

# A Highly Luminous $\text{LiCaPO}_4:\text{Eu}^{2+}$ Phosphor Synthesized by a Solution Method Employing a Water-Soluble Phosphate Ester

Minsung Kim, Makoto Kobayashi, Hideki Kato, Masato Kakihana\*

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan

Email: \*kakahana@tagen.tohoku.ac.jp

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## ABSTRACT

A  $\text{LiCaPO}_4:\text{Eu}^{2+}$  phosphor with high photoluminescence was synthesized using a polymerizable complex (PC) method employing a water-soluble polyethylene glycol-conjugated phosphate ester (PEG-P). PEG-P could be obtained from a reaction among polyethylene glycol 300, phosphorus pentoxide, and pyrophosphoric acid. The PEG-P prepared was stable in an aqueous condition. A transparent solution and gel were obtained when the PEG-P was used as a source of P during the PC method, whereas the use of  $\text{H}_3\text{PO}_4$  caused an undesirable precipitate. The  $\text{LiCaPO}_4:\text{Eu}^{2+}$  obtained via the PC method employing the PEG-P showed higher emission intensity than those synthesized by a solid state reaction method and the PC method employing  $\text{H}_3\text{PO}_4$ . The high luminescence properties of the sample synthesized using the PEG-P may be attributed to high homogeneity of constituents in the sample.

**Keywords:** Solution Method; Stable Phosphate Ester; Homogeneity;  $\text{LiCaPO}_4:\text{Eu}^{2+}$

## 1. Introduction

Phosphate phosphors have been well-known as one of the most important luminescence materials because of their excellent thermal stability and high emission intensity as well as lower temperature synthesis [1,2]. Among them,  $\text{Eu}^{2+}$ -activated  $\text{ABPO}_4$  phosphors (A and B are mono- and divalent cations, respectively) have been reported as blue-emitting phosphors excited by near UV-LEDs. For instance,  $\text{KSrPO}_4:\text{Eu}^{2+}$ ,  $\text{KBaPO}_4:\text{Eu}^{2+}$ , and  $\text{LiCaPO}_4:\text{Eu}^{2+}$  have excellent luminescence properties including quantum efficiency and thermal quenching behavior. Therefore, they are considered to be potential application as phosphors for the white light emitting diodes [3-5].

Several kinds of methods were applied to synthesis of inorganic powders, such as solid state reaction (SSR), solution-based method, and combustion process. In the synthesis of phosphors, the SSR method is the most extensively used. However, the SSR method includes some drawbacks such as low homogeneity, and non-uniform particles morphology and size. Generally, solution-based synthesis is considered to be a desirable approach be-

cause it can produce highly homogeneous compounds in the atomic level [6,7]. Homogeneity of constituents and control of morphology and size of particles are requisites for highly efficient phosphors. One of limitations in a synthesis of phosphate phosphors using solution methods is requirement of appropriate P source, which is soluble and stable in an aqueous condition. The use of conventional phosphate reagents such as phosphoric acid or ammonium phosphate produce precipitates with metal ions in an aqueous condition [8]. Precipitates would lead to samples with inhomogeneous composition accompanying by secondary phases. In ion-activated type phosphors, distribution of an activator is closely connected to luminescence intensity in the view of concentration quenching. It indicates that inhomogeneity results in low performance of phosphor. Additionally, in a highly homogeneous sample, high amount of rare-earth can be doped, and as a result, high luminescence intensity would be achieved.

Solution-based synthesis highly requires the use of appropriate raw materials, which do not produce precipitate with any metals present in a given aqueous solution. Therefore, development of a new water-soluble P source that does not form precipitates with other metal ions is

\*Corresponding author.

