Modulation of the optical properties of Pr\textsuperscript{3+}-doped Y\textsubscript{2}O\textsubscript{3} ceramics by Zr doping

Yumiko KATAYAMA, Hideki TOMIMOTO, JumpeiUEDA and Setsuhisa TANABE

Graduate School of Human and Environmental Studies, Kyoto University, Yoshida, Sakyo, Kyoto 606–8501, Japan

The photoluminescence properties of 0.2\% Pr\textsuperscript{3+}-doped (Y\textsubscript{1–x}Zr\textsubscript{x})\textsubscript{2}O\textsubscript{3} (x = 0, 0.1, 1, 3, 4.5, 6) ceramics were investigated. The luminescence intensity due to the transition from the \textit{3P}_0 level increased drastically when the Zr content \textit{x} increased, which is completely quenched in Y\textsubscript{2}O\textsubscript{3}:Pr\textsuperscript{3+} (\textit{x} = 0) due to the thermal relaxation through the lowest 5d level of the Pr\textsuperscript{3+} ion. By monitoring at 630 nm (1\textit{D}_2\rightarrow3\textit{H}_4), we found that the 4f–5d photoluminescence excitation bands for Pr\textsuperscript{3+} in the two six-fold sites (C\textsubscript{2} and S\textsubscript{6} in the Y\textsubscript{2}O\textsubscript{3}:Pr\textsuperscript{3+} (\textit{x} = 0) were observed at approximately 300 and 340 nm. On the other hand, when monitored at 510 nm (1\textit{P}_0\rightarrow3\textit{H}_4), the Zr-doped samples showed an additional 4f–5d band at 280 nm. Based on these results, we concluded that the \textit{3P}_0 luminescence is from Pr\textsuperscript{3+} in a seven-fold site, which is generated by incorporation of an additional oxygen via a defect chemical reaction, 2ZrO\textsubscript{2} \rightarrow \textit{Zr}_7\textsuperscript{4+} + O\textsubscript{6} + 3O\textsubscript{4}.

Key-words : Y\textsubscript{2}O\textsubscript{3}, Zr, Pr\textsuperscript{3+}, Luminescence

1. Introduction

Cubic rare earth oxide Y\textsubscript{2}O\textsubscript{3} is a well-known host material for trivalent rare earth active centers. For example, Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} phosphors are widely used in fluorescent tubes,\textsuperscript{3,4} and transparent Y\textsubscript{2}O\textsubscript{3} doped with Nd\textsuperscript{3+} and Yb\textsuperscript{3+} are used for the laser medium.\textsuperscript{5–11} Y\textsubscript{2}O\textsubscript{3} shows several advantages for optical applications such as a low phonon energy, a high thermal conductivity, a wide transparency range and a high refractive index. However, because Y\textsubscript{2}O\textsubscript{3} has a high melting point (above 2400°C) and shows a phase transformation from a hexagonal to cubic structure at approximately 2280°C, the growth of Y\textsubscript{2}O\textsubscript{3} single crystals is technically difficult. Therefore, transparent polycrystalline Y\textsubscript{2}O\textsubscript{3} ceramics have been widely investigated by adding sintering aids, such as HfO\textsubscript{2}, ThO\textsubscript{2} and ZrO\textsubscript{2}.\textsuperscript{3,5–7}

Y\textsubscript{2}O\textsubscript{3} crystallizes in cubic bixbyite under ambient conditions, which is a derivative of the fluorite structure. An eightfold coordination of cations in the form of a cube is reduced to a lower sixfold coordination in the bixbyite structure. There are two different symmetric sites, C\textsubscript{2} and S\textsubscript{6}, with an abundance ratio 3:1, where the relative positions of the two oxygen vacancies are different. For the C\textsubscript{2} site, the vacancies stack along the face diagonal to the cube, while for S\textsubscript{6} sites they are along the main diagonal (Fig. 1).\textsuperscript{3,5,9}

It is reported that when Pr\textsuperscript{3+} ion is doped into the cubic Y\textsubscript{2}O\textsubscript{3}, the red luminescence from the \textit{3P}_0 level is completely quenched and the \textit{3P}_0 level is observed, while blue and red luminescence bands from the \textit{3P}_0 level occur in many other host materials.\textsuperscript{10–12} This quenching phenomenon is explained as a thermal relaxation process across the low-lying 5d excited state of Pr\textsuperscript{3+}.\textsuperscript{10,13,14}

In this paper, we report strong luminescence from the \textit{3P}_0 level in the Y\textsubscript{2}O\textsubscript{3}:Pr\textsuperscript{3+} with a small amount of Zr doping. This phenomenon was discovered in the course of preparing trans-

\textsuperscript{1} Corresponding author: Y. Katayama; E-mail: katayama.yumiko.48a@st.kyoto-u.ac.jp

Fig. 1. Schematic diagram of the cubic Y\textsubscript{2}O\textsubscript{3} crystal structure.
3. Results

3.1 X-ray diffraction and lattice constant

Based on the XRD measurements, the cubic bixbyite structure in the obtained samples was confirmed. With increasing Zr content $x$, diffraction peaks shifted to higher angles. The lattice constants of the obtained samples were 0.5481 nm for $x = 0$, 0.5476 nm for $x = 3$ and 0.5470 nm for $x = 6$.

