

Synthesis of $\text{KSrPO}_4\text{:Eu}$ by polymerized complex method and its reduction process by microwave irradiation

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$\text{KSrPO}_4\text{:Eu}^{2+}$ was synthesized by polymerized complex microwave reduction method, which is a new method utilizing microwave reduction for precursor prepared by polymerized complex method. $\text{KSrPO}_4\text{:Eu}^{2+}$ without any other phase was successfully obtained by the new method. The grain size prepared by the new method was small and homogeneous in comparison with usual method utilizing solid state reaction. Blue emission band around 427 nm was observed under UV excitation around 320 ~ 350 nm. Eu concentration quenching was found to occur above 0.5%. Temperature dependence of photoluminescence showed good thermal stability. Phonon energy coupled with excited state was estimated to be 23 ~ 26 meV using configuration coordinate model.

Key words: Phosphor, Polymerized complex method, $\text{KSrPO}_4\text{:Eu}$, Microwave reduction.

Introduction

Recent years, white light LEDs have become popular remarkably as lighting, because of the high efficiency, electrical power saving and long lifetime compared with conventional lighting. The most general structure of white light LEDs is the combination of blue emitting LEDs with blue excited yellow emitting phosphors, $\text{Y}_3\text{Al}_5\text{O}_{12}\text{:Ce}^{3+}$. This structure has a drawback of poor color rendering properties and high color rendering LEDs emitting natural light are required. High color rendering properties can be attained by exciting blue, green and red phosphors with UV-LEDs. However, the efficiency of these LEDs becomes low compared with the general white light LEDs. One of the simple solutions of the problem is a boost of the input power for LED chip. Consequently, the exploration of phosphors which have high temperature stability is necessary.

UV-excited blue emitting phosphor, $\text{KSrPO}_4\text{:Eu}^{2+}$ is known to have excellent thermal stability because of its phosphate crystal structure [1, 2]. Usually $\text{KSrPO}_4\text{:Eu}^{2+}$ was synthesized by solid state reaction (SSR) and subsequent high temperature reduction process in H_2 atmosphere. On the other hand, SSR synthesis and reduction of $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} using microwave-heated activated carbon were reported [3]. Because the microwave heating is rapid and selective, the synthesis and reduction time is expected to become drastically shorter than that of usual method.

In this study, we use the microwave reduction method with a double crucible filled with activated carbon for the

reduction of the Eu ions in KSrPO_4 . Furthermore, to synthesize $\text{KSrPO}_4\text{:Eu}$, we used polymerized complex method (PCM) using citric acid that has an advantage over SSR for uniformity of structure and composition around Eu ions [4]. The luminescent properties of $\text{KSrPO}_4\text{:Eu}^{2+}$ prepared by this combined method, here after we call as polymerized complex microwave reduction method (PCMR), is compared with those by usual method.

Experimental

Sample preparation

As starting materials for the synthesis of $\text{KSr}_{(1-x)}\text{PO}_4\text{:Eu}_x^{2+}$ ($x = 0.3 \sim 100\%$), stoichiometric amounts of KH_2PO_4 , SrCO_3 and Eu_2O_3 were dissolved in diluted nitric acid. As a chelating agent, citric acid monohydrate was added and chelated at 80 °C. To dehydrate and polymerize the chelate complexes, propylene glycol was added, leading to the formation of a yellow polyester resin. The resin was decomposed at 300 ~ 350 °C by a mantle heater and calcinated at 800 °C for 3 hours to obtain white precursor of $\text{KSrPO}_4\text{:Eu}$. For comparison, the precursor was prepared by usual SSR method with the same starting materials at 600 °C for 3 hours.

The precursor was set into an inner crucible of double crucibles (10 and 50 ml) and the space between inner and outer crucibles was filled with activated carbon as microwave absorber and source of reducing agent. Furthermore, the double crucible was set into a heat-insulating brick in a domestic microwave oven (2.45 GHz, 800 W). The microwave oven was operated for 15 minutes to reduce the Eu ions in KSrPO_4 precursor by carbon monoxide gas generated from the activated carbon in oxygen deficient atmosphere. For comparison, usual H_2 gas reduction was done at

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Table 1. Combination of the precursor synthesis and reduction method.

Precursor \ Reduction	H ₂ reduction	Microwave reduction
SSR	Sample 1	Sample 2
PCM	Sample 3	Sample 4

1200 °C for 3 hours using tube furnace with H₂(5%)/N₂ atmosphere. Four kinds of samples with combination of two kinds of precursors and two reduction methods were obtained as summarized in table 1.

