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Luminescent properties of Eu^{3+}-doped $YTaO_4$ powders

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Abstract

$YTaO_4$:Eu^{3+} powders were synthesized by a flux method with LiCl. The use of a flux in the synthesis of M′–$YTaO_4$ facilitated the reaction of raw materials, leading to lowering the heating temperature, but not effective at the high firing temperature. The red emission peaks were observed around 613 nm with an excitation wavelength of 254 nm. Emission peaks were composed of two sets around 613 nm and 590 nm, which originated from $^5D_0$–$^7F_2$ and $^5D_0$–$^7F_1$, respectively. PL intensity of $YTaO_4$:Eu^{3+} prepared with a small amount of LiCl (10 wt%) significantly depended on the firing temperatures, while that with a larger amount of LiCl (40 wt%) slightly relied on firing temperatures. The highest PL intensity could be obtained at the firing conditions of 1300 °C and 10 wt% LiCl.

Keywords: A. Powders: solid state reaction; C. Optical properties; D. Tantalates

1. Introduction

$YTaO_4$ has been known as a candidate for X-ray phosphors instead of $CaWO_4$ [1–3]. $YTaO_4$ itself is activated under X-ray excitation and emits a broad band ultraviolet (UV) emission at 330 nm. Furthermore, doping rare-earth ions to $YTaO_4$ enables not only PL (photoluminescence) emissions in the visible ranges, but also CL (cathodoluminescence) at the low accelerating voltage for FED (field emission display).

$YTaO_4$ has three crystal structures; scheelite (tetragonal, T), fergusonite (monoclinic, M), and another monoclinic form, called M′ [4,5]. M′ structure can be synthesized at the low temperature below 1400 °C, and T around 1450 °C. T structure transforms to M by cooling process. Generally, M′ structure is used for the luminescent material. The crystal structure of M′ $YTaO_4$ is shown in Fig. 1. The unit cell parameters are $a = 5.30$ Å, $b = 5.45$ Å, $c = 5.11$ Å, and $\beta = 96.5°$, and the density is 7.57 g cm^{-3}. Y atoms are 8-cordinated with oxygen atoms forming a distorted cube. Ta atoms are surrounded by 4 + 2 coordination with oxygen atoms, which means four shorter Ta–O bonds leading to a distorted octahedral coordination. Distorted TaO_6 units construct strings by sharing the edges one another.

It was reported that PL of $Y_{1-x}Eu_xTaO_4$ and $Y_{1-x}Bi_xTaO_4$ showed red and blue emission around 613 nm and 420 nm, respectively under 254 nm excitation [2]. Gd-doped $YTaO_4$ has UV emission nearby 312 nm [6,7]. $YTa_{1-x}Nb_xO_4$ shifts the emission wavelength from UV (330 nm) to blue region (410 nm) [3]. However, PL (photoluminescence) properties of Eu^{3+}-doped $YTaO_4$ have not been studied in detail.

In this work, the Eu^{3+}-doped $YTaO_4$ was synthesized by solid state reaction method with a flux. The effects of firing conditions and a flux on the crystalline formations were investigated, and then the correlations between PL properties and the formed phases were examined.

2. Experimental procedure

Y_2O_3 (Sigma–Aldrich, 99.99%), Ta_2O_5 (Sigma–Aldrich, 99.99%, <5 μ), and Eu_2O_3 (Sigma–Aldrich, 99.99%) were used as starting materials. As a flux, H_3BO_3 (High Purity Chemical, 99.99%) and LiCl (Sigma–Aldrich, 99.99+%) were added to compare their contributions to the crystalline formations each other. The mixture was ball-milled for 24 h and fired for 12 h at 1000–1300 °C in air atmosphere. Doping concentration was changed from 0.3 mol% to 20 mol%.

The crystalline phases of prepared powders were determined by XRD (X-ray diffractometer, SIEMENS D5005) using Cu Kα radiation (λ = 1.5406 nm). PL (photoluminescence)

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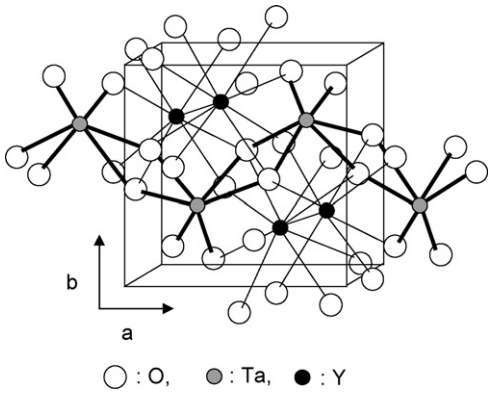

Fig. 1. Monoclinic structure of M′–$YTaO_4$ [3].

properties were measured by PL (PSI Darsa 5000) system using a xenon lamp as an excitation source.

