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Luminescence of YPO_4:Zr and YPO_4:Zr,Mn under Vacuum Ultraviolet Excitation

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Novel UV and blue phosphors, YPO_4:Zr and YPO_4:Zr,Mn, respectively, are synthesized and investigated. YPO_4:Zr shows the emission about 290 nm assigned to the charge transfer transition of O-Zr. The excitation spectrum of the emission has main band peaked at 175 nm. The codoped phosphor YPO_4:Zr,Mn shows the emission peaked at 477 nm assigned to the d-d transition of Mn^{2+} within $3d^5$ configuration. The excitation bands of the blue emission are around 152 and 193 nm. YPO_4:Mn does not show any emission and the 290 nm emission observed for YPO_4:Zr is diminished for YPO_4:Zr,Mn. It is suggested that Zr plays an important role in the excitation of the Mn blue emission of YPO_4:Zr,Mn. The emission wavelength of YPO_4:Zr,Mn is remarkably short compared with the usual Mn^{2+} activated phosphors.

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Recently, the luminescence of the phosphors in the vacuum ultraviolet (VUV) region has become important for the improvement of plasma display panels (PDP) and the development of the Hg-free, rare-gas discharge lamps. The light of 147 and 172 nm emitted by Xe plasma is used in both devices for the excitation of phosphors. In the case of the 147 nm excitation, since the wavelength is shorter than the absorption edge of the host crystal, the penetration depth of the excitation light into phosphor particles is so shallow that most of the excitation light is absorbed by the host crystal. Therefore it is necessary for VUV phosphors to have a high energy-transfer rate from the host to the activator.

On the other hand, at the present time PDP blue-emitting phosphors activated with Eu^{2+} are used, for the phosphors emit brightly and have a suitable color. Among such phosphors, the most popularly used is $BaMgAl_{10}O_{17}$:Eu (BAM). BAM has the problem of how to reduce the drop of luminance during the panel fabrication process and in the use of the panels. Some approaches to solve this problem have been made through the improvement of the process of preparation of the phosphor.[1] An alternative host activated with Eu^{2+}, $CaMgSi_2O_6$, *e.g.*, has also been proposed.[2] The authors have the question, however, whether an activator other than Eu^{2+} is possible for the VUV-excited blue phosphor.

To our knowledge, there are not many elements that show efficient light emission in the visible range when doped with transparent host crystals. Mn^{2+} seems to be a candidate for alternative to Eu^{2+}. The emission wavelength of the known Mn-activated phosphors is distributed in a rather wide range, from green to red.[3] In addition, there are some efficient Mn-activated phosphors known, although some of them need to be codoped with an element (sensitizer) together with Mn. In this report, the luminescence of YPO_4 phosphors activated by Zr^{4+} and/or Mn^{2+} under VUV excitation is investigated.

Experimental

Preparation of phosphors.— As a starting material for the phosphor preparation, yttrium phosphate (YPO_4) was precipitated by mixing an aqueous solution of yttrium chloride into a solution of phosphoric acid that contains an excess of the acid at 350 K. The precipitate was then filtrated, dried, and calcined in air at 1073 K. Manganese oxalate (MnC_2O_4) was obtained as the precipitate through the reaction of manganese chloride and ammonium oxalate in aqueous solution. The precipitate was air-dried. The chemical analyses of the prepared materials were carried out in order to quantify the content of Y, Mn and P in the materials.

Phosphor samples, YPO_4:Zr and/or Mn, were synthesized as follows. Calculated amounts of above obtained materials, ZrO_2 and $(NH_4)_2HPO_4$ were mixed in a mortar. The mixture was fired in nitrogen flow at 1473 K for 3 h. All samples were a white-powder although some that contained a large amount of Mn were slightly pink, which is evidence that manganese is doped as Mn^{2+}. For the purpose of comparison, the samples, YPO_4:Zr,Mg and YPO_4:Zr,Zn, were also prepared, using MgO or ZnO instead of MnC_2O_4. ZrP_2O_7:Mn and $Mn_2P_2O_7$ samples were also prepared, in a similar method except the calcination temperature was 1273 K.

