Paper

Photoluminescence Enhancement in $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ Phosphor

Mamoru KITAURA*, Yohei INADA** and Kazutoshi FUKUI**

*Fukui National College of Technology, General Education

**University of Fukui, Department of Electrical and Electronics Engineering, Faculty of Engineering

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ABSTRACT

The phosphor of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ has been synthesized in order to increase the photoluminescence (PL) intensity of the blue-green (BG) band at 2.52 eV in $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ phosphor. PL properties of this material have been investigated. A PL band is predominantly observed at 2.34 eV in $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$. This green (G) band is most likely caused by the intra-3d transition of the Mn^{2+} ion occupying a Sc^{3+} site, in analogy with PL properties of the BG band. The G band surpasses the BG band in PL intensity. Discussions are conducted on the change of PL properties in $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ phosphor.

KEYWORDS: Mn^{2+} phosphor, $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$, PL and PLE spectra, ESR spectra, PL intensity enhancement

1. Introduction

Photoluminescence (PL) properties of divalent manganese ions are sensitive for the structure of host crystals. An adjustment of the environment around Mn^{2+} ions by the choice of host materials leads to the improvement of PL properties; the diversification of emission color and the increase in PL intensity. It is thus expected that Mn^{2+} activated phosphors still have the potential controlling PL properties artificially on demand. Actually, a number of Mn^{2+} phosphors have been synthesized for practical use of newly developed excitation sources¹⁾.

Recently, Kaneyoshi and Nakazawa have developed a blue-green (BG) phosphor²⁾. This phosphor is realized by codoping of Zr^{4+} ions into $\text{YPO}_4\text{:Mn}^{2+}$ ³⁾. One of the authors (M.K.) has investigated the effect of Zr^{4+} codoping on PL properties of $\text{YPO}_4\text{:Mn}^{2+}$. The PL spectra of $\text{YPO}_4\text{:Mn}^{2+}$ were dominated by the red (R) band at 1.91 eV. The R band was changed to the BG band at 2.52 eV by Zr^{4+} addition, the PL intensity of which was increased several ten times. From the analysis of electron spin resonance (ESR) spectra, it was pointed out that Mn^{2+} ions occupy Y^{3+} sites and interstitial spaces in YPO_4 lattice. Since the ESR signals of the former are remarkably enhanced by Zr^{4+} addition, it is likely that the change of the PL spectra is due to the change of the lattice site occupied by a Mn^{2+} ions. That is to say, the BG and R bands originate from the Mn^{2+} ions in the Y^{3+} site and interstitial site, respectively.

In order to more increase the PL intensity of the BG band in $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$, it is supposed that the

suppression of orthorhombic Mn^{2+} ions is an important key, because it results in the increase of tetragonal Mn^{2+} ions. Such suppression is possible by narrowing the interstitial space: hence the replacement of Y^{3+} ions by others is most effective. On the other hand, ScPO_4 has the xenotime structure which is the same as YPO_4 ⁴⁾. The interstitial space in this material is smaller than that in YPO_4 . There is the possibility that the PL band from tetragonal Mn^{2+} ions is more enhanced in $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ than in $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$. Therefore, it is worthwhile to investigate the PL properties of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$.

In the present study, PL and PL-excitation (PLE) spectra of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ have been measured. Furthermore, an ESR experiment has been carried out at 300 K. Comparison of PL and ESR properties are performed between $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ and $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$. On this basis, the effect of host lattice on PL properties is discussed.

2. Experimental

Samples of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ were synthesized by the solid state reaction with the reagent of Sc_2O_3 , $(\text{NH}_4)_2\text{HPO}_4$, ZrO_2 , and MnC_2O_4 . The concentration of Mn^{2+} and Zr^{4+} ions were adjusted to be 2.5 mol% in preparation. The powders were mixed by a ball mill, and then fired at 800 °C in air for 5 hours. The powders thus obtained were sintered at 1200 °C in nitrogen atmosphere for 3 hours. The samples of $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ were also prepared by the procedure mentioned above. The crystal structures and compositions of samples were checked by a powder X-ray diffraction (XRD) using Cu $K\alpha$ radiation. The XRD patterns of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ and

Figure 1 XRD patterns of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ (a) and $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ (b). The powder simulation patterns of ScPO_4 and YPO_4 in the ICSD were also shown.

$\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ samples are shown in the upper part of Figures 1(a) and 1(b), respectively. The powder simulation patterns of ScPO_4 and YPO_4 in the inorganic crystal structure database (ICSD) are represented in the lower part of Figures 1(a) and 1(b). For the peak positions and intensity ratios, agreement between ours and ICSDs are fairly good. No other peaks are observed, indicating that our samples are composed of the single phases of ScPO_4 and YPO_4 with xenotime structure.