3. Results and discussion

Fig. 2 shows XRD patterns of $YTaO_4$:Eu^{3+} (0.3 mol%) as a function of firing temperatures with 10 wt% LiCl as a flux. It has been well-known that a flux method is very effective to prepare the commercial X-ray phosphors such as M′–$YTaO_4$ [2,8–10] by one-step fabrication process,

$$Ta_2O_5 + Y_2O_5 \overset{1100-1300^\circ C,\ 12\ h,\ flux}{\longrightarrow} 2M' - YTaO_4 \quad (1)$$

At 1000 °C, M′–$YTaO_4$ phase could be achieved, but the secondary phase of $LiTaO_3$ and un-reacted Y_2O_3 due to low temperature appeared. Even though LiCl was employed as a flux, it reacted with Ta_2O_5, resulting in $LiTaO_3$ secondary phase. At low temperature, with chloride fluxes, rare-earth oxychloride, and metal-tantalate intermediate phases can be synthesized, while at high temperature, M′–$YTaO_4$ formation can be completed following the Eqs. (2) and (3) [3,10]:

$$Y_2O_3 + Ta_2O_5 + 2LiCl \overset{low\ temperature}{\longrightarrow} 2YOCl + 2LiTaO_3 \quad (2)$$

$$2YOCl + 2LiTaO_3 \overset{high\ temperature}{\longrightarrow} 2YTaO_4 + 2LiCl \quad (3)$$

This result indicated that 1000 °C in our experiment was a transient temperature for the phase transformation from $LiTaO_3$ to $YTaO_4$, which caused the coexistence of these two phases. With increase in the firing temperature, $LiTaO_3$ and Y_2O_3 phases decomposed and disappeared, and $Y_{10}Ta_4O_{25}$ phase newly appeared. At 1100–1300 °C, strong $YTaO_4$ peaks were observed, while a little $Y_{10}Ta_4O_{25}$ still existed as a secondary phase. The FWHM (full width of half maximum) values of the main peak of $YTaO_4$ at 28.2° were 0.1, 0.08, 0.08, and 0.05 at 1000 °C, 1100 °C, 1200 °C, and 1300 °C, respectively. This indicated that the crystallinity was enhanced with increasing temperature.

To investigate the effects of the amount of LiCl, $YTaO_4$ powders were synthesized at 1300 °C with various amounts of LiCl as shown in Fig. 3. LiCl did not contribute to the crystallinity of $YTaO_4$, while the peak intensity of $Y_{10}Ta_4O_{25}$ apparently decreased with increasing the amount of LiCl. It demonstrated that the effects of LiCl flux on the formation of $YTaO_4$ were insignificant at high temperature, because the high temperature (1300 °C) already supplied enough thermal energy for the synthesizing $YTaO_4$ regardless of the amount of LiCl.

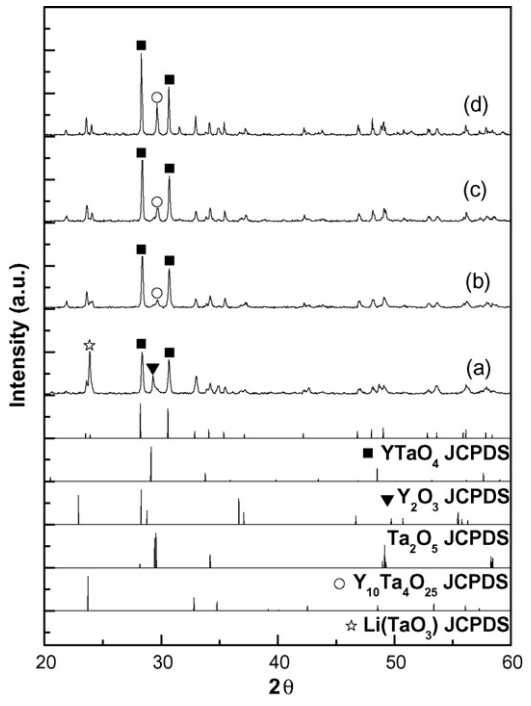

Fig. 2. XRD patterns of $YTaO_4$:Eu (0.3 mol%) powders fired with 10 wt% LiCl flux at various temperatures. (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C.

