Nanoscale mapping of ZnO–TiO$_2$ up-conversion phosphor containing Yb$^{3+}$ and Er$^{3+}$

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Abstract

Up-conversion phosphors have attracted considerable attention for their visible-light emission. In this study, a ZnO–TiO$_2$ up-conversion phosphor containing Yb$^{3+}$ and Er$^{3+}$ ions was prepared; its emission characteristics and crystal structure were analyzed, and its nanoscale elemental mapping was examined. The metal organic decomposition (MOD) method was used to fabricate the samples. After firing the sample at 1000 °C, the emission intensity showed a maximum when the molar ratio was Ti/Zn/Yb/Er = 1/1/0.06/0.02. Finally, the function of each element was considered from the viewpoint of the crystal structure and nanoscale mapping.

1. Background

Up-conversion (UC) phosphor provides visible-light emission at a low excitation energy through a multi-step excitation process [1]. In particular, the UC of near infrared (NIR) light to visible-light emissions is considered appropriate for solar cell [2–6] and biomarker [7–11] applications. In recent years, the materials and technology required for the synthesis of UC phosphors have attracted considerable attention. In 2018, Das et al reported metal–insulator–metal nanostructures that show over a thousand-fold increase in their photoluminescence (PL) [12]; in early 2019, Jadczyk et al demonstrated a room temperature UC PL process in a monolayer semiconductor WS$_2$ [13]. The latest developments include a unique study by Gupta et al, who demonstrated that UC nanoparticles fluoresce 50 times more on a gold coated cicada wing [14]. Thakur et al demonstrated a hybrid UC nanoparticle/graphene composite that works as a high sensitivity and high gain photodetector [15].

UC phosphors consist of a host material and a doping material. Rare earth (RE) metals such as ytterbium (Yb), erbium (Er), and thulium (Tm) are adopted as doping materials. Yb–Er and Yb–Tm type materials are often used for co-doping. For the host material, halides such as NaYF$_4$ are often used to obtain high emission intensities [16–25], but these halides have problematic hygroscopicity. Using a metal oxide as a host material is a possible alternative, as metal oxides such as ZnO and TiO$_2$ are highly stable in the ambient atmosphere.

ZnO–TiO$_2$ oxides are a multifunctional material that have been used in gas sensors [26] and photocatalysts [27, 28]. And, we have reported that the PL intensity is increased by mixing TiO$_2$ and ZnO in comparison to only TiO$_2$ or only ZnO [29]. However, the luminescence efficiency of a metal oxide is generally lower than that of a halide. Thus, UC metal oxide phosphors typically have low efficiency, limiting their practical applications. However, if the problem of luminescence efficiency can be solved by analyzing each element in the metal oxide, then a metal oxide could be an effective host material in comparison to a halide.

In this study, visible-light emissions are obtained from NIR light by using an UC phosphor material. A metal oxide consisting of ZnO and TiO$_2$, both of which are highly stable in the ambient atmosphere, was adopted as the host material. Yb and Er oxides were adopted as doping materials. In reference to Luitel et al [30], our previous work identified the best molar ratio for this UC phosphor as Ti/Zn/Yb/Er = 1/1/0.06/0.02 is best [31]. However, to increase the luminescence efficiency, each element of the metal oxide must be analyzed in more...
Table 1. Molar ratio of each element.

| RE ratio (Yb/Er) | Ti | Zn | Yb | Er |
|------------------|----|----|----|----|
| Er only          | 1  | 1  | 0  | 0.06|
| 1/3              | 1  | 1  | 0.02 | 0.06|
| 1/1              | 1  | 1  | 0.06 | 0.06|
| 3/1              | 1  | 1  | 0.06 | 0.02|
| Yb only          | 1  | 1  | 0.06 | 0.06|

There are some prior studies that adopted nanoscale mapping as one of the evaluation methods [32–34], but there are few studies that considered deeply by using high-resolution nanoscale mapping. Therefore, the purpose of this study is to consider the function of each element and compounds based on high-resolution nanoscale mapping.

2. Experimental

2.1. Synthesis procedure

Metal organic decomposition (MOD) was adopted in this study to synthesize all samples. The advantages of MOD are that the sample can be fabricated in an ambient atmosphere, and multiple materials are easy to synthesize. Moreover, the process of complex liquid synthesis is unnecessary, and a thin film can be fabricated at a low cost. The synthesis of UC phosphors using MOD is described in detail in a past report [35]. Four MOD solutions (TiO2, ZnO, Yb2O3, Er2O3) sold by Kojundo Chemical Laboratory Co., Ltd were used in this study. Each of the MOD solutions were mixed at an arbitrary ratio and stirred; the mixed solution was spread on the entire surface of the Si substrate and dried for 10 min at 100 °C in atmosphere. This drying process was repeated 5 times, and finally, the sample was fired for 4 h at 1000 °C in atmosphere. Each of the UC phosphors was prepared by these above steps. The structure of the obtained samples comprises (from top to bottom) the UC phosphor powder, UC phosphor thin film, and Si substrate.