indispensable to realization of synthesis of extremely homogeneous phosphate compounds with high performance by aqueous solution-based methods. It is known that precipitates between phosphorus and metals could be prevented by introduction of condensed chain-structured phosphates [9,10]. Recently, we have succeeded in a synthesis of a phosphor with high luminescence by a solution method using such a phosphate oligomer [11]. The prepared oligomer had good solubility and stability in an aqueous condition, though approximately 50%  $\text{H}_3\text{PO}_4$  unreacted remained. Therefore, it can be expected that if a phosphorus source with further less  $\text{H}_3\text{PO}_4$  can be prepared, the range of synthesis of phosphate phosphors with even better photoluminescence properties can be greatly expanded. The condensed chain-structured phosphates are commercially available and are synthesized from a rather simple reaction among alcohol, phosphorus pentoxide, and polyphosphoric acid [12]. Especially, polyethylene glycol (PEG) is considered to be a good candidate for its condensation with the phosphate moiety because PEG is widely used as a cross-linking agent for promoting formation of “gel” in a variety of “sol-gel”-based solution methods. Polyethylene glycol-conjugated phosphate ester (PEG-P) is considered to be soluble and stable in an aqueous solution, and also PEG-P may have a role as a cross-linking agent. In this study, we report the synthesis of PEG-P whose chemical structures are deduced from  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR measurements, and then we stress the great advantage of the use of PEG-P as a P source for the synthesis of  $\text{Eu}^{2+}$ -doped  $\text{LiCaPO}_4$ , chosen as a model among phosphate-based phosphors, by demonstrating the superior photoluminescence properties of the target phosphor synthesized by the polymerizable complex (PC) method employing the PEG-P instead of the conventional P source, that is  $\text{H}_3\text{PO}_4$ .

## 2. Experimental Section

### 2.1. Synthesis of PEG-P

Pyrophosphoric acid (10 mmol phosphorus, Kanto Chemical) and polyethylene glycol 300 (PEG300, 10 mmol Kanto Chemical) were mixed at 323 K and kept for 2 h. Phosphorus pentoxide  $\text{P}_4\text{O}_{10}$  (10 mmol phosphorus, Wako Chemical) was weighed in an inert atmosphere to prevent its hydrolysis, and then slowly added into the mixture. After  $\text{P}_4\text{O}_{10}$  was dispersed homogeneously, temperature of the mixture increased to 358 K and kept for 5 h. Finally, 10 mmol of PEG300 was added, and the reaction was continued for 12 h at 358 K. The entire reaction was conducted in  $\text{N}_2$  atmosphere. Gel with high viscosity was formed and it was dissolved in distilled water. The gel was dissolved in  $\text{D}_2\text{O}$ , and pH was adjusted to 13 using 10 M NaOH to prepare a solution

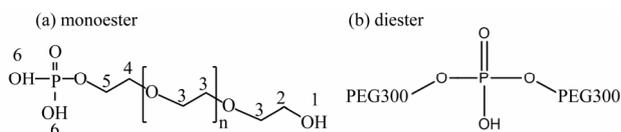
for NMR analysis.  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the prepared PEG-P were recorded on a Bruker AVANCE 400 spectrometer (400 MHz for  $^1\text{H}$  resonance) to analyze the chemical structure of PEG-P. The phosphorus concentration of diluted PEG-P was determined using an inductively-coupled plasma (ICP) method (Perkin Elmer; Optima 3300XL) prior to its use for the synthesis of  $\text{Eu}^{2+}$ -doped  $\text{LiCaPO}_4$  by the PC method described in the following section.

### 2.2. Preparation of $\text{Eu}^{2+}$ -Doped $\text{LiCaPO}_4$

A  $\text{Eu}^{2+}$ -doped  $\text{LiCaPO}_4$  phosphor was synthesized via the PC method employing the PEG-P as a P source.  $\text{LiNO}_3$  (99%, Kanto Chemical),  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (99.5%, Kanto Chemical), and  $\text{Eu}(\text{NO}_3)_3$ , which was prepared by dissolution of  $\text{Eu}_2\text{O}_3$  in  $\text{HNO}_3$ , were dissolved in a citric acid (CA) solution at a ratio of  $\text{Li}:\text{Ca}:\text{Eu}:\text{CA} = 1:0.97:0.03:8$ . The mixture was firstly heated at 353 K to allow chelation for 2 h, and then, the PEG-P and propylene glycol (PG) were added into the solution at a molar ratio of 1:8. The temperature was subsequently increased to 423 K to promote gel formation. The formed gel was heated at 1123 K in air to remove the organic content, and then it was reduced at 1373 K under a flow of Ar containing 4%  $\text{H}_2$  for 3 h. To enhance the phase purity, post-heat treatment was conducted at 1073 K for 18 h in an Ar/4% $\text{H}_2$  atmosphere. A  $\text{Eu}^{2+}$ -doped  $\text{LiCaPO}_4$  phosphor was also synthesized by the PC method using  $\text{H}_3\text{PO}_4$  as the P source. In addition, synthesis using the SSR method was carried out for comparison by stoichiometric mixing raw materials including  $\text{Eu}_2\text{O}_3$  (Furuuchi Chemical), and  $\text{Li}_2\text{CO}_3$  (Wako Chemical),  $\text{CaCO}_3$ , and  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  (both from Kanto Chemical). X-ray diffraction analysis (XRD, Bruker AXS; D2 Phaser) was conducted. Excitation and emission spectra of phosphors were recorded using a fluorescence spectrometer (Hitachi; F-4500) at room temperature. Quantum efficiencies of the samples were evaluated using fluorescence spectrometer (Jasco; FP-6500).