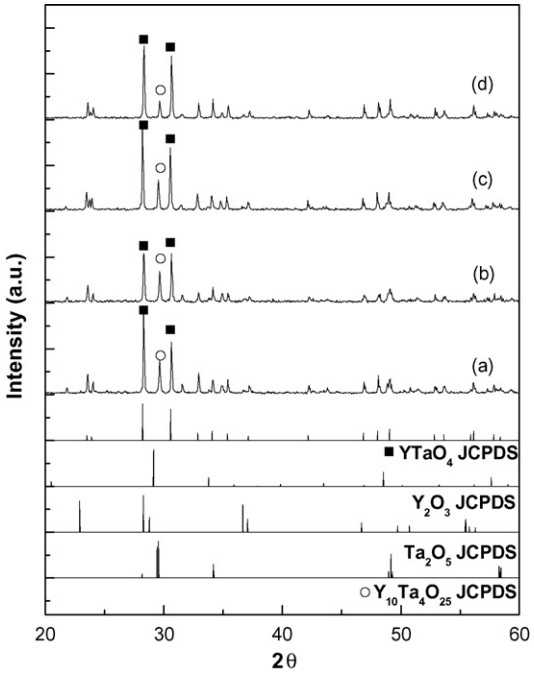

Fig. 3. XRD patterns of $YTaO_4$:Eu (0.3 mol%) powders fired at 1300 °C with various LiCl contents. (a) 10 wt%, (b) 20 wt%, (c) 30 wt%, and (d) 40 wt%.

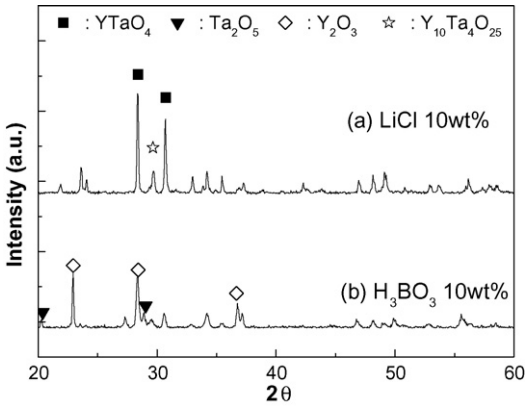

Fig. 4. XRD patterns of $YTaO_4$:Eu (0.3 mol%) powders fired at 1200 °C with (a) LiCl 10 wt% and (b) H_3BO_3 10 wt%.

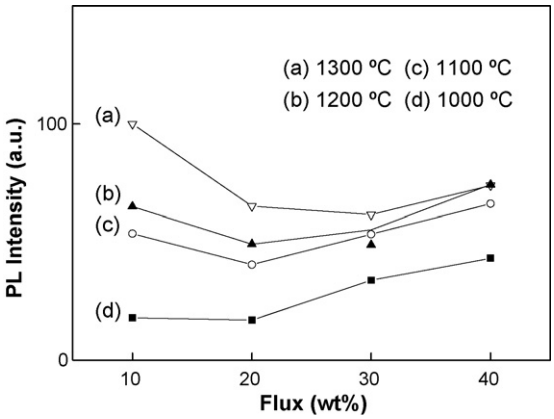

Fig. 6. PL intensity of 0.3 mol% Eu-doped $YTaO_4$ as a function of firing temperature and LiCl amounts. (a) 1300 °C, (b) 1200 °C, (c) 1100 °C, and (d) 1000 °C.

A flux method is well-known for a single-crystal growth and accelerates the kinetics of the formation of the desired compounds by enhancing diffusion coefficients. For phosphors, it enables spherically shaped powders, leading to the enhancement of luminescent properties [11–12]. The use of flux in the synthesis of M′–$YTaO_4$ facilitates the reaction of raw materials and so lowers the heating temperature. Without a flux, it is necessary to heat more than 1300 °C several times with intermediate grindings for the synthesis of M′–$YTaO_4$, but we could obtain it by only one-step process at 1100 °C with a flux, LiCl.

Fig. 4 shows XRD patterns of Y_2O_3–Ta_2O_5 mixture fired at 1200 °C with LiCl and H_3BO_3 as a flux. With LiCl, $YTaO_4$ could be synthesized, but with H_3BO_3, the raw materials, Y_2O_3 and Ta_2O_5, remained un-reacted. H_3BO_3 is a well-known flux for the synthesis of many oxides, but it was not effective in this experiment. The melting point of H_3BO_3 is about 185 °C, and that of LiCl is 610 °C. In our experimental firing conditions of 1000–1300 °C, it was thought that the high firing temperature caused highly rapid evaporation of H_3BO_3 prior to acting as a flux due to a low melting point. Accordingly, LiCl is more appropriate for high temperature process than H_3BO_3.