Powder X-ray diffraction was carried out for the YPO_4-based phosphor samples. All the pattern was composed mainly of the peaks assigned to YPO_4 (xenotime). The pattern of the sample that has 2.5 mol % Zr/Y + Zr, however, contains the trace of ZrP_2O_7, and the ZrP_2O_7 peaks are obvious in the pattern of the sample with 5.0 mol % of Zr. Thus it is considered that the solubility of Zr into YPO_4 is limited to the extent of a few mol percents of the Y sites. On the other hand, the peaks assigned to $Mn_2P_2O_7$ appear in the pattern of the sample that contain 5.0 mol % of Mn. The solubility of Mn into YPO_4 is estimated at less than 5 mol % of Y sites.

Measurement of luminescence.— Luminescence emission spectra and excitation spectra of each samples were recorded using the vacuum ultraviolet spectrofluorometer (Bunko Keiki Co., Ltd.), which was equiped with a deuterium lamp and the Seya-Namioka-type monochromator. All the measurements were carried out at room temperature. The luminescence of the commercial BAM:Eu phosphor (NP-107-06, Nichia Corporation) was also measurerd. The excitation spectra were calibrated, and the influence of the spectrum distribution of the light source is compensated, using sodium salicylate as the standard.

Results and Discussion

YPO_4:Zr.— Yttrium phosphate (YPO_4) activated only with Zr shows a broad emission in the ultraviolet region under vacuum ultraviolet excitation. Figure 1 shows the emission spectra of the sample with a Zr content of 2.5 mol % (Zr/Y + Zr). The peak of the emission is at 291 nm. The luminescence excitation spectrum of the sample, which was measured for the emission peak, is shown in Fig. 2, in which the excitation peak is at 176 nm and the shoulder is at about 155 nm.

The luminescence is obviously originated from Zr. YPO_4 has the zircon-type crystal structure (space group $I4_1$/amd).[4] The Zr ion doped in YPO_4 is thought to replace the Y site eightfold coordinated by oxygen ions, as it occupies in isostructural $ZrSiO_4$ (zircon). The luminescence of Zr as an emitting center has been reported for Cs_2ZrCl_6,[5] although there is no such example of the oxide materials. The emission peak and excitation peak of the chloride have been reported to be 451 and 258 nm. The luminescence of the present study can be understood by analogy with luminescence of oxygen-

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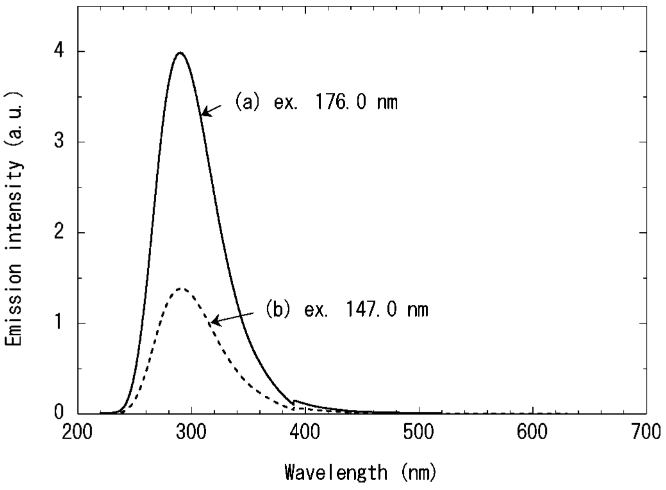

Figure 1. Emission spectra of YPO_4:Zr (2.5 mol %): (a) $\lambda_{ex} = 176.0$ nm (solid line), (b) $\lambda_{ex} = 147.0$ nm (broken line).