## 3. Results and Discussion

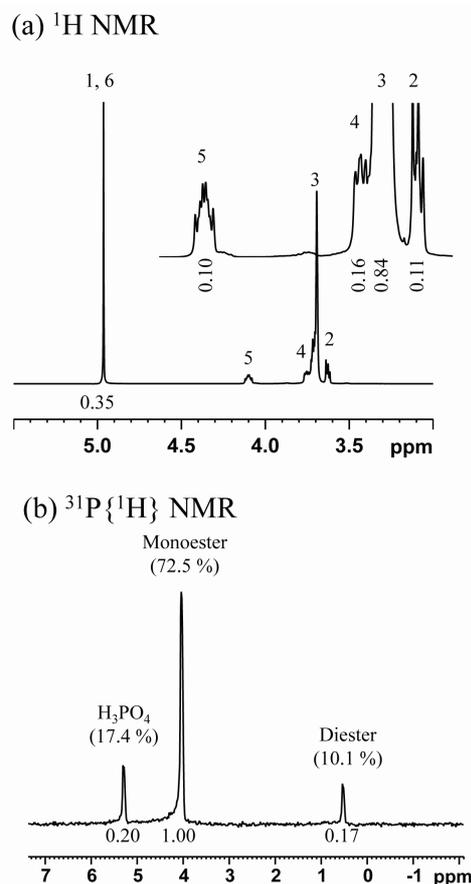
**Scheme 1** shows estimated chemical structures of the synthesized PEG-P; (a) mono- and (b) di-esters, and **Figure 1** shows  $^1\text{H}$  (a) and  $^{31}\text{P}\{^1\text{H}\}$  (b) NMR spectra of the obtained PEG-P. In the  $^1\text{H}$  NMR spectra (**Figure 1(a)**), each peak was assigned to each hydrogen marked with “1 - 6” in **Scheme 1(a)**. No peaks of “4” and “5” were observed in  $^1\text{H}$  NMR spectra of PEG and  $\text{H}_3\text{PO}_4$  (not shown here), which in turn indicates that the observation of these peaks evidences formation of a conjugation between PEG300 and phosphate. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (**Figure 1(b)**) indicates that only one side OH group of PEG was conjugated with phosphate. The integration



**Scheme 1. Estimated chemical structures of synthesized PEG-P: (a) monoester, (b) diester.**

area corresponding to the peak “2” was greatly decreased after the reaction, and finally, it could be estimated that more than 90% of PEG 300 was bonded with phosphate. From the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, it could be confirmed that the PEG-P contained  $\text{H}_3\text{PO}_4$ , monoester, and diester with ratio of 17.4:72.5:10.1 (**Figure 1(b)**). Previously, we reported preparation of a phosphate oligomer starting from ethylene glycol and phosphoric acid by promoting their esterification reaction under reflux [11]. The yield of the phosphate oligomer was about 55.4% with 44.6% of unreacted  $\text{H}_3\text{PO}_4$ . This indicates that the present method can produce the condensed chain-structured phosphate with less  $\text{H}_3\text{PO}_4$  than the reported method. The use of such a P source having a large proportion of esters containing a small amount of  $\text{H}_3\text{PO}_4$  is considered to be suitable for solution-based synthesis of phosphate-based phosphors because of less opportunity that precipitates form resulting from interaction between  $\text{H}_3\text{PO}_4$  and metal ions present in a given solution. Another important characteristic of PEG-P is its stability in  $\text{H}_2\text{O}$ , which was confirmed by the fact that the initial small proportion of  $\text{H}_3\text{PO}_4$  remained unchanged over 2 months.

