Sintering Condition and Optical Properties of Zn$_3$V$_2$O$_8$ Phosphor

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ABSTRACT

One of promising phosphors in vanadium oxide family, Zn$_3$V$_2$O$_8$, was successfully synthesized by a solid state reaction of ZnO and V$_2$O$_5$. Characterization by XRD, photoluminescence (PL) and SEM was done for samples with different temperature and time in the sintering process. Residual percentage of secondary Zn$_2$V$_2$O$_7$ phase, subsidiary ZnO and Zn$_4$V$_2$O$_9$ phases was dependent on the sintering condition. The crystalline purity (CP) was defined by the integral intensity ratio of Zn$_3$V$_2$O$_8$ phase and that of residual phases in XRD spectra, which showed a reasonable correspondence to the PL quantum yield (QY) of each sample. The highest QY exceeding 50% was obtained by the sintering condition of 750°C for 48 h. It turned out that the CP value is a good measure of high QY, which can be utilized for developing phosphor materials and controlling their processes.

Keywords: Zn$_3$V$_2$O$_8$ Phase; XRD; Crystalline Purity; Internal Quantum Efficiency; Photoluminescence

1. Introduction

Development of phosphor materials has been accelerated with the expansion of lighting and display applications as well as the progress on material science [1]. Through continuous efforts for improving efficiency and stability, BaMg$_2$Al$_{16}$O$_{27}$:Eu$^{3+}$, CeMgAl$_{11}$O$_{19}$:Tb$^{3+}$, Y$_2$O$_3$:Eu$^{3+}$ etc. were utilized for fluorescent lamps [2], and CaWO$_4$:Pb$^{2+}$, Zn$_2$SiO$_4$:Mn$^{2+}$, YVO$_4$:Eu$^{3+}$ etc. for plasma display panels [3]. The evolution of InGaN/GaN blue light emitting diode (LED) [4-6] provided cost-effective LED lamps in combination with yellowish phosphor YAG:Ce$^{3+}$ and its variations [7]. The excitation density of such phosphor materials is higher than that of previous applications due to small emission volume and adjacent location of LED chips. As these LED lamps substitute for incandescent lamps, the quality of white light was added to one of key issues as well as efficiency and reliability. It is of crucial importance, therefore, to develop phosphor materials suitable for LED lamp applications with higher color rendering and reliable properties.

Unlike sharp emission lines due to 4f transitions of rare earth ions as Eu$^{3+}$, Tb$^{3+}$ etc., a family of vanadates, Zn$_V$O$_S$, CsVO$_3$ et al., shows efficient and broad emission spectrum in a visible wavelength region. Each VO$_4$ tetrahedron in Zn$_3$V$_2$O$_8$ 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 [8]. A two-component oxide system, zinc oxide and vanadium pentoxide, ZnO-V$_2$O$_5$, has been studied by many researchers [8-15]. With different mixing ratio of Zn, V and O, and different sintering conditions, there exists a number of different compositional phases as Zn$_4$V$_2$O$_9$, Zn$_2$V$_2$O$_7$ and Zn$_V$O$_S$, etc. [9]. Though the Zn$_3$V$_2$O$_8$ phase is preferable for an efficient visible light emission, detailed study on the crystalline purity and light emission properties of the Zn$_3$V$_2$O$_8$ phosphor was rarely reported.

In this work, we fabricated an efficient Zn$_3$V$_2$O$_8$ phosphor by controlling the temperature and time duration of the sintering process and obtained a reasonable correspondence between crystalline and luminescent properties.

2. Material and Methods

2.1. Preparation of Zn$_3$V$_2$O$_8$

The Zn$_3$V$_2$O$_8$ phosphor was synthesized by a solid-state reaction of ZnO and V$_2$O$_5$, both with 99.99% purities. The mixing ratio of constituent source materials was fixed to the stoichiometric value as ZnO:V$_2$O$_5$ = 3:1. They were ground 4 h by a mortar, pressed into pellets, and then transferred into a crucible which was put into a sintering oven. The sintering was performed in the air with atmospheric pressure. The sintering temperature was varied between 600°C and 800°C, and the sintering time between 12 and 72 h. We obtained a slightly yellowish white powder of Zn$_3$V$_2$O$_8$ after sintering, which
was characterized by the following schemes.

