

# Photoluminescence Characterization of Zn- and Cs-Vanadate Phosphors

Tingting Li, Zentaro Honda, Takeshi Fukuda, Jiaolian Luo and Norihiko Kamata  
Graduate School of Science and Engineering, Saitama University, 255 Shimo-Ohkubo,  
Sakura-ku, Saitama 338-8570, Japan

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Abstract: We synthesized  $Zn_3V_2O_8$ ,  $CsVO_3$  and  $Cs_3VO_4$  by sol-gel process and studied their crystalline and luminescent properties. By optimizing the sintering conditions, pure phases of aim samples including  $Cs_3VO_4$  were obtained. The annealing temperatures of 450°C for  $CsVO_3$ , 600°C for  $Cs_3VO_4$ , respectively, are lower than that of 750°C for  $Zn_3V_2O_8$  at the same duration of 12h. The  $Cs_3VO_4$  showed quantum yield of 90% with the half-width of 120nm. It became clear that the Cs-V-O system, especially  $Cs_3VO_4$ , is promising for white LED applications.

## 1 INTRODUCTION

White light-emitting diodes (W-LEDs) are replacing traditional incandescent and fluorescent lamps due to their superior efficiency, lifetime, and controllability of lighting environment (Li et al., 2013). However, recent widespread W-LEDs, realized by blue LED and yellow phosphor of Ce-doped yttrium aluminum garnet, lack red emission component and show a low color rendering index (CRI) (Kim et al., 2009). It is necessary, therefore, to find phosphor materials with higher CRI together with keeping efficiency and reliability. As a kind of efficient phosphor materials, a family of vanadates has been widely investigated for various types of W-LEDs and flat-panel displays due to their better chromaticity (Huang et al., 2012); (Nakajima et al., 2009).

The  $VO_4$  unit of a central vanadium ion and coordinating four oxygen ions in a tetrahedral (Td) symmetry is known as the luminescent center of the vanadate group. Unlike sharp emission lines due to 4f transitions of rare earth ions as  $Eu^{3+}$ ,  $Tb^{3+}$  etc., a family of zinc and cesium vanadates,  $Zn_3V_2O_8$ ,  $CsVO_3$  and  $Cs_3VO_4$ , shows efficient and broad emission spectra in a visible wavelength region. Each  $VO_4$  tetrahedron in  $Zn_3V_2O_8$  is isolated in an orthorhombic structure, while that in  $CsVO_3$  is two-dimensionally arrayed as the  $VO_4$  sheet in an orthorhombic pyroxene structure (Nakajima et al.,

2010).

In the present work, we synthesized  $Zn_3V_2O_8$ ,  $CsVO_3$  and  $Cs_3VO_4$  by a sol-gel method and studied their X-ray diffraction (XRD) patterns, surface images, photoluminescence (PL), PL excitation (PLE) spectra and the value of PL-quantum yield (QY). The synthesized  $Cs_3VO_4$  was most efficient with the PL-QY of 90%. Different luminescence properties and synthesis conditions among three phosphors were discussed.

## 2 EXPERIMENTAL

### 2.1 Preparation

We chose  $Zn(CH_3COO)_2 \cdot 2H_2O$ ,  $Cs_2CO_3$  and  $NH_4VO_3$  as starting materials of  $Zn_3V_2O_8$ ,  $CsVO_3$  and  $Cs_3VO_4$  by a sol-gel process. First, we weighed these starting materials, and dissolved them in aqueous ammonia, respectively. The first stirring step was performed for two hours with 250 rpm at room temperature (RT) in order to prevent the evaporation of aqueous ammonia and make sure that materials fully react with each other in ionic states. Then the temperature was increased to 80°C with keeping 250 rpm stirring until the solution became a semitransparent gel. Second, the semitransparent gel was dried at 120°C about 4h, then ground thoroughly by a mortar, and transferred into a crucible which

was put into a sintering oven. After the sintering process, a yellowish powder of CsVO<sub>3</sub> (450°C, 12h) or a white powder of Cs<sub>3</sub>VO<sub>4</sub> (600°C, 12h) were obtained.