2.2. Experimental conditions

Five samples were fabricated with the experimental molar ratios shown in table 1. The molar ratio of the host materials was fixed at Ti/Zn = 1/1, and the mixing ratio of the RE elements was varied. For the doping materials, we initially used the best ratio of RE elements (Yb, Er) from a past study, i.e., Ti/Zn/Yb/Er = 1/1/0.06/0.02 [31], and varied the RE molar ratio around that to identify the optimum condition.

2.3. Evaluation method

The fabricated samples were analyzed by measuring their PL characteristics. An NIR laser of 980 nm was used as the excitation light source. The power of the laser was 200 mW and the diameter was about 1.5 mm. The details of the evaluation are described in a past report [35]. Next, the crystal states of all the samples were analyzed using the 2θ–θ X-ray diffraction (XRD) method. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) images were also recorded, and the samples were observed via electron back-scattered diffraction (EBSD) to determine the local distributions of each compound. Finally, the elements were mapped using energy dispersive X-ray spectroscopy (EDX).

3. Results

3.1. Emission characteristics

The PL spectrum of the UC phosphor is shown in figure 1. The emission intensity is greatest when the mixing ratio of the RE is Yb/Er = 3/1. As the content of Yb is reduced, the emission intensities changed at 555 nm (4S3/2 → 4I15/2) and 672 nm (4F9/2 → 4I15/2). Our past study examined the energy-transfer process in detail [31]. In Yb and Er doped samples, the emission intensities of the green component at 555 nm (4S3/2 → 4I15/2) are close to each other. On the other hand, the emission intensity of the red component at 672 nm (4F9/2 → 4I15/2) clearly changes in the Yb and Er doped samples. Thus, the ratio of green to red components changes the emitted color.

Figure 2 indicates the energy bands of Yb3+ and Er3+ ions [1, 36–40]. When the excitation wavelength is 980 nm, bi-photonic absorption takes place with efficient excitation to the 4F7/2 level; the electron then decays to the 2H11/2 level and produces green light of 534 nm. A green light of 555 nm is also seen due to the shift between 2H11/2 and 4S3/2. Kumar et al report that no multi-photonic transition can happen at the energy gap between...
and \( \frac{4S_3/2}{4F_9/2} \) transition is thought to be radiative. Part of the population decaying to the \( \frac{4F_9/2}{4I_{15/2}} \) level appears at 672 nm as a red light. The major process to the \( \frac{4F_9/2}{4I_{15/2}} \) level of Er\(^{3+}\) ion is expressed by the following formula (1) [39].

\[
\frac{2F_{5/2}({\text{Yb}}^{3+})}{2F_{7/2}({\text{Yb}}^{3+}} + \frac{4I_{15/2}({\text{Er}}^{3+})}{4F_{9/2}({\text{Er}}^{3+})} 
\]

(1)

3.2. Crystal structure analysis

In order to analyze the crystal structures of the UC phosphors, they were examined using XRD with an angle of incidence from 20° to 60°. The results are shown in figure 3. The obtained peaks were compared with those in the International Crystal Structure Database (ICSD) to analyze the compound and crystal structures. The standard patterns are shown at the bottom of figure 3 for TiO\(_2\) (ICSD:165924), Er\(_2\)Ti\(_2\)O\(_7\) (ICSD:24152), Yb\(_2\)Ti\(_2\)O\(_7\) (ICSD:154077), and Zn\(_2\)TiO\(_4\) (ICSD:37433). The peak analyses revealed Zn\(_2\)TiO\(_4\), RE\(_2\)Ti\(_2\)O\(_7\), and TiO\(_2\) phases. These results are similar to those reported by Luitel \textit{et al} [30]. Because the Yb\(_2\)Ti\(_2\)O\(_7\) and Er\(_2\)Ti\(_2\)O\(_7\)
phase peaks are present at the same positions, identifying the compounds from the peak angles is difficult. Therefore, RE$_2$Ti$_2$O$_7$ is used to generically represent Yb$_2$Ti$_2$O$_7$ and Er$_2$Ti$_2$O$_7$ in this study. The results of figure 3 reveal that changing the ratio of RE elements does not greatly affect the XRD peaks, which can be attributed to the fact that the host materials of the UC phosphors occupy most of the sample. These UC phosphors have RE contents of 2% to 6% relative to the host components, which is why the crystal structure does not significantly change.

Therefore, according to the results of Section 3.1 and the results thus far in Section 3.2, the emission spectra of the UC phosphors with TiO$_2$ and ZnO change depending on the RE ratio, but this ratio negligibly affects the crystal structures.

4. Discussion

4.1. EBSD analysis

Electron backscattered diffraction (EBSD) is a method which analysis the crystal orientation and crystal structure a local region by irradiating one point on the sample surface with an electron beam. EBSD is typically performed by scanning the electron beam across an area on the sample surface, taking measurements at equal intervals. Hence, the crystal orientation data of each point is measured with two-dimensional coordinates. As a result, various crystal structures are visually presented within a material, which describes the crystal orientation [41, 42].