2.2. Scheme of Measurement

The powder of Zn$_3$V$_2$O$_8$ was ground again and then transferred onto a glass plate, and the X-ray diffraction (XRD) measurement was performed by using a RINT-UltimaIII (RIGAKU) diffractometer with Cu Kα radiation (40 kV × 40 mA). The surface morphology was observed by using a S-4100 (HITACHI) scanning electron microscope (SEM).

The photoluminescence (PL) and PL excitation (PLE) measurements of each sample, pressed inside a circular dip of 4mm diameter with 1mm depth on a Cu-holder, were performed by a FluoroMax-3 (Horiba Jovin-Yvon) spectrophotometer [16]. The excitation wavelength of PL measurement was 340 nm with the density of 5 mW/cm$^2$, and the observation wavelength of PLE was set in the PL spectral peak of 585 nm.

The PL quantum yield (QY) was determined by a QEMS-2000 (Systems Engineering) PL quantum yield measurement system, which was composed of an LED with the peak wavelength of 375 nm, a calibrated integrating sphere, and a multichannel spectrometer. Here, either a standard diffuser or the sample on the same quartz glass-holder was placed at the window of the integrating sphere and irradiated by the LED. The photon number absorbed by the sample $N_a$ was calculated from the spectral difference between two cases at the irradiation wavelength, and the emitted photon number $N_e$ was obtained by the PL spectrum from the sample. The value of QY was defined by the ratio $N_e/N_a$. All measurements were performed at room temperature.

3. Results and Discussion

3.1. XRD Patterns

Figure 1 shows the XRD patterns of samples with different sintering temperature between 600°C and 800°C at the fixed sintering time of 12 h. The principal XRD peak positions of all samples coincided with those of the Zn$_3$V$_2$O$_8$ phase according to Joint Committee on Powder Diffraction Standards (JCPDS card) [17]. Its crystallographic structure is the orthorhombic space group Cmca with lattice parameters $a = 6.28(8)$ Å, $b = 11.53(6)$ Å and $c = 8.28(2)$ Å [Z = 4] (JCPDS 34-0378): the (1 2 2) diffraction peak is dominant among others. The secondary phase observed in every spectrum was attributed to the Zn$_2$V$_2$O$_7$ phase (JCPDS 016-0830) as shown by asterisks in the figure: the (0 2 2) peak is the highest one. The intensity ratio of the (0 2 2) peak to the (1 2 2) peak of the Zn$_3$V$_2$O$_8$ phase showed a minimum point at the temperature of 750°C.

Besides these Zn$_3$V$_2$O$_8$ and Zn$_2$V$_2$O$_7$ phases, subsidiary phases which bring forth residual peaks were dependent on the sintering temperature. At the temperature from 600°C to 750°C, peaks of ZnO (JCPDS 65-3411) were resolved in the XRD pattern as shown by arrows, while those of Zn$_2$V$_2$O$_7$ phase (JCPDS 01-077-1757) appeared above 760°C as shown by stars in the figure. With increasing temperature, the former intensity decreased but that of the latter increased, showing their minimum point at the temperature around 750°C.

Next, we fixed the sintering temperature to the 750°C, and varied the sintering time from 12 h to 72 h as shown in Figure 2. Here the peak intensity of the Zn$_2$V$_2$O$_7$ phase decreased and that of ZnO phase disappeared with increasing the time from 12 h to 48 h. It became clear from the experiment that an enough sintering time of 48 h is necessary for reducing the Zn$_2$V$_2$O$_7$ and other phases at the temperature of 750°C.

3.2. Photoluminescence Characteristics

The optical properties of Zn$_3$V$_2$O$_8$ powder samples were characterized by PL and PLE measurements. At the fixed time of 12 h, PL and PLE spectra of samples with different sintering temperature were shown in Figure 3. In the PLE spectrum, each sample showed a broad absorption band centered at around 340 nm. A sub-peak at 380 nm, which was attributed to ZnO, was clearly observed in samples treated below 740°C. The PL spectra showed a broad emission band between 450 nm and 750 nm with a peak wavelength at about 585 nm [18]. The full width at half maximum (FWHM) of the emission band was 180 nm. The highest PL intensity was obtained at the sintering condition of 750°C from this experiment.