3.2 Photoluminescence properties

Figure 2 shows the PL spectra of the $(Y_{1-0.01}Zr_{0.01}x)_{0.998}Pr_{0.002}O_3$, $(x = 0, 0.1, 1, 3, 6)$ samples under 478 nm excitation. The intensities of all the spectra were normalized at the PL peak at approximately 630 nm ($Pr^{3+}:3H_4 \rightarrow 3H_6$). In particular, the sample with $x = 0$ showed five transition peaks at 619, 630, 635, 646 and 657 nm, which are consistent with the literature.[10,12] The Zr-doped samples showed the transitions from the $Pr^{3+}:3P_J$ levels at 510 nm ($3P_0 \rightarrow 3H_4$), 550 nm ($3P_1 \rightarrow 3H_5$), 668 nm ($3P_0 \rightarrow 3H_6$) and 750 nm ($3P_0 \rightarrow 3F_J$) while the Zr-free sample ($x = 0$) showed only transitions from the $Pr^{3+}:1D_2$ level.

With increasing Zr content $x$, the relative intensity of 510 nm ($3P_0 \rightarrow 3H_4$) luminescence to 630 nm ($1D_2 \rightarrow 3H_4$) luminescence increased, and the $1D_2$ luminescence band at approximately 630 nm was broadened. In the sample with $x = 6$, the luminescence intensity from the $3P_0$ level at 510 nm was approximately three times higher than that from the $1D_2$ level at 630 nm.

Figure 3 shows the PL and PLE spectra of the sample with $x = 0$ and $x = 3$. The sample with $x = 0$ showed two different PL spectra ($1D_2 \rightarrow 3H_4$ transition) under 300 and 340 nm excitations. The peak wavelength under 300 nm excitation was 630 nm while that by 340 nm excitation was 620 nm. PLE monitoring at 630 nm showed two broad bands at 300 and 340 nm, and sharp lines at approximately 450 to 520 nm and at approximately 580 nm. By monitoring at 600 nm, only one UV band at 340 nm and sharp lines at approximately 450 to 520 nm were observed. The broad UV bands were assigned to the $4f - 5d$ transitions of $Pr^{3+}$. The sharp lines are attributed to $4f - 4f$ transitions, $3H_4 \rightarrow 3PJ$, $1I_6$ (approximately 450 to 520 nm) and $3H_4 \rightarrow 1D_2$ (approximately 580 nm).

The PL and PLE spectra of the sample with $x = 3$ are shown in Fig. 3(b). PLE monitoring at 600 and 630 nm showed the same structure as the PLE value of the sample $x = 0$, with two broad $4f - 5d$ bands at 300 and 340 nm, and $4f - 4f$ transitions, $3H_4 \rightarrow 3P_J$, $1I_6$ (approximately 450 to 520 nm) and $3H_4 \rightarrow 1D_2$ (approximately 580 nm). By monitoring the luminescence at 510 nm (appeared by Zr doping), the splitting of the $3H_4 \rightarrow 3P_J$, $1I_6$ lines was different from the PLE monitoring at 600 and 630 nm luminescence. One additional UV band was observed at 280 nm, which is a shorter wavelength than that observed by monitoring at 600 and 630 nm.

The PL spectra were recorded by three different excitations of the $4f - 5d$ transitions. Under 340 nm excitation, only the luminescence from the $1D_2$ level was observed, which had a peak wavelength at 620 nm. By excitation at 300 and 270 nm, both the...
Vink notation as follows.15,16) replace the lattice sites of \( \text{Y} \), which can be expressed in Kröger-von Slogman notation. Electrical neutrality, one interstitial oxygen forms as two Zr atoms in \( \text{Y}_2\text{O}_3 \). Based on the result of PLE, the lowest 5d level in the additional site with \( \text{CN} = 7 \) increased compared with that in \( \text{CN} = 6 \) (\( \text{C}_2 \) and \( \text{S}_6 \)). Thus, the nonradiative transition probability from the \( \text{Pr}^3^+ \) level to the 1D2 level decreased because of the higher energy barrier and the luminescence from the \( \text{Pr}^3^+ \) level was observed [Fig. 5(b)].

The PLE band at 280 nm showed a negligible wavelength shift, the PLE bands at 300 and 340 nm both shifted to the longer wavelength with increasing Zr content. The observed luminescence from the \( \text{Pr}^3^+ \) level in Zr-doped \( \text{Y}_2\text{O}_3 \) ceramics is from the \( \text{Pr}^3^+ \) ions in \( \text{C}_2 \) and \( \text{S}_6 \) sites, resulting in lowering of the lowest 5d state.10) The configuration coordinate diagram of \( \text{Pr}^3^+ \) in \( \text{Y}_2\text{O}_3 \) is depicted in Fig. 5(a).