Sample characterization

The obtained samples were analyzed with X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) and photoluminescence excitation (PLE). XRD patterns were measured using Cu K α radiation of X-ray diffractometer (Shimadzu, XRD-7000). SEM image was monitored with field emission scanning microscope (Hitachi, S-4000). The PL and PLE measurements were done in temperature range of 16 ~ 586 K. For low temperature range (16 ~ 300 K), the samples were attached to the cold finger of an optical cryostat coupled to a refrigerator (Iwatani, Cryo-Mini D105). For high temperature range (293 ~ 586 K), samples were attached to a metal plate mounted at end of a soldering iron. The PL excitation was done by the 325 nm line of a He-Cd laser (Omnichrome, 3056-M10, 10 mW). Photoluminescence was dispersed by a spectrometer (Nalumi, RM23) in conjunction with a photomultiplier (Hamamatsu, R943-02) coupled to a photon counter (Hamamatsu, C767). The PLE spectrum was taken by combining the spectrometer and a double monochromator (Ritsu, MC-30NW) to obtain mono-chromatic light from a high pressure Xe lamp (Hamamatsu, L2175, 150 W) for the excitation. PL and PLE spectra shown below were corrected for the spectral sensitivity of the detection system for the former, and intensity distribution of the exciting system for the latter, respectively.

Results and Discussion

XRD and SEM characterization

Fig. 1 shows the XRD patterns of sample 1 ~ 4 (Eu concentration is 0.5%). Almost all peaks of the sample 2 and 4 with microwave reduction correspond to the ICDD data of K₂SrPO₄, while the sample 1 and 3 with H₂ gas reduction show the peaks corresponding to the second phase of Sr₃(PO₄)₂ due to evaporation of K⁺ ions during the long time and high temperature reduction process in H₂ atmosphere.

SEM images of sample 1 ~ 4 are shown in Fig. 2. The particle size of sample 4 (PCM and microwave reduction) is most homogeneous and smallest of the all samples. This feature is owing to the advantage of PCM producing homogenous and small precursors and the short time reduction process with microwave avoiding

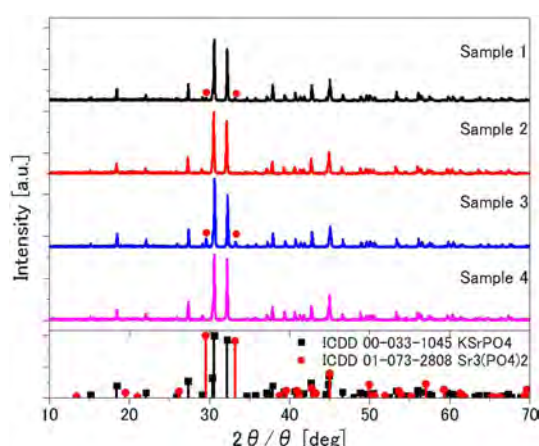


Fig. 1. XRD patterns of sample 1 ~ 4 and ICDD data of K₂SrPO₄ and Sr₃(PO₄)₂. Closed circles indicate lines of the different phase, Sr₃(PO₄)₂.

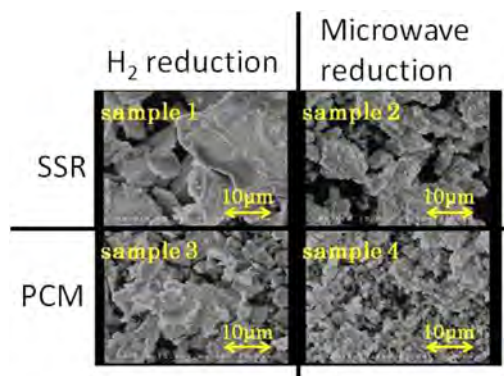


Fig. 2. SEM images of sample 1 ~ 4. The grain size of sample 4 is small and homogenous compared with other samples.

the agglomeration of precursors.