In case of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> (750°C, 24 h), it also contained the phase of Zn<sub>2</sub>V<sub>2</sub>O<sub>7</sub> or Zn<sub>4</sub>V<sub>2</sub>O<sub>9</sub>. (Li et al., 2013) In order to obtain a uniform crystalline phase, the inchoate sample was placed into ethanol solution again. It was stirred first at 250 rpm for 2h at RT, then raised the temperature to 80°C until the ethanol solution was completely removed. After that, we sintered it again at the temperature of 750°C during 24h, and at last obtained a yellowish powder of pure Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>.

## 2.2 Characterization

Synthesized samples were ground again and then transferred onto a glass plate, and the X-ray diffraction (XRD) patterns were measured by using a RINTUltimaIII (RIGAKU) diffractometer with Cu K $\alpha$  radiation (40 kV 9.40 mA). The samples were identified by Joint Committee on Powder Diffraction Standards (JCPDS) files, and the relative percentages of each phase were estimated from the total area under the most intense diffraction peaks (Francisco et al., 2007). The surface morphology was observed by using a S-4100 (HITACHI) scanning electron microscopy (SEM).

The photoluminescence (PL) and PL excitation (PLE) spectra of each sample, pressed inside a circular dip of 4 mm diameter with 1 mm depth on a Cu-holder, were measured by a FluoroMax-3 (Horiba Jovin-Yvon) spectrophotometer. The PL-QY was determined by a QEMS-2000 (Systems Engineering) by an excitation light of an LED with the peak wavelength of 375 nm. The PL-QY was obtained by a comparison between the PL spectrum of the sample and the scattered excitation light when a standard diffuser was placed at the sample position (Li et al., 2013). All measurements were performed at room temperature.

## 3 RESULTS AND DISCUSSION

### 3.1 Crystalline Phase Formations

Figure 1 shows the XRD patterns of synthesized samples with corresponding homologous databases. We can see that our experimental data of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> and CsVO<sub>3</sub> agreed well with the standard PDF cards of No.34-0378 (Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>) and No.033-0381 (CsVO<sub>3</sub>), respectively. No PDF data were found as

for the case of Cs<sub>3</sub>VO<sub>4</sub> phosphor, but the principal patterns of our synthesis were consistent with those of a commercial powder from Alfa.

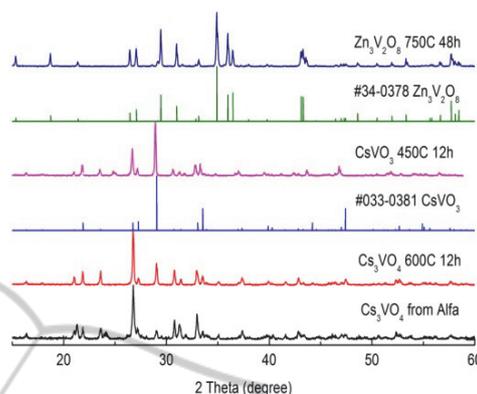


Figure 1: XRD patterns for vanadates.

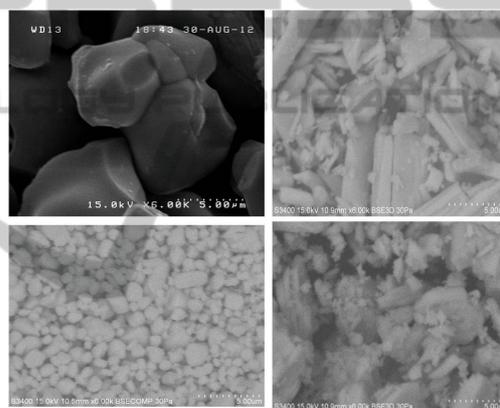


Figure 2: SEM images for vanadate phosphors: (a) Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> 750°C 12h, (b) CsVO<sub>3</sub> 450°C 12h, (c) Cs<sub>3</sub>VO<sub>4</sub> 600°C 12h, and (d) Cs<sub>3</sub>VO<sub>4</sub> 450°C 12h.

Surface morphologies of synthesized samples were observed by SEM. Resultant images of synthesized vanadates were shown in Figure 2(a)-(d). In case of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub> (750°C 12h), each block throughout the observing volume seems to be homogeneously crystallized with a typical size of several  $\mu$ m as shown in Fig. 2(a).