In the measurements of PL and PLE spectra, samples were molded in the disk of 10 mm diameter and 3 mm thickness, and then attached at the sample holder of a cryostat in a cryogenic refrigerator system. They were excited by ultraviolet (UV) or visible light from a 150 W xenon lamp passed through a grating monochromator (Nikon G250). PL from samples was detected by the combined system of two quartz lenses, a grating monochromator (SPEX 270M) and a photomultiplier tube. The PL spectra were not corrected for the spectral response and sensitivity of the detecting system. The PLE spectra were corrected for the spectral distribution of the excitation light by a rhodamine B ethanol solution.

In ESR experiment, samples were put into high quality quartz tubes, and then inserted into the cavity of a X-band spectrometer (Joel JES-TE300). The magnetic field modulation was performed at 100 KHz. The saturation effect of ESR signals was checked by measuring the dependence of microwave power on them. It was confirmed that ESR signals do not saturate below 1 mW microwave power.

Figure 2 PL spectra of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ and $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ at 14 K under excitation with photons at 6.5 eV

Figure 3 PLE spectra for the G band of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ (a) and the BG band of $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ (b) at 14 K. The PL intensities were normalized to unity at their maxima.

3. Results

The PL spectrum of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ at 14 K is shown in Figure 2. In this figure, the PL spectrum of $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ at 14 K was also shown as a reference. These spectra were obtained under excitation with 6.5 eV photons. In $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$, a PL band appears at 2.34 eV. This green (G) band was enhanced by adding Zr^{4+} ions. It surpasses the BG band of $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$; its intensity is about twice as large as the intensity of the BG band. Furthermore, the half width of the G band is smaller than that of the BG band. In the high-energy side, a weak band is observed in both spectra. They are ascribed to the PL bands related to Zr^{4+} ions²⁾⁵⁾.

The PLE spectra of the G and BG bands at 14 K are shown in Figures 3(a) and 3(b), respectively. Several peaks are observed in both PLE spectra. These peaks are considered to be the absorption bands due to the intra-3d transition of Mn^{2+} , because they are caused by photons in the visible range. The lowest energy peak is located at 3.08 eV in $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ and at 3.15 eV in $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$. The peak energy is lower in $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ than in $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$. The visible absorption due to the intra-3d transitions of Mn^{2+} can be stimulated using near UV LEDs. However, the PL efficiency is not so high, because the intra-3d transitions are basically spin-forbidden. Actually, the peak intensities of the G and BG bands excited at the prominent peaks were ten percent of those excited at 6.5 eV. As the temperature is raised from 14 K into 290 K, the G and BG bands decreased their intensities to 55 and 65 %, respectively.

Figures 4(a) and 4(b) show ESR spectra of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ and $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ at 300 K, respectively. The microwave frequency was 9.3992 GHz in our measurement. ESR spectra are composed of sharp lines on a broad structure. The sharp lines have been observed in ESR spectra of the samples with a dilute concentration of Mn^{2+} , suggesting the existence of isolated Mn^{2+} ions. They are ascribed to the hyperfine structures characteristics of Mn^{2+} with the ^6S ground state, which originates from the interactions between electrons of Mn 3d orbitals and a ^{55}Mn nucleus (100 % abundance) of spin $I = 5/2$. On the other hand, the broad structure has been observed in ESR spectra of the samples doped with a high concentration of Mn^{2+} . This is connected to the formation of clustered Mn^{2+} ions, which causes an exchange broadening in ESR spectra by spin-spin interaction.

4. Discussions

As seen from the PL and PLE spectra, the G band of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ has the PL properties similar to the BG band of $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$. This finding suggests that the G band originates from the intra-3d transition of Mn^{2+} ions. As mentioned in the previous section, the addition of Zr^{4+} ions is apparently connected to an appearance of the G band in PL spectra. ESR spectra also clearly exhibited sharp lines by adding Zr^{4+} ions, as shown in Figure 4(a). It is most likely that the G band originates in isolated Mn^{2+} ions. According to ref. 6, Mn^{2+} ions can occupy Sc^{3+} sites in the tetragonal structure. Therefore, the origin of the G band is reasonably ascribed to the Mn^{2+} ions occupying a Sc^{3+} site. Hereafter, this Mn^{2+} center is called tetragonal Mn^{2+} ion. The ratio of sharp lines to a ESR spectrum are larger in $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ than in

$\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$. The intensity enhancement of the G band is attributed to the increase in the number of tetragonal ions.