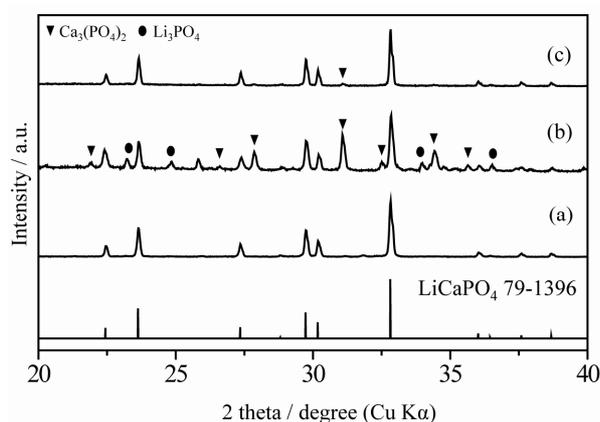
To demonstrate the advantages of the use of PEG-P in a solution-based method, a  $\text{LiCaPO}_4$  doped with  $\text{Eu}^{2+}$  phosphor was synthesized by the PC method employing the PEG-P. **Figure 2** shows XRD patterns of  $\text{LiCaPO}_4:\text{Eu}_{0.03}$  synthesized by the PC method employing the PEG-P under various conditions; (a) 1123 K for 3 h in air, (b) 1373 K for 3 h in  $\text{Ar}/4\%\text{H}_2$  atmosphere, and (c) post-heating of (b) at 1073 K for 18 h. No precipitate was formed when the PEG-P was added into an aqueous solution containing  $\text{LiNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{Eu}(\text{NO}_3)_3$ . When the sample obtained after the heat-treatment at 1123 K in air, a single phase  $\text{LiCaPO}_4$  was formed without any impurity phases as shown in **Figure 2(a)**. Synthesis of a single phase  $\text{LiCaPO}_4:\text{Eu}^{2+}$  phosphor was rarely achieved in previous studies, and they suffered from significant contamination by impurities, such as  $\text{Li}_3\text{PO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$  [13-15]. It should therefore be stressed here that it was possible to obtain a single phase of  $\text{LiCaPO}_4$  resulting from the achievement of highly homogeneous distribution of constituents. Reduction at 1373 K for 3 h gave the sample exhibiting the highest emission intensity among various reduction temperatures (1073 - 1473 K). However, at this relatively higher temperature, strong reflections due to impurity phases such as  $\text{Li}_3\text{PO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$  showed up (**Figure 2(b)**).



**Figure 1.  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of PEG-P in  $\text{D}_2\text{O}$  at pH 13.**

This is due to decomposition of  $\text{LiCaPO}_4$  at such a high temperature. Reaction between  $\text{Li}_3\text{PO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$  appears to be possible when the corresponding phase diagram for these two compounds is taken into account [15,16]. The post-heat treatment of the above-mentioned sample at 1073 K for 18 h (**Figure 2(c)**) resulted in almost complete elimination of  $\text{Li}_3\text{PO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$ , which accompanied formation of  $\text{LiCaPO}_4$  resulting from a back reaction between the two impurities, and consequently an almost single phase of  $\text{LiCaPO}_4$  was formed with a very tiny amount of  $\text{Ca}_3(\text{PO}_4)_2$ .