Then PL and PLE spectra were compared in Figure 4 as a function of the sintering time at the fixed temperature of 750°C. By increasing the sintering time from 12 h to 48 h, the PL intensity increased with the ratio of...
24.3%. Further increase in time, longer than 60 h, changed the purity of the Zn$_3$V$_2$O$_8$ phase, and decreased the PL intensity. Therefore, it is confirmed that both the temperature and the time of sintering process affect light emission properties, indicating the necessary condition of 750°C and 48 h.

3.3. SEM Observation

Surface morphology of synthesized samples was observed by SEM. Resultant images of samples sintered at 700°C, 750°C and 760°C, all during 12 h, were shown in Figures 5(a)-(c). With increasing the sintering temperature, dregs-like particles at the surface of each block became less dominant and the size of each block increased. Figure 5(d) shows the image of the sample sintered at 750°C for 48 h. With increasing the sintering time from 12 h to 48 h, such dregs-like particles in Figure 5(b) completely disappeared and the size of each block increased, even larger than that of 760°C of Figure 5(c). No significant difference was observed between samples sintered at 750°C and 760°C in case of 48 h duration. The SEM image of the sample under suitable sintering process, shown in Figure 5(d), yielded a typical size of several µm, and was almost homogeneous throughout the observing volume [19-21]. Above result of SEM observation is considered to have direct correspondence with the crystallization process of Zn$_3$V$_2$O$_8$ [9], indicating its sintering temperature and time dependence distinctly.

3.4. Crystalline Purity and PL Quantum Yield

In order to determine the dominance of Zn$_3$V$_2$O$_8$ phase over other phases quantitatively, we defined a crystalline purity (CP) as the integral intensity ratio of Zn$_3$V$_2$O$_8$
peaks and that of the residual peaks including Zn$_2$V$_2$O$_7$, ZnO and Zn$_2$V$_2$O$_9$ phases in the diffraction angle between 15 and 45 degree of XRD spectra. Calculated CP values of samples sintered at 750°C with different time were listed together with their values of QY in Table 1. The highest CP of 97.5% was obtained for the sample sintered during 48 h. It is quite important that the sample showed highest value of QY: the highest QY value of 51% is similar to the previous report [13].

Combining the result of SEM observation, the correspondence between the CP and the QY implies that the crystal growth of Zn$_3$V$_2$O$_8$ phase with an enough scale is indispensable for an efficient light emission. The sintering process at 750°C with time duration of 48 h is necessary for such high CP value. In the course of improving Zn$_3$V$_2$O$_8$ phosphor and controlling its process, the CP value can be utilized as a good measure of high QY. Such continuing steps toward optimization lead us to fabricate efficient and stable phosphor materials suitable for LED lamp applications.

4. Conclusions

One of promising vanadate phosphor Zn$_3$V$_2$O$_8$ was synthesized by solid reaction of ZnO and V$_2$O$_5$. Crystallographic and optical characterization was performed with varying the sintering temperature between 600°C and 800°C and the sintering time between 12 h and 72 h. Aside from the principal Zn$_3$V$_2$O$_8$ phase, there observed secondary Zn$_2$V$_2$O$_7$ phase and subsidiary ZnO and Zn$_2$V$_2$O$_9$ phases, depending on the sintering condition.

The CP value, defined by the ratio of the integrated intensity of Zn$_3$V$_2$O$_8$ phase and that of residual phases in the diffraction angle between 15 and 45 degree in the XRD spectra, showed a reasonable correspondence with the value of QY. In order to obtain high QY, the sintering temperature at 750°C with the duration of 48 h is preferable. It turned out, therefore, that the CP value can be utilized as a good measure of high QY in Zn$_3$V$_2$O$_8$ phosphor materials.

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REFERENCES


Table 1. Crystalline purity (CP) and PL quantum yield (QY) as a function of sintering time at 750°C.

<table>
<thead>
<tr>
<th>Sample (750°C)</th>
<th>12 h</th>
<th>24 h</th>
<th>36 h</th>
<th>48 h</th>
<th>60 h</th>
<th>72 h</th>
</tr>
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<tr>
<td>CP (%)</td>
<td>88.5</td>
<td>95.9</td>
<td>96.6</td>
<td>97.5</td>
<td>96.6</td>
<td>96.7</td>
</tr>
<tr>
<td>QY (%)</td>
<td>24</td>
<td>36</td>
<td>48</td>
<td>51</td>
<td>49</td>
<td>48</td>
</tr>
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