coordinated, closed-shell-type transition-metals (M^{m+} or MO_x^{n-} M: V, W, Nb, Mo, Ti, etc.).[6-8] It is known that their emission peaks are mainly in blue region. The luminescence of the present study is ascribed to the charge-transfer (CT) transition, the excitation to electron transfer O → Zr and the emission to Zr → O. Both the emission and excitation band are situated in a shorter wavelength region than in the above M-O system. The reason is thought to be that Zr^{4+} attracts electrons less than W^{6+}, Nb^{5+}, etc., and even Ti^{4+} because of its smaller positive charge or shielding effect by 3d, 4p, 5s electrons. Compared with the Zr-Cl system, the fact that O is more electronegative than Cl results in the larger transition energy and shorter luminescent wavelength in this work. Another example of the VUV excited luminescence of the closed-shell cation, has recently been reported for BO_3^{3-}, which emits at 310 nm.[9]

The Zr concentration dependence of emission intensities of YPO_4:Zr is shown in Fig. 3. The maximum of the intensity is situated around the point that Zr/Y + Zr = 2.5 mol %, and beyond that point, the intensity is gradually weakened.

YPO_4:Mn.—YPO_4 activated with Mn, concentrations of 0.5 and 2.5 mol %, were prepared and their luminescence studied. They both did not show any emission in the range from 250 to 750 nm under the VUV or UV excitation from 130 to 330 nm. The reason is thought to be that the absorption by which Mn^{2+} can be excited to the emitting level of luminescence is very weak, because it is a forbidden d-d transition. It is not the rare case that a phosphor activated only with Mn, without any sensitizer, does not show photoluminescence and only emits under excitation by electrons.[3]

YPO_4:Zr,Mn.—YPO_4 activated with both Zr and Mn shows ultraviolet and blue emission under VUV excitation. The emission spectra of a sample are shown in Fig. 4. The peak of the blue emission is at 477 nm and that of the UV emission is at 291 nm. The ratios of the height of the two peaks change under the excitation at different wavelengths. The excitation spectra of the same sample are shown in Fig. 5. The spectrum for the blue emission has two bands, the peaks of which are 152 and 193 nm. Additionally, the emission intensity is rising at 130 nm, the limit of measurement, which suggests that possibly there is another excitation band at <130 nm. The UV emission has an excitation band around 175 nm.

First, the blue emission is considered to originate from Mn^{2+} that replaces the Y site of YPO_4. A confirmation is the fact that neither

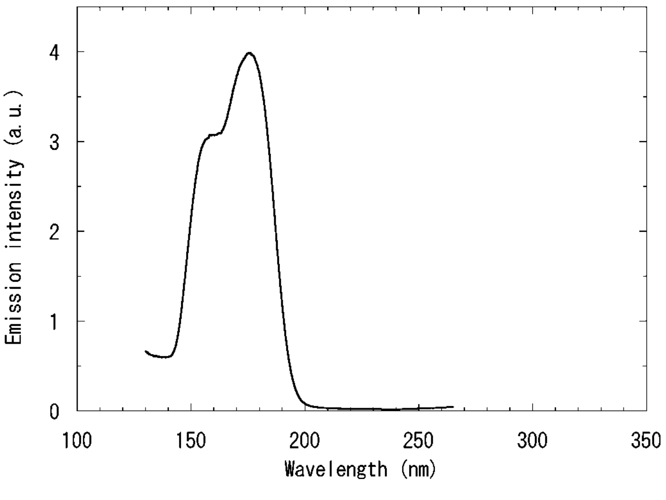

Figure 2. Excitation spectrum of YPO_4:Zr (2.5 mol %). $\lambda_{em} = 290.2$ nm.