**Figure 3** shows XRD patterns of  $\text{LiCaPO}_4:\text{Eu}_{0.03}^{2+}$  synthesized by the PC method employing PEG-P or  $\text{H}_3\text{PO}_4$  and the SSR method after post-heat treatment at 1073 K for 18 h. All the samples mainly consisted of  $\text{LiCaPO}_4$  as assigned to the JCPDS Card ( $\text{LiCaPO}_4$ , No. 79-1396). The sample synthesized by the PC method employing PEG-P was the almost single phase  $\text{LiCaPO}_4$  with negligible extent of impurity phase, whereas the samples synthesized by the PC method using phosphoric acid and SSR method contained a large amount of impurities, which were  $\text{Li}_3\text{PO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$ . During the PC method employing  $\text{H}_3\text{PO}_4$ , precipitate was observed in

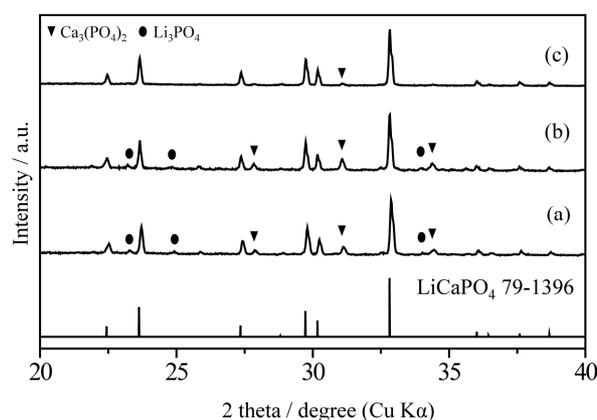


**Figure 2.** XRD patterns of  $\text{LiCaPO}_4:\text{Eu}_{0.03}$  phosphors synthesized by the PC method; (a) calcination at 1123 K for 3 h, (b) reduction at 1373 K for 3 h, and (c) post-heating at 1073 K for 18 h.

the mixture solution while PEG-P didn't make any precipitate. It can be expected that low homogeneity led to formation of a large amount of  $\text{Li}_3\text{PO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$  and these phases remained even after post-heat treatment. As mentioned above, phase purity is closely related to photoluminescence properties. The use of a novel PEG-P as a P source in the PC method could improve phase purity of  $\text{LiCaPO}_4$ , and it is one of advantages of the PEG-P in the PC method.

**Figure 4** shows the SEM and the corresponding EDS maps of Eu in  $\text{LiCaPO}_4:\text{Eu}_{0.07}^{2+}$  phosphors prepared by the SSR method (a, b) and the PC method employing PEG-P (c, d) after the post-heat treatment. The state of Eu distribution is closely related to the photoluminescence properties of given phosphors [7]. 7 mol% Eu-doped samples were analyzed to obtain clearer images of Eu distribution. As to the sample synthesized using the SSR method, inhomogeneity, especially, deficient Eu area as marked with the white arrow in **Figure 4(b)** corresponding to the black arrow in **Figure 4(a)** could be observed. On the other hand, as to the sample prepared using the PC method, the EDS mapping image showed uniform distribution of Eu without observation of deficient and localization of Eu ions. These results suggest that the PC method allowed highly homogeneous distribution of each element throughout the  $\text{Eu}^{2+}$ -doped  $\text{LiCaPO}_4$  phosphor, which may result in improvement of the corresponding photoluminescence properties.

**Figure 5** shows excitation and emission spectra of the  $\text{LiCaPO}_4:\text{Eu}_{0.03}^{2+}$  phosphors synthesized using the SSR method and the PC method employing the PEG-P or  $\text{H}_3\text{PO}_4$  after post-heat treatment at 1073 K for 18 h. The sample synthesized by the PC method using  $\text{H}_3\text{PO}_4$  showed the lowest emission intensity. As stated above, the emission intensity of materials is closely related to the homogeneity of each element. The formation of pre-

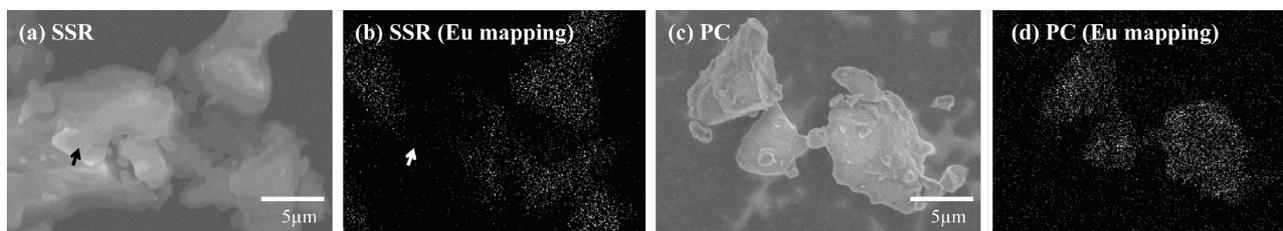


**Figure 3.** XRD profiles of  $\text{LiCaPO}_4:\text{Eu}_{0.03}^{2+}$  phosphors after post-heating synthesized by the SSR method (a) and PC method employing  $\text{H}_3\text{PO}_4$  (b) and PEG-P(c).