As generally accepted, the PL band of Mn^{2+} originates from the transition from the $^6\text{A}_1$ (^6S) ground state to the $^4\text{T}_1$ (^4G) excited state. The $^4\text{T}_1$ state has the $(t_2)^2(e)^3$ configuration which is different from the $(t_2)^3(e)^2$ configuration of the $^6\text{A}_1$ ground state. Since the energy difference between the $^6\text{A}_1$ and $^4\text{T}_1$ states is dependent on the $\text{Mn}^{2+}\text{-O}^{2-}$ distance, the width of the PL band will be changed by the local vibration at Mn^{2+} sites. As referring to the lattice constants⁴⁾, the $\text{Mn}^{2+}\text{-O}^{2-}$ distance is shorter in ScPO_4 lattice than in YPO_4 lattice. The local vibration should be more suppressed in $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$. Thus, the G band is narrower than the BG band.

In Figure 3(a), one can see a prominent peak at 3.08 eV with a low-energy shoulder. The similar structure is seen in the PLE spectrum for the BG band, as shown in Figure 3(b). The energy of the lowest PLE peaks is close to the energy difference between the ^6S and ^4G states⁷⁾. The ^4G state splits into the lower-lying level of $^4\text{A}_1$, ^4E , and $^4\text{T}_2$, and the higher-lying level of $^4\text{T}_1$ under a cubic approximation. Since the $^4\text{A}_1$ and ^4E states have the same $(t_2)^3(e)^2$ configuration as the $^6\text{A}_1$ ground state, a sharp peak is expected for the $^6\text{A}_1 \rightarrow ^4\text{A}_1 + ^4\text{E}$ transition. Therefore, the lowest PLE peaks in Figures 3(a) and 3(b) are assigned to the $^6\text{A}_1 \rightarrow ^4\text{A}_1 + ^4\text{E}$ transition. The low-energy shoulders are the nearest to the PL band of Mn^{2+} , and thus it is regarded as the reverse process of the transition giving rise to the PL band, namely, the $^6\text{A}_1 \rightarrow ^4\text{T}_1$ transition.

Figure 4 ESR spectra of $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ (a) and $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ (b) at 300 K. The microwave frequency was 9.3992 GHz in our measurements.

As the host material is changed from YPO_4 to ScPO_4 , the lowest PLE peak shifts into low-energy side. It is well known that the ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1 + {}^4\text{E}$ transition is scarcely influenced by the crystal field potential⁸⁾. This fact suggests that the peak shift is not due to the change in the crystal field strength at the Mn^{2+} site. One plausible effect for the peak shift is the change in electrostatic interaction, which is caused by the change in covalent bonding between a Mn^{2+} ions and O^{2-} ligands. According to refs. 3 and 6, the hyperfine splitting constant A of tetragonal Mn^{2+} ions in ScPO_4 is small, compared to that in YPO_4 . Considering that the value of A is proportional to the electron density at a tetragonal Mn^{2+} ion, the 3d wave functions of Mn^{2+} may spread out in ScPO_4 lattice more than YPO_4 lattice. The increase of covalent bonding results in the reduction of electron-electron repulsion, reducing the energy difference between ${}^6\text{S}$ and ${}^4\text{G}$ multiplet states. Consequently, the lowest peak from the ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1 + {}^4\text{E}$ transition is lowered in $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$.

5. Summary

In the present study, PL and PLE spectra and ESR spectra have been measured in $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ and $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ phosphors synthesized by a solid state reaction. The PL spectra were dominated by the G band at 2.34 eV in $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ and the BG band at 2.52 eV in $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$. The G band exceeded the BG band in PL intensity. ESR spectra of both phosphors exhibited sharp lines on a broad structure. It was revealed that the proportion of sharp lines in a ESR spectrum is larger in $\text{ScO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ than in $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$. Since an appearance of them indicates the existence of isolated Mn^{2+} ions in the tetragonal structure, the intensity enhancement of the G band is interpreted as an increase in the number of the tetragonal Mn^{2+} ions. In addition to such a PL intensity enhancement, the narrowing of PL band and the low-energy shift of the lowest PLE peak were found by changing the host crystal from YPO_4 to ScPO_4 . These results are qualitatively explained by considering the effect of host lattice on the multiplet levels of a Mn^{2+} ion.

The phosphors of $\text{YPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ and $\text{ScPO}_4\text{:Zr}^{4+},\text{Mn}^{2+}$ may not be favorable to the phosphors for white LEDs, because of low PL efficiency in the visible range. However, this problem will be solved by replacing Zr^{4+} ions into the tetravalent ions which shows allowed transitions in

the near ultraviolet or visible range. Investigations are now in progress.

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