PL excitation and emission spectra of $YTaO_4$:Eu^{3+} (0.3 mol%) is shown in Fig. 5. The maximum excitation peak was observed at 254 nm for 613 nm red emission. Emission peaks were composed of two sets. One is two peaks around 613 nm and one another is three peaks around 590 nm, which originated from $^5D_0$–$^7F_2$ and $^5D_0$–$^7F_1$, respectively. An excitation peak at 254 nm corresponds to Eu^{3+} charge-transfer band that is situated at high energy [13].

The effects of the amount of a flux, LiCl and the firing temperatures on the luminescent properties are shown in Fig. 6. PL intensity of $YTaO_4$:Eu^{3+} prepared with a small amount of LiCl (10 wt%) significantly increased with firing temperatures, while those with a larger amount of LiCl (40 wt%) slightly depended on firing temperatures. Conclusively, the dependence of PL intensity on firing temperatures was noticeable with decreasing the amount of a flux. This result was in well accordance with the structural changes as discussed in Figs. 2 and 3, which mentioned that the flux was not effective on the structure at high temperatures. In our experiment, the highest PL intensity could be obtained at the firing conditions of 1300 °C and 10 wt% LiCl. Fig. 7 exhibited PL intensity of $YTaO_4$:Eu^{3+} as a function of doping concentrations. PL intensity peaked at 5 mol%, and slightly decreased with

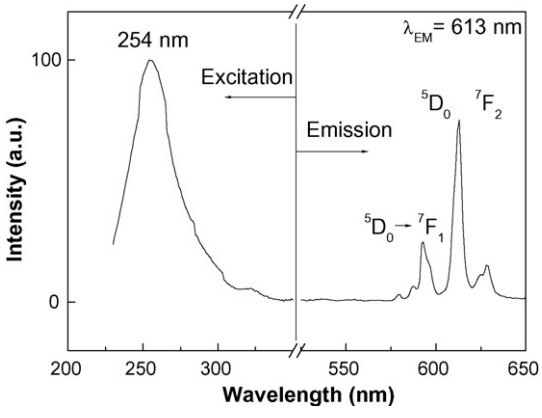

Fig. 5. Excitation and emission spectra of $YTaO_4$:Eu (0.3 mol%) fired at 1300 °C with 10 wt% LiCl.

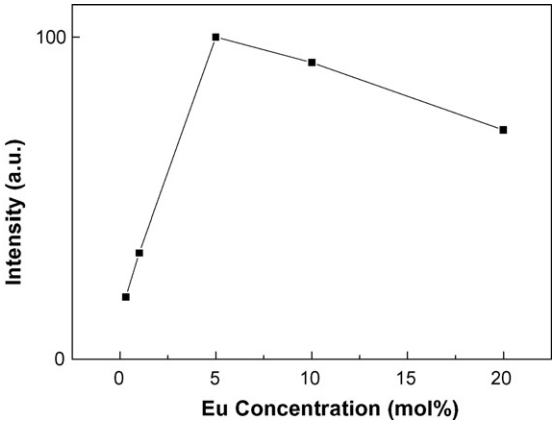

Fig. 7. PL intensity of $YTaO_4$:Eu^{3+} fired at 1300 °C with 10 wt% LiCl as a function of Eu contents.

increasing doping concentration more than 5 mol% due to concentration quenching effects. It was speculated that high Eu concentration in $YTaO_4$ caused irregular distributions of Eu, resulting in pairing and/or coagulation, and then led to concentration quenching in PL.

4. Conclusions

$YTaO_4$:Eu^{3+} powders were synthesized by solid state reaction method with a flux, LiCl. The phase formation and PL strongly depended on the firing conditions such as temperature, flux amount, Eu doping concentration. The maximum excitation peak was observed at 254 nm for 613 nm red emission. Emission peaks were composed of two sets around 613 nm and 590 nm, which originated from $^5D_0$–$^7F_2$ and $^5D_0$–$^7F_1$, respectively. PL intensity of $YTaO_4$:Eu^{3+} prepared with a small amount of LiCl (10 wt%) significantly depended on the firing temperatures, while that with a larger amount of LiCl (40 wt%) slightly relied on firing temperatures. The highest PL intensity could be obtained at the firing conditions of 1300 °C and 10 wt% LiCl.

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