PL and PLE characterization

PL and PLE spectra of sample 1 ~ 4 at room temperature are shown in Fig. 3. The inset shows normalized spectra. PL spectra of sample 2 and 4 consist of single broad band around 427 nm due to 4f⁶5d¹ → 4f⁷5d⁰ transition of Eu²⁺, indicating the Eu ions are successfully reduced by microwave irradiation. The sample 1 and 3 with H₂ gas reduction show strong emission, however, a shoulder appears around 480 nm and the main peak shift to 430 nm. These spectral changes are explained by Eu ions on interstitial site in non-stoichiometric K₂SrPO₄ [5], resulting from evaporation of K⁺ ions during the long time and high temperature reduction process in H₂ atmosphere. The crystal field at interstitial site is weaker than that of Sr site, leading to longer wavelength emission. Sample 2 and 4 with microwave reduction shows weaker emission than sample 1 and 3. And furthermore, sharp lines around 620 nm due to f-f transitions of Eu³⁺ ions remain slightly, indicating the reduction process is incomplete due to the shorter reduction time. PLE spectra of the sample 2 and 4 consist of a broad band around 320 ~ 350 nm, while those of the sample 1 and 3 are around

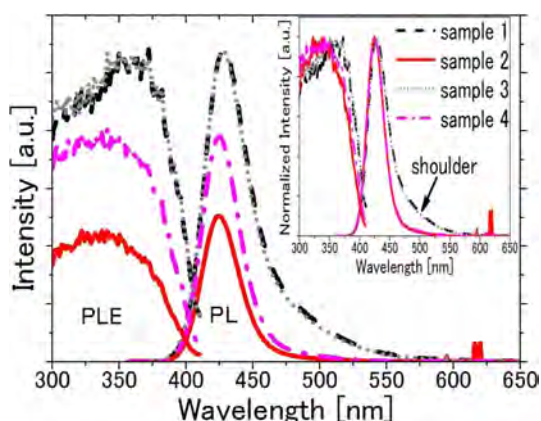


Fig. 3. PL and PLE spectra of sample 1 ~ 4 at room temperature. Excitation wavelength λ_{ex} for PL spectra is 325 nm and observation wavelength λ_{em} for PLE spectra is 427 nm. The inset shows normalized PL and PLE spectra.

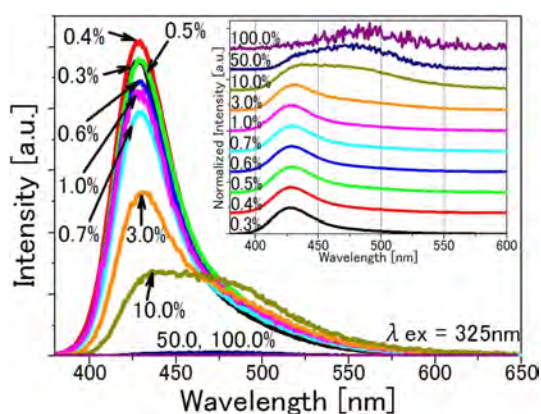


Fig. 4. PL spectra of the sample prepared by the same method of sample 3 with various Eu concentration (0.3 ~ 100%).

350 ~ 370 nm. This spectral change also may be explained by the evaporation of K^+ ions.

Eu concentration dependence of PL spectra

Eu concentration dependence of PL spectra was investigated using samples prepared by the same method of sample 3 (PCM + H_2 gas reduction) because the Eu ions was expected to be distributed homogeneously and the PL intensity was relatively stronger.

Fig. 4 shows the Eu concentration dependence of PL spectra of the range of 0.3 ~ 100% and the inset shows that of normalized spectra. The PL intensity has a maximum at 0.4% and concentration quenching occurs above 0.5%. The peak wavelength shifts to longer gradually with concentration increase above 10% and reaches to 490 nm at 100%. This red shift is explained by the enhancement of crystal field due to the expansion of lattice parameters caused by the difference of ion radius between Eu (1.30 Å) and Sr (1.31 Å) where the coordination number is 9 [6, 7].

Temperature dependence of PL and PLE spectra

Temperature dependence of PL spectra was investigated

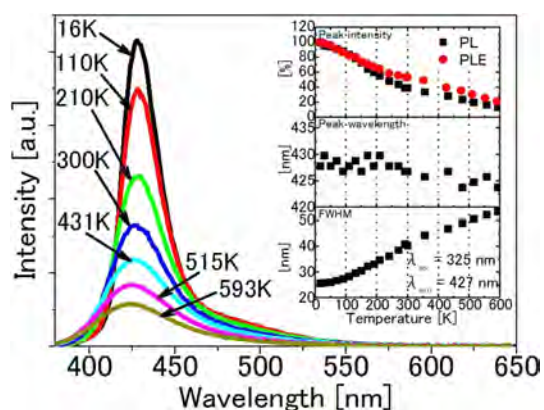


Fig. 5. PL spectra of the sample prepared by the same method of sample 3 at various temperature (16 ~ 586 K). The inset shows temperature dependence of peak intensity of PL and PLE bands, peak wavelength of PL band and FWHM of PL band.