EBSD analysis was conducted to locally observe the distribution of each compound. Two samples were analyzed, Ti/Zn/Yb/Er = 1/1/0.06/0.02 and 1/1/0.06/0.06, both of which exhibited high luminance in the emission characteristics, as described in section 3.1. The results of Ti/Zn/Yb/Er = 1/1/0.06/0.02 and 1/1/0.06/0.06 are shown in figures 4 and 5. In the figures 4 and 5(a)–(d) show the image quality (IQ) maps, phase + IQ maps, EDX + IQ map (Blue: Zn, green: Yb, Red: Ti), EDX + IQ map (Blue: Zn, green: Er, Red: Ti) respectively. In the figure 4(b), Zn$_2$TiO$_4$ (red color) is observed to exist throughout the sample, and small grains of RE$_2$Ti$_2$O$_7$ (green color) are dispersed in the sample. Figure 4(c) shows the same result as figure 4(d). If Yb and Er are present in Zn$_2$TiO$_4$, the whole is considered to become white color. Therefore, it is considered that Yb and Er exist only in RE$_2$Ti$_2$O$_7$.

Meanwhile, in the figure 5(b), linearly connected areas of RE$_2$Ti$_2$O$_7$ appear. Figure 5(c) shows the same result as figure 5(d). From the results of figures 5(c) and (d), it is considered that Yb and Er exist only in RE$_2$Ti$_2$O$_7$. Therefore, when the molar ratio of Er is changed from 0.02 to 0.06, the amount of RE$_2$Ti$_2$O$_7$ increases and the grains change to a linear shape.
4.2. Cross-sectional STEM image and elemental mapping

Elemental mapping was performed using EDX on the cross-sectional STEM images of the UC phosphor. Two samples were analyzed, Ti/Zn/Yb/Er = 1/1/0.06/0.02 and 1/1/0.06/0.06, both of which exhibited high luminance in the emission characteristics, as described in section 3.1, and the results are shown in figures 6 and 7. Figure 6(a) shows the cross-sectional STEM image of the UC phosphor thin film, and figures 6(b)–(f) show the
mapping results of O, Ti, Yb, Er, and Zn, respectively. In the same as figures 6, 7 (a) shows the cross-sectional STEM image of the UC phosphor thin film, and figures 7(b)–(f) show the mapping results of O, Ti, Yb, Er, and Zn, respectively.

The results in figures 6(b), (c), 7(b) and (c) demonstrate that O and Ti are distributed throughout the sample, which is consistent with the XRD results in figure 3. It has now been established that three of the components of Zn2TiO4, TiO2 and RE2Ti2O7 that are present in the XRD results in figure 3 are also present in the results in figures 4 and 5. The results in figures 6(d), (e), 7(d), and (e) indicate that Yb and Er are present at the same positions. Therefore, Yb and Er can transfer the energy of the excitation.

Notably, in figures 6(d)–(f), 7(d)–(f), Zn and RE elements (Yb, Er) are present at different positions. These results reveal that the RE elements are not dissolved in the Zn2TiO4 host material and are present in large amounts in RE2Ti2O7, RE elements are thought to substitute the Zn2+ sites of the Zn2TiO4 octahedron to produce luminescence [43, 44], but, in fact, RE2Ti2O7 may be emitting light. There is a prior work that has reported the emission of upconversion by adding Er to Yb2Ti2O7 [45–47]. If RE2Ti2O7 is a luminescent material, then Zn is not necessary for the UC phosphor. However, the luminescence efficiency severely decreases when Zn is not introduced. Therefore, Zn is concluded to move Yb and Er to the same positions, as observed in
figures 6(d), (e), 7(d), and (e). Further, for the UC phosphor to emit light, it is desirable for a large amount of RE2Ti2O7 to be present. However, in sections 3.1 and 4.1, the emission intensity was seen to decrease when RE2Ti2O7 showed a linear shape. The reason is considered to be related to the shape of RE2Ti2O7 because there is an example in which the phosphor is finely patterned to improve the emission intensity [12]. The evidence presented in section 4.2 suggests that RE2Ti2O7 may be a luminescent compound. Therefore, in our future research, we intend to fabricate a thin film UC phosphor that emits high-intensity light. Then, the light-emitting compound will be specified by comparing microscopy images of the light emission states and the surface SEM images.

5. Conclusions

UC phosphor prepared using the MOD method exhibited high luminance when the molar ratio was Ti/Zn/Yb/Er = 1/1/0.06/0.02. According to the XRD analysis, UC phosphor comprised of Zn2TiO4, RE2Ti2O7, and TiO2. And, from the results of the EBSD analysis, when the molar ratio was Ti/Zn/Yb/Er = 1/1/0.06/0.02, RE2Ti2O7 was observed to be dispersed in a granular form. In contrast, when the molar ratio was Ti/Zn/Yb/Er = 1/1/0.06/0.06, RE2Ti2O7 was observed to be linearly connected. The nanoscale elemental mapping revealed that the energy could be transferred because Yb and Er are present at the same positions. Moreover, Zn and the RE elements (Yb, Er) were found to exist at different positions.

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Conflicts of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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