Fairly irregular particles both on size and shape were observed in CsVO<sub>3</sub> (450°C 12h) as shown in Figure 2 (b). In contrast, the morphology of Cs<sub>3</sub>VO<sub>4</sub> (600°C 12h) was relatively homogeneous with particle sizes about 1-3 $\mu$ m as shown in Figure 2 (c). At 450 °C 12h, however, the dregs-like particles were found at the surface of the Cs<sub>3</sub>VO<sub>4</sub> as shown in Figure 2(d).

### 3.2 The Excitation and Emission Spectra

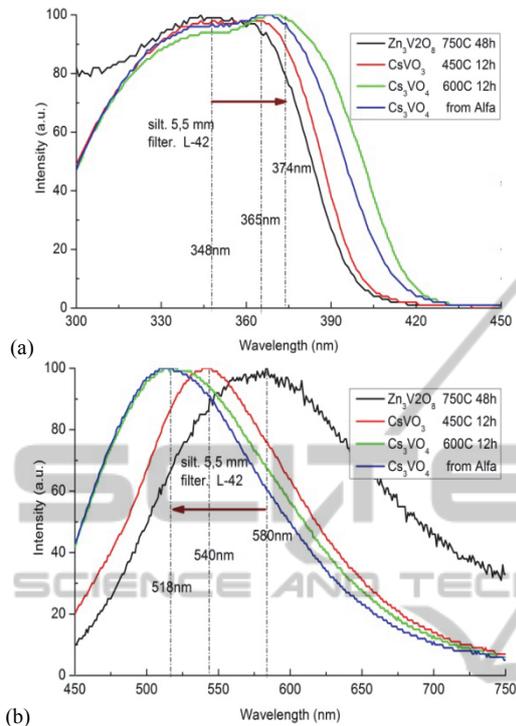


Figure 3: The PLE (a) and PL (b) spectra of the vanadate phosphors.

Figure 3(a) and (b) show the PLE and PL spectra of these vanadate phosphors, respectively. The broad PLE band ranging from 300nm to 400nm enables these vanadates to be combined with UV or blue LEDs. Meanwhile, Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, CsVO<sub>3</sub> and Cs<sub>3</sub>VO<sub>4</sub> produce intense emission from yellowish white to mid white band with the FWHM of 180, 110 and 120nm, respectively. Meaningful spectral shifts were observed, though these originate from the same luminescence center VO<sub>4</sub> at transitions among 3T<sub>2</sub>, 3T<sub>1</sub> and 1A<sub>1</sub> levels. Compared with the PLE and PL peaks of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, those of CsVO<sub>3</sub> shift about 20 and 40nm, and those of Cs<sub>3</sub>VO<sub>4</sub> about 30 and 60nm, respectively.

### 3.3 The PL-Quantum Yield (PL-QY)

The PL-QY at 375nm excitation is listed in Table 1 together with the synthesis condition, the FWHM, the peak wavelengths of the PLE and PL spectra. The QY value of 90% was obtained in the case of Cs<sub>3</sub>VO<sub>4</sub> which is higher than that of 76% obtained by commercial powder from Alfa. We consider that the difference between Cs<sub>3</sub>VO<sub>4</sub> and CsVO<sub>3</sub> is

important for their application to W-LEDs.

## 4 CONCLUSIONS

In conclusion, vanadate phosphors of Zn<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, CsVO<sub>3</sub> and Cs<sub>3</sub>VO<sub>4</sub> were synthesized by the sol-gel method. By comparing the difference of crystalline structure and luminescence properties among the three, the Cs<sub>3</sub>VO<sub>4</sub> with the heating process at 600°C during 12h showed highest PL-QY of 90% and is promising for the application to the W-LEDs.

Table 1: Comparison between the three vanadate phosphors.

Samples	Zn <sub>3</sub> V <sub>2</sub> O <sub>8</sub>	CsVO <sub>3</sub>	Cs <sub>3</sub> VO <sub>4</sub>
Synthesis conditions	750 °C 48h	450 °C 12h	600 °C 12h
FWHM (nm)	180	110	120
λ <sub>ex</sub> (nm)	348	365	374
λ <sub>em</sub> (nm)	580	540	518
PL-QY (%)	52	81	90

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