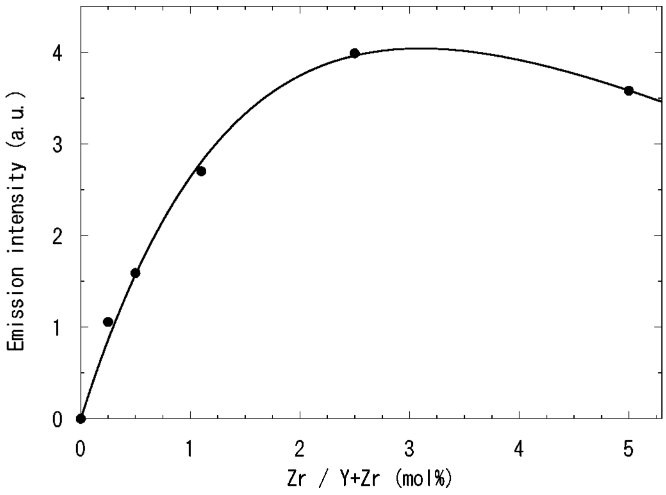

Figure 3. Concentration dependence of the emission intensity of YPO_4:Zr. 290 nm emission, $\lambda_{ex} = 175$ nm.

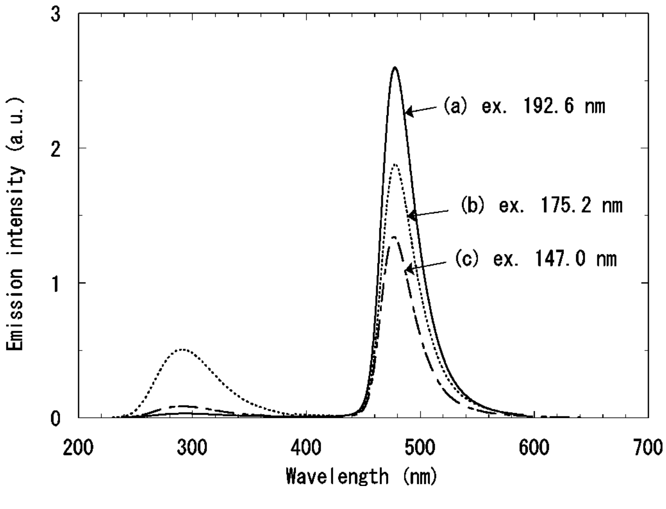

Figure 4. Emission spectra of YPO_4:Zr (1.1 mol %), Mn (1.1 mol %): (a) $\lambda_{ex} = 192.6$ nm (solid line), (b) $\lambda_{ex} = 175.2$ nm (dotted line), (c) $\lambda_{ex} = 147.0$ nm (dash-dotted line).

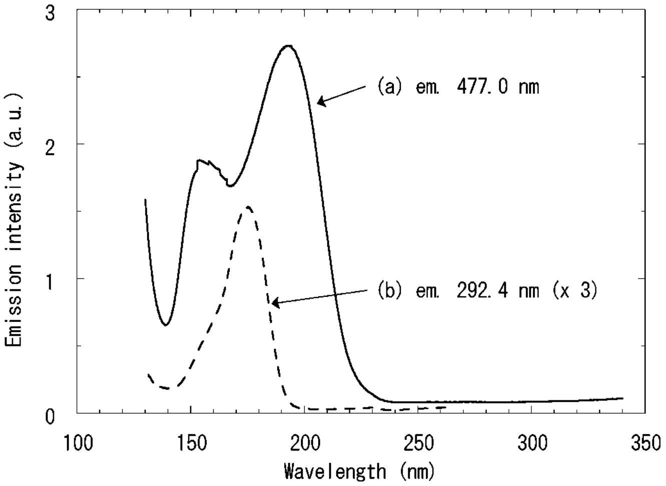

Figure 5. Excitation spectra of YPO_4:Zr (1.1 mol %), Mn (1.1 mol %): (a) $\lambda_{em} = 477.0$ nm (solid line), (b) $\lambda_{em} = 294.2$ nm, three times as measured data (broken line).

