Low-temperature synthesis of white-light-emitting CsVO₃ nanoparticles by an aqueous solution route

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CsVO₃ nanoparticles were synthesized by the evaporation of aqueous solutions of peroxo-isopolyvanadic acid and cesium carbonate. The resulting phosphor showed white light Photoluminescence (PL) property with a broad peak in the range of 400–700 nm at an excitation wavelength of 350 nm. The as-prepared CsVO₃ was heat-treated at 200 and 400°C, and an increase in the particle size and PL intensity was observed with increasing heat-treatment temperatures.

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1. Introduction

Metavanadate phosphors, AVO₃ (A: K, Rb, and Cs), show white light Photoluminescence (PL) emission upon UV irradiation^{1)–3)} and have been attracting considerable attention for LED applications. CsVO₃ has a broad absorption range corresponding to excitation between 250 and 390 nm and white PL emission with a broad peak between 380 and 800 nm. It shows two PL peaks at 514 nm (Em1) and 600 nm (Em2).³⁾ The quantum efficiency of CsVO₃ measured at room temperature was 87% in the previous report,³⁾ which is a very large value.³⁾ Therefore, CsVO₃ phosphor can be applied in the white-light-emitting (white LED) devices.

CsVO₃ can be synthesized by a solid state reaction³⁾ or a hydrothermal⁴⁾ method. The reaction temperature should be above 450°C to prepare CsVO₃ via the solid state reaction, or a high pressure (close to 1×10^4 hPa) with a reaction temperature of 180°C is needed to prepare CsVO₃ by the hydrothermal method. Nakajima et al. reported synthesizing a white-light-emitting RbVO₃ phosphor by a solution route at room temperature,³⁾ but there are no reports of CsVO₃ synthesis at room temperature in the literature.

In our previous work, we synthesized the Zn₃V₂O₈ phosphor by a solution route using peroxo-isopolyvanadic acid (V-IPA).⁵⁾ V-IPA is readily soluble in water,⁶⁾ and hence, various vanadate compounds can be synthesized by a solution route using V-IPA. In the present study, we prepared CsVO₃ by a solution route using V-IPA at room temperature, and the PL property of the obtained CsVO₃ was evaluated. Furthermore, in the present investigation, we analyze the merits of the synthesis method based on the solution route.

2. Experimental procedure

V-IPA was prepared according to a previous report,⁵⁾ and the method was as follows. Vanadium powder (Wako, Osaka, Japan) was mixed with an H₂O₂ aqueous solution, and cooled using an ice bath. The resulting orange solution was dried using a rotary evaporator in a water bath at 40°C, and the V-IPA powder was obtained.

V-IPA and Cs₂CO₃ powders (Wako, Osaka, Japan) were dissolved in ion-exchanged water at a 0.01 M vanadium concentration, and the Cs/V molar ratio in the solution was 1:1. The resulting solution was dried using a rotary evaporator at 40°C, where the evaporator pressure was less than 1 kPa. The resulting samples were heat treated at 200 and 400°C for 1 h in air.

The crystal structures of the resulting powders were determined using X-ray diffraction (XRD; Miniflex, Rigaku, Japan) with Cu K α radiation (30 kV, 15 mA). The microstructures of the powders were observed using transmission electron microscope (TEM, EM-002B; Topcon Corp., Japan) and scanning electron microscope (SEM, JEOL JSM-6510, Japan). The PL properties of the powders were evaluated at room temperature using a conventional fluorescence spectrophotometer (RF 5300PC, Shimadzu, Japan) with a Xe lamp.

3. Results and discussion

Figure 1 shows the XRD patterns for the as-prepared sample, and the samples with the heat-treated at 200 and 400°C. All the powders can be assigned to single-phase CsVO₃ (JCPDS: 70-0680). A halo peak at around $2\theta = 20^\circ$ was observed for the as-prepared sample, indicating that the crystallinity of the as-

Fig. 1. The XRD patterns for (a) the as-prepared powder, (b) the powder heat-treated at 200°C and (c) the powder heat-treated at 400°C.