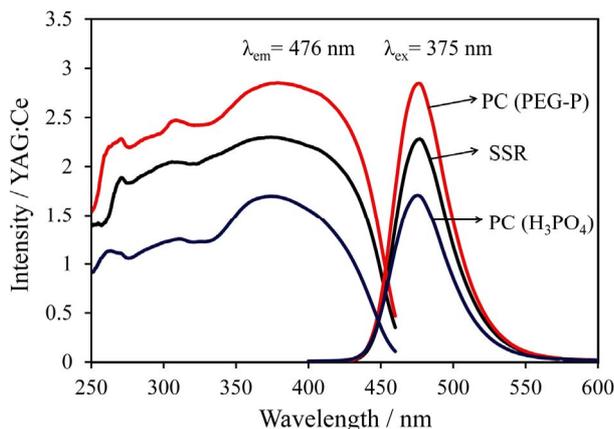
cipitate between  $\text{H}_3\text{PO}_4$  and metals during the mixing step in the PC method implies poor homogeneity despite of a solution-based method. The SSR method could produce better condition of sample compared to that of the PC method employing  $\text{H}_3\text{PO}_4$ , because it exhibited higher emission intensity. Formation of undesirable precipitate in the PC method is thought to be a critical factor for homogeneity. The strongest emission intensity was observed from the sample synthesized via the PC method using the PEG-P as a P source. The internal quantum efficiencies of  $\text{LiCaPO}_4:\text{Eu}_{0.03}^{2+}$  prepared using the SSR method and the PC method employing PEG-P under excitation at 375 nm were 53.7% and 67.6%, respectively, although the corresponding absorption rate (81.3%) of the sample prepared by the PC method using PEG-P was slightly smaller than that of the one prepared by the SSR method (82.7%). The PEG-P was stable in the aqueous condition and the use of PEG-P didn't produce any precipitates with coexisting metal ions, and it allowed us to obtaining a highly homogeneous phosphor sample. As a result, despite of a lower absorption rate, the sample obtained from the PC method using PEG-P showed the high emission intensity and enhanced quantum efficiency.

## 4. Conclusion

A stable and water soluble phosphate ester was prepared by the reaction using pyrophosphoric acid, phosphorus pentoxide, and PEG300. The method could produce P source with less  $\text{H}_3\text{PO}_4$ . It was confirmed that the synthesized PEG-P didn't make any precipitate in a mixture of metal salts while the use of  $\text{H}_3\text{PO}_4$  resulted in formation of a precipitate. An almost single phase of  $\text{LiCaPO}_4$  was obtained using the PEG-P, while SSR and PC method using  $\text{H}_3\text{PO}_4$  led to formation of impurity phases, which were  $\text{Li}_3\text{PO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$ . As a result, the phosphor prepared by the PC method using the synthesized



**Figure 4.** SEM micrographs and corresponding EDS mapping images of Eu ion in  $\text{LiCaPO}_4:\text{Eu}_{0.07}^{2+}$  phosphors prepared by (a), (b) SSR method, and (c), (d) PC method using PEG-P.



**Figure 5.** Excitation and Emission spectra of  $\text{LiCaPO}_4:\text{Eu}_{0.03}^{2+}$  phosphors synthesized by SSR and PC method employing  $\text{H}_3\text{PO}_4$  or PEG-P.

PEG-P exhibited enhanced photoluminescence properties, such as the highest emission intensity and quantum efficiency compared to other methods. Enhanced photoluminescence properties seemed to be attributed to homogeneous distribution of constituents in the atomic level. Therefore, the PEG-P is expected to be applicable in the solution-based synthesis of various kinds of phosphate-based ceramic compositions with enhanced material properties.

## 5. Acknowledgements

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