

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*

Keywords: $Zn_3V_2O_8$, $CsVO_3$, Cs_3VO_4 , Sol-gel Process, Quantum Yield.

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 CsVO₃ (450°C, 12h) or a white powder of Cs₃VO₄ (600°C, 12h) were obtained.

In case of Zn₃V₂O₈ (750°C, 24 h), it also contained the phase of Zn₂V₂O₇ or Zn₄V₂O₉. (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 Zn₃V₂O₈.

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 α 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 Zn₃V₂O₈ and CsVO₃ agreed well with the standard PDF cards of No.34-0378 (Zn₃V₂O₈) and No.033-0381 (CsVO₃), respectively. No PDF data were found as

for the case of Cs₃VO₄ phosphor, but the principal patterns of our synthesis were consistent with those of a commercial powder from Alfa.

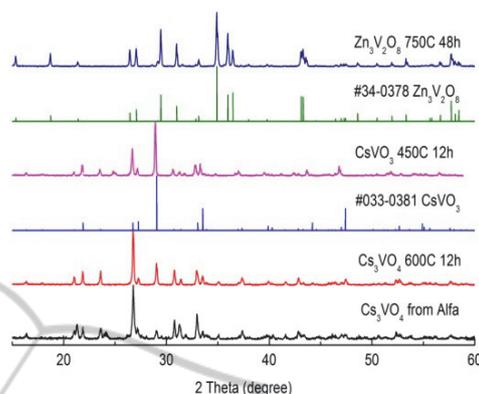


Figure 1: XRD patterns for vanadates.

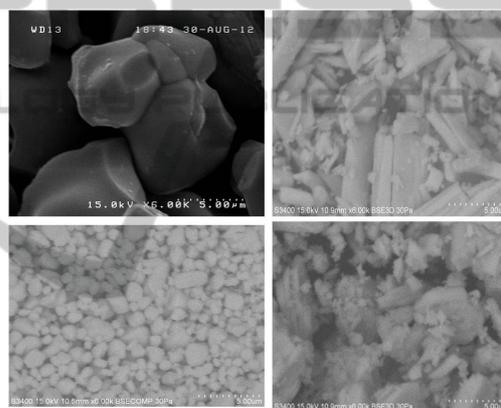


Figure 2: SEM images for vanadate phosphors: (a) Zn₃V₂O₈ 750°C 12h, (b) CsVO₃ 450°C 12h, (c) Cs₃VO₄ 600°C 12h, and (d) Cs₃VO₄ 450°C 12h.

Surface morphologies of synthesized samples were observed by SEM. Resultant images of synthesized vanadates were shown in Figure 2(a)-(d). In case of Zn₃V₂O₈ (750°C 12h), each block throughout the observing volume seems to be homogeneously crystallized with a typical size of several μ m as shown in Fig. 2(a).

Fairly irregular particles both on size and shape were observed in CsVO₃ (450°C 12h) as shown in Figure 2 (b). In contrast, the morphology of Cs₃VO₄ (600°C 12h) was relatively homogeneous with particle sizes about 1-3 μ m as shown in Figure 2 (c). At 450 °C 12h, however, the dregs-like particles were found at the surface of the Cs₃VO₄ as shown in Figure 2(d).

3.2 The Excitation and Emission Spectra

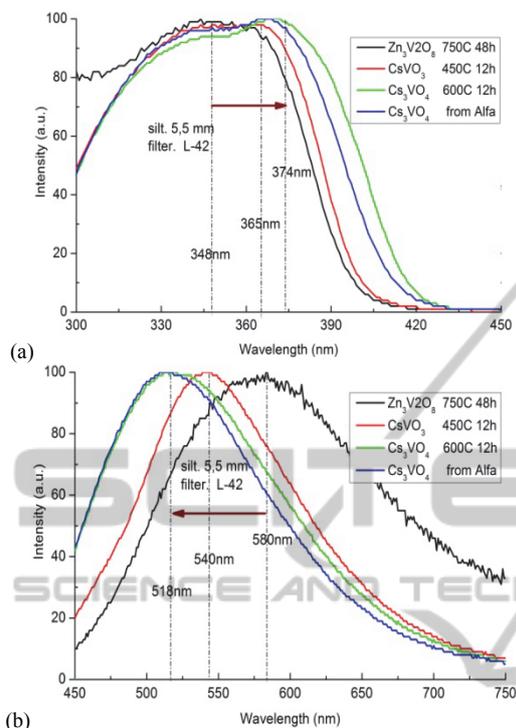


Figure 3: The PLE (a) and PL (b) spectra of the vanadate phosphors.

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, $Zn_3V_2O_8$, $CsVO_3$ and Cs_3VO_4 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_4 at transitions among $3T_2$, $3T_1$ and $1A_1$ levels. Compared with the PLE and PL peaks of $Zn_3V_2O_8$, those of $CsVO_3$ shift about 20 and 40nm, and those of Cs_3VO_4 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_3VO_4 which is higher than that of 76% obtained by commercial powder from Alfa. We consider that the difference between Cs_3VO_4 and $CsVO_3$ is

important for their application to W-LEDs.

4 CONCLUSIONS

In conclusion, vanadate phosphors of $Zn_3V_2O_8$, $CsVO_3$ and Cs_3VO_4 were synthesized by the sol-gel method. By comparing the difference of crystalline structure and luminescence properties among the three, the Cs_3VO_4 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	$Zn_3V_2O_8$	$CsVO_3$	Cs_3VO_4
Synthesis conditions	750 °C 48h	450 °C 12h	600 °C 12h
FWHM (nm)	180	110	120
λ_{ex} (nm)	348	365	374
λ_{em} (nm)	580	540	518
PL-QY (%)	52	81	90

REFERENCES

- C. Li et al, 2013. 'Photoluminescence and energy transfer studies on Ce^{3+}/Eu^{2+} co-doped $Ba_3Si_6O_{12}N_2$ phosphor for white light emitting diodes'. *Opt. Communications* 295, pp. 129-133.
- J. Kim et al, 2009. 'Nanocrystalline $Y_3Al_5O_{12}:Ce$ phosphor-based white light-emitting diodes embedded with $CdS:Mn/ZnS$ core/shell quantum dots'. *Mater Lett* 63, pp. 614-616.
- Y. Huang et al, 2012. 'Novel yellow-emitting phosphors of $Ca_5M_4(VO_4)_6$ ($M=Mg, Zn$) with isolated VO_4 tetrahedra'. *Opt. Express* 20(4), pp. 4360-4367.
- T. Nakajima et al, 2009. 'A revisit of photoluminescence property for vanadate oxides AVO_3 ($A:K, Rb$ and Cs) and $M_3V_2O_8$ ($M:Mg$ and Zn)'. *J. Lumin.* 129(12), pp. 1598-1601.
- T. Nakajima et al. 2010. 'Correlation between Luminescence Quantum Efficiency and Structural Properties of Vanadate Phosphors with Chained, Dimerized, and Isolated VO_4 Tetrahedra'. *J. Phys. Chem. C*, 114, pp. 5160-5167.
- T. Li, Z. Honda et al, 2013. 'Fabrication and characterization of $Zn_3V_2O_8$ phosphor by sol-gel process'. *J Sol-Gel Sci Technol* 66, pp. 225-230.
- M. M. Francisco, J. V. Miriam, P. Heriberto, 2007. 'Micro-structural development of ZnO pellets doped with different Vanadium Oxides (V_2O_5 and V_2O_3)'. *Int. J. Appl. Ceram. Technol.*, 4(6), pp. 564-570.