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Table 1. Calculated lattice constant of the resulting samples

Lattice constant	a (nm)	b (nm)	c (nm)	Cell volume (nm ³)
As-prepared	0.5462	1.235	0.5786	0.3903
200°C	0.5416	1.230	0.5814	0.3873
400°C	0.5398	1.231	0.5799	0.3852

Fig. 2. TEM images of (a) the as-prepared CsVO₃ powder and (b) the CsVO₃ powder heat-treated at 200°C, and (c) SEM image of the CsVO₃ powder heat-treated at 400°C.

prepared powder is not high. However, the peaks of the powders heat-treated at 200 and 400°C were sharp, and no halo pattern was observed for these powders. Calculated lattice constants of these samples were depicted in **Table 1**. The cell volume of the samples decreased with increasing of the heat-treatment temperature. Heat treatment is assumed to result in the removal of the residual water from the as-prepared sample and improvement in crystallinity. We carried out the heat treatment of the samples at temperatures >500°C, leading to the melting of powders. Thus, CsVO₃ cannot be synthesized by heat treatment at temperatures greater than 500°C.

Figures 2(a) and 2(b) depict the TEM images of the samples that were as-prepared and heat-treated at 200°C, and **Fig. 2(c)** shows the SEM image of the sample heat-treated at 400°C. The particle sizes of the as-prepared sample and of those heat-treated at 200 and 400°C were 200–300, 400–500 nm, and 1–3 μm, respectively. The particle size of the resulting CsVO₃ phosphor increased with increasing heat-treatment temperature, demonstrating that the particle size of CsVO₃ can be controlled from sub-hundred nanometer to sub-micrometer scale by changing the heat-treatment temperature. Controlling the CsVO₃ phosphor

Fig. 3. PL properties of (a) the as-prepared CsVO₃ powder, (b) the CsVO₃ powder heat-treated at 200°C and (c) the CsVO₃ powder heat-treated at 400°C.

particle size assumed to cause easily CsVO₃ phosphor to implementation on a white light LED and EL devices.

Figure 3 shows the PL spectra of the resulting CsVO₃ powders under various heat-treatment temperatures, and the inset image is obtained from phosphor subjected to heat treatment at 200°C under UV irradiation with a wavelength of 365 nm using a Hg lamp. Where, the around 250 nm peaks on the excitation spectra and the around 700 nm spectra on the emission spectra was attributed to the Xe lamp source. From the PL spectra, it is evident that the excitation at 350 nm produced white luminescence of the CsVO₃ phosphor, with a broad peak at 510 nm for all the phosphor samples. The PL intensities of samples heat-treated at 200 and 400°C were 1.5 times and 1.8 times larger than that of the as-prepared sample. This increase in PL intensities was attributed to the removal of residual water from the phosphor, improvement of the crystallinity, and enlargement of the particles. The XRD, TEM, SEM, and PL results reveal that CsVO₃ nanoparticles can be synthesized at temperatures from room temperature to 400°C by the solution route.

In previous reports,³⁾ CsVO₃ phosphor was synthesized by a conventional solid-state reaction, and the PL peak position of

Fig. 4. The deconvoluted PL pattern (Em1 and Em2, dashed lines) of the CsVO₃ powder heat-treated at 200°C.

these particles was around 520–530 nm. On the other hand, the PL peak position of the sample in the present study was 510 nm, and the peak value shifted to the low-wavelength region. CsVO₃ shows two PL peaks (Em1, Em2),⁷⁾ and we too observed these Em1 and Em2 peaks. We carried out deconvolution of the PL spectrum of the sample heat-treated at 200°C, and the result is shown in **Fig. 4**. The Em2/Em1 peak area ratio for the phosphor was 0.20. Where, The Em1 and Em2 peaks were 2.43 and 2.05 eV, respectively. We evaluated the Em2/Em2 value of the previous study⁷⁾ in which the phosphor was synthesized by a solid-state reaction, and that value was 0.53. In the present study, Em1 of the phosphor was much larger than Em2, so the peak positions in the present study shifted to lower-wavelength region. Thus, the synthesis method for the CsVO₃ phosphor determines the PL peak positions. Furthermore, the V-IPA (peroxo-isopolyvanadic acid) was used as vanadium source, the source V-IPA material include excess oxygen. Thereby the resulting CsVO₃ phosphor

assumed to be low oxygen defect, and assumed to cause varying the Em2/Em1 ratio comparison with the Em2/Em1 ratio in the previous report.⁷⁾

4. Conclusion

White-light-emitting CsVO₃ nanoparticles were successfully synthesized by a solution route using V-IPA at around room temperature. The CsVO₃ phosphor was prepared within a wide range of heat-treatment temperatures, and the particle size of the phosphor could be controlled by varying the heat-treatment temperatures. The resulting CsVO₃ showed white light luminescence. For the CsVO₃ prepared by the present method, the Em1 PL peak intensity was higher than the Em1 PL peak intensity. This result is different from that for the phosphor prepared by the other method. The synthesis method is therefore assumed to affect the PL properties and Em1 and Em2 peak positions for CsVO₃ phosphor.

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