ZrP_2O_7:Mn nor $Mn_2P_2O_7$ show this blue emission. In addition, the blue emission is not likely to originate from the Zr center of YPO_4:Zr,Mn. Luminescence of YPO_4:Zr (2 mol %), Mg (2 mol %), and YPO_4:Zr (2 mol %), Zn (2 mol %) was measured. Both samples showed emissions only in the UV region under VUV excitation, which is very similar to the emission of YPO_4:Zr, though the intensity of the emission was weaker. Neither sample showed a blue emission like YPO_4:Zr,Mn. Therefore the possibility that the circumstances of the Zr center were changed by the addition of Mn and the wavelength of Zr emission shifted is rejected. For the incorporation of Mg^{2+} or Zn^{2+}, which has an ionic radius similar to Mn^{2+}, is likely to give a similar change to the circumstances of Zr center. There are numerous examples of the phosphor for practical use that employ Mn^{2+} as the activator.[3] The emission is usually explained as the transition $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ of Mn^{2+} within the $3d^5$ configuration. It is known that the peak wavelength of the emission of Mn^{2+} phosphor varies according to its host crystal. The emission peak in the present study, 477 nm, is one of the shortest, very close to 471 nm for $SrSb_2O_6$:Mn, the shortest that is reported.[10] On the basis of what the crystal field theory teaches, the weaker the field strength at the site which Mn^{2+} occupies, the shorter the emission wavelength is.[11-14] On the other hand, the crystal field at the site of YPO_4 was reported to be rather weak, in connection with the absorption and emission of YPO_4:Ce.[15]

Second, the excitation bands for the blue emission are discussed. The band peaking at 152 nm corresponds to the absorption of the host crystal or PO_4 group.[16] The other excitation band is located around 193 nm. This is near to the excitation band of YPO_4:Zr but does not overlap with it. One should remember the fact that YPO_4:Mn without Zr does not show any emission. In addition, the codoping of Mn to YPO_4:Zr has resulted in diminishing the Zr emission at 290 nm (see also Fig. 6). Therefore we claim that Zr plays an important role in the excitation of the Mn blue emission of YPO_4:Zr,Mn, although the mechanism for the excitation cannot be determined only by the data of emission and excitation spectra. The possibility that the excitation bands originate from ZrP_2O_7:Mn or MnP_2O_7 is again rejected, for those samples do not show a blue emission.

Third, the UV emission band in Fig. 4 is quite similar to that of YPO_4:Zr in Fig. 1, and the excitation spectra for these UV emissions in Fig. 2 and Fig. 5 are also similar to each other. We claim that the UV emission of YPO_4:Zr,Mn occurs from Zr^{4+} that does not have a Mn neighbor and thus its environment is similar to Zr^{4+} in YPO_4:Zr.

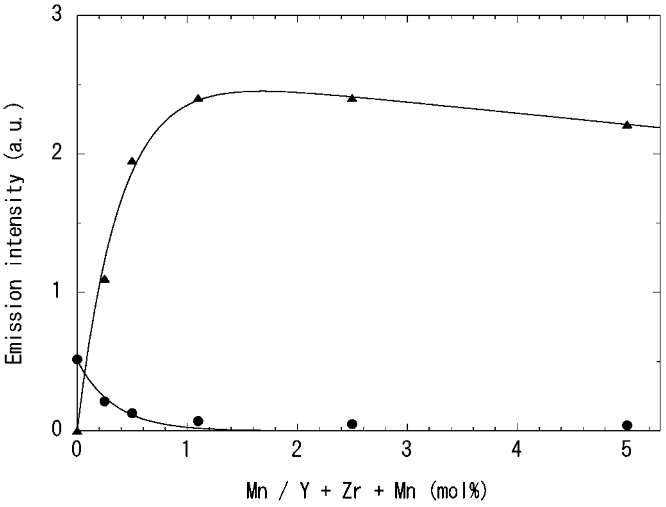

Figure 6. Mn concentration dependences of emission of YPO_4:Zr, Mn ($\lambda_{ex} = 193$ nm). Triangles are for blue emissions, and circles are for UV emissions. Zr conc. = 2.5 mol %. Note that 193 nm is not at the peak but skirts the excitation band for the UV emission.