The luminescence from the \( \text{Pr}^3^+ \) level in Zr-doped \( \text{Y}_2\text{O}_3 \) ceramics \((x = 0, 1, 3, 6)\) was investigated. In the sample with Zr, the luminescence from the \( \text{Pr}^3^+ \) level was observed and the corresponding PLE showed the different 4f-4f splitting and 4f-5d energies at 280 nm from that monitoring the 1D2 luminescence (Figs. 3 and 4). These results indicate that there is an additional (the third) coordination environment for \( \text{Pr}^3^+ \) ions in the Zr-doped \( \text{Y}_2\text{O}_3 \) samples. Considering the incorporation of \( \text{ZrO}_2 \) into \( \text{Y}_2\text{O}_3 \), to preserve electrical neutrality, one interstitial oxygen forms as two Zr atoms replace the lattice sites of \( \text{Y} \), which can be expressed in Kröger-Vink notation as follows.15,16)

\[
2\text{ZrO}_2 + \text{Y}^3^+ + 2\text{O}^{2-} \rightarrow 2\text{Zr}^{4+} + \text{O}_2^0 + 3\text{O}_2^0
\]

In the cubic bixbyite \( \text{Y}_2\text{O}_3 \) structure, there are two tetrahedral voids around each yttrium site (Fig. 1). It is believed that an interstitial oxygen was incorporated into one of the two voids in the low doping of \( \text{ZrO}_2 \). In this case, the coordination number of the four nearest neighbor yttrium sites is converted from six to seven. Based on the result of PLE, the lowest 5d level in the additional site with \( \text{CN} = 7 \) increased compared with that in \( \text{CN} = 6 \) (\( \text{C}_2 \) and \( \text{S}_6 \)). Therefore, the nonradiative transition probability from the \( \text{Pr}^3^+ \) level to the 1D2 level decreased because of the higher energy barrier and the luminescence from the \( \text{Pr}^3^+ \) level was observed [Fig. 5(b)]. For the Zr content dependence of the lowest 4f-5d bands, the band at 280 nm showed a negligible wavelength shift, while the other two bands (\( \text{Pr}^{3+} \) in \( \text{C}_2 \) site at 300 nm and \( \text{S}_6 \) at 340 nm) showed a redshift. With increasing smaller cation Zr doping, the lattice constant decreased and the spatial size of the yttrium sites also decreased. In this case, the overlapping between the \( \text{Pr}^{3+} \) 5d wave functions and \( \text{O}^{2-} \) ligands wave functions increases and induces a higher electron repulsion. Consequently, the larger 5d orbital splitting and the lower energy difference between the lowest 5d level and the ground level are observed. This phenomenon has been observed in Pr-doped \( \text{Ln}_2\text{O}_3 \) (Ln = Sc, Y, Gd).10) In the sites with \( \text{CN} = 7 \) introduced by \( \text{ZrO}_2 \), however, the 4f-5d band at 280 nm showed little wavelength shift due to Zr doping. This is possibly because the spatial size effect was reduced by an inverse effect, such as distortion, which eliminates the Zr content dependence on the energy differences of the 4f-5d transition in the site \( \text{CN} = 7 \).

For a complete understanding of the luminescence properties by Zr doping, further investigation is required, particularly with regard to the crystallography.

## 5. Conclusion

The photoluminescence properties of \( \text{Pr}^{3+} \)-doped \((\text{Y}_{1-x}\text{Zr}_x\text{O}_3)\) ceramics \((x = 0, 0.1, 1, 3, 4.5, 6)\) were investigated. The luminescence from the \( \text{Pr}^{3+} \) level was observed in \((\text{Y},\text{Zr})_2\text{O}_3\) samples. Based on the PL and PLE results, the luminescence is from the \( \text{Pr}^{3+} \) ion in an additional site. Zr doping has two effects on the \( \text{Pr}^{3+} \) optical properties in \( \text{Y}_2\text{O}_3 \): one is oxygen incorporation, which leads to the formation of a seven-coordinate site (\( \text{CN} = 7 \)). The \( \text{Pr}^{3+} \) ions in the \( \text{CN} = 7 \) site, the energy gap between the lowest 5d level and the ground level increased. The other is the effect of Zr doping on the crystal field of \( \text{Pr}^{3+} \) in the \( \text{C}_2 \) and \( \text{S}_6 \) sites, resulting in lowering of the lowest 5d levels with increasing Zr doping. These results provide new insight into the optical properties of the \( \text{Pr}^{3+} \) ion.
Acknowledgements This work is financially supported by Japan Science and Technology Agency-Precursory Research for Embryonic Science and Technology (JST-PRESTO) and Grant-in-aid for Scientific Research from JSPS Fellows (No. 24-943).

References