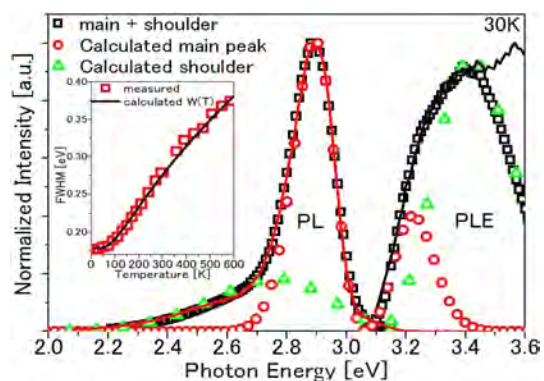


Fig. 6. PL and PLE spectra at 30 K. Open circles, triangles and squares are results of fitting (see text). The solid line in the inset shows the result of curve fitting for the temperature dependence of FWHM of PL band.

using samples prepared by the same method of sample 3 (Eu concentration was 0.4%). Fig. 5 shows the temperature dependence of PL spectra and the inset shows the temperature dependence of peak intensity of PL and PLE bands, peak wavelength of PL band and FWHM of PL band. Although the temperature quenching is occurring, the peak intensity keeps 19% and 47% at high temperature of 586 K in comparison with 16 K and 300 K, respectively, proving the excellent thermal stability of phosphate crystal structure. The peak wavelength becomes shorter and FWHM becomes broader with increase of temperature. This red shift is due to the thermal expansion of the host lattice. The broadening of PL band is due to a change of population in the excited state, and the temperature dependence is related with the phonon energy of excited state (5d) as discussed below.

Fig. 6 shows the PL and PLE spectra of the same sample shown in Fig. 5 at low temperature of 30 K. According to the configuration coordinate model, the shapes of the PL and PLE bands at low temperature reflect the phonon energies of ground (4f) and excited (5d) states, respectively. The shapes of the bands can

be expressed by the Poisson distribution function [8] as follows,

$$f(E) \propto \frac{S^{\frac{E_0-E}{\hbar\omega}} e^{-S}}{\left(\frac{E_0-E}{\hbar\omega}\right)!}, \quad (1)$$

where E_0 is the zero-phonon energy (which is taken to be 3.06 eV, the intersection of the PL and PLE bands), S is the Huang-Rhys factor and $\hbar\omega$ is the phonon energy. The open circles in Fig. 6 show the results of fitting using Eq. (1) to the main PL and PLE band. The values of fitting parameters S and $\hbar\omega$ are 6.9 and 26 meV for the PL band, and 6.8 and 26 meV for the PLE band, respectively. The open triangles show the results of fitting to the shoulder components of PL and PLE. The open squares in Fig. 6 show superposition of the open circles and triangles, reproducing the whole PL and PLE bands well.

As mentioned above, the FWHM of the PL band is related with the phonon energy of the excited state (5d) and expressed by the following equation [9],

$$W(T) = 2.36\hbar\omega\sqrt{S} \sqrt{\coth\frac{\hbar\omega}{2kT}}, \quad (2)$$

where kT is the thermal energy. The solid line in the inset of Fig. 6 is the result of curve fitting using Eq. (2) and is in good agreement with the measured data up to 586 K. The value of phonon energy obtained by the curve fitting is 23 meV which is close to the value of 26 meV, obtained from the shape of PLE band. This results shows that the phonon energy coupled with the excited state (5d) is 23 ~ 26 meV.

Summary

$\text{KSrPO}_4\text{:Eu}^{2+}$ without any other phase was successfully obtained by microwave reduction using activated

carbon for the precursor prepared by polymerized complex method. Blue PL band around 427 nm was observed under UV excitation around 320 ~ 350 nm. Although the reduction time was drastically shortened to less than a tenth of the usual reduction time using H_2 gas, the PL intensity was 70% compared with the usual method using H_2 gas reduction for the precursor prepared by solid state reaction. On the other hand, the grain size prepared by polymerized complex method was small and homogeneous compared with solid state reaction. From the measurement of Eu concentration dependence, the concentration quenching was found to occur above 0.5%. From the measurement of temperature dependence, the peak intensity keeps 19% and 47% at high temperature of 586 K in comparison with 16 K and 300 K, respectively, suggesting the feasibility to combine with high power LEDs. Applying the configuration coordinate model to the PL properties, the phonon energy coupled with excited state was found to be 23 ~ 26 meV.

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