The Mn concentration dependence of emission intensities of YPO_4:Zr,Mn is shown in Fig. 6. The intensity of the blue emission shows its maximum at 1.1 mol % Mn, and beyond that point, the intensity is gradually weakened. The UV emission intensity decreases rapidly as the Mn concentration increases. The Zr concentration dependence of emission intensities of YPO_4:Zr,Mn is shown in Fig. 7. The intensity of the blue emission increases rapidly in low Zr concentration and is saturated in at 0.6 mol %.

The emission under 147 nm excitation of the commercial BAM:Eu phosphor was measured. The emission peak is at 456 nm and the half width is 55 nm. When the Zr (1.1 mol %), Mn (1.1 mol %) sample (see Fig. 4), which shows the brightest blue emission among the series of YPO_4:Zr,Mn, is compared with the commercial BAM:Eu for the emission under 147 nm excitation, the peak height is 25% of the BAM:Eu one and the half width is 63%. In order to be evaluated for practical use, YPO_4:Zr,Mn should im-

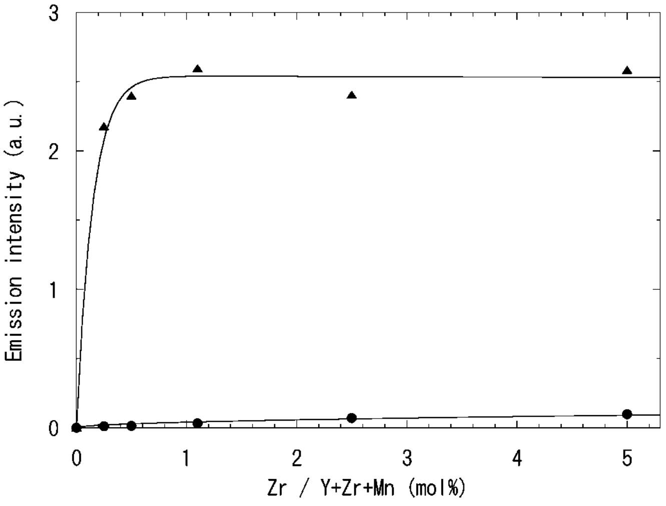

Figure 7. Zr concentration dependences of emission of YPO_4:Zr, Mn ($\lambda_{ex} = 193$ nm). Mn conc. = 1.1 mol %. See captions of Fig. 6.

prove in luminosity. The study of other luminescent properties, such as fluorescence life-span, thermal quenching, and chromatic coordinates, is also necessary.

Conclusions

YPO_4:Zr shows the UV emission peaked at about 290 nm. The excitation spectrum of this emission has the main band peaked at 175 nm and with a shoulder at 155 nm. This luminescence is assigned to the CT transition of O-Zr.

The Zr, Mn codoped material, YPO_4:Zr,Mn shows a blue emission peaked at 477 nm, which is assigned to the transition $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ of Mn^{2+} within $3d^5$ configuration. The excitation spectrum of the emission has two bands, the peaks of which are 152 and 193 nm. The excitation band at 152 nm corresponds to the absorption of the host crystal. YPO_4:Mn does not show any emission, and the 290 nm emission due to Zr is diminished in YPO_4:Zr,Mn. It is suggested that Zr plays an important role in the excitation of the Mn blue emission of YPO_4:Zr,Mn.

The emission wavelength (477 nm) of YPO_4:Zr,Mn is remarkably short, which is similar to the known shortest record.

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