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Effect of Thulium Doping on Luminescence Properties of $YAlO_3$ and YTa_7O_{19}

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Thulium (Tm) has been incorporated into $YAlO_3$ and YTa_7O_{19} host materials to obtain blue phosphors. Tm^{3+}-doped $YAlO_3$ and YTa_7O_{19} phosphors were prepared by the conventional solid state reaction method. According to the results of excitation and emission spectra measured at room temperature, the blue emission intensity of Tm^{3+}-doped YTa_7O_{19}, peaking at 455 nm was much higher than that of Tm^{3+}-doped $YAlO_3$, peaking at 458 nm. The maximum of relative intensity of Tm^{3+}-doped $YAlO_3$ and YTa_7O_{19} was obtained at the doping concentration of 0.016 and 0.120 mol% Tm^{3+}, respectively. These emission spectra revealed the concentration quenching effect.

Key words : Tm^{3+}, $YAlO_3$, YTa_7O_{19}, Luminescence, Quenching

I. Introduction

In recent years blue phosphors have been actively investigated due to the importance of these materials for the development of full color display panels. However, the blue phosphor had many disadvantages: insufficient color purity, brightness saturation at a high current density and poor chemical stability, etc. Therefore, the ideal phosphor should have a line emission spectrum.

It is well-known that the Tm^{3+} ion plays an important role in the phosphor and the laser-type solid state materials. It can be used directly as an active center in the visible region, or in the infrared spectral region around 2 μm. The electron configuration of Tm^{3+} is $5s^25p^6$. Due to emission by the 4f-4f transition only, it is expected to obtain the very sharp spectra. Thulium is of particular interest among all rare earth ions because it shows the most efficient luminescence in the blue emission region. Therefore, many investigations have been performed on the luminescence properties of Tm^{3+}-doped compounds, e. g., Y_2SiO_5,[1] $NaYF_4$,[2] etc.

In the Y_2O_3-Al_2O_3 system, $YAlO_3$ (perovskite: YAP) doped with various ions is known to be an efficient laser host and numerous spectroscopic studies have been performed on these materials.[3] $YAlO_3$ is described as metastable, because crushed single crystals or polycrystals from the melt, both of which are single phase $YAlO_3$ initially, convert to $Y_3Al_5O_{12}$ (garnet: YAG) and an unidentified phase or to $Y_3Al_5O_{12}$ and $Y_4Al_2O_9$ (monoclinic: YAM) when subjected to heat-treatment.[4,5] Powder samples prepared through the solid state reaction below 1600°C contain $Y_3Al_5O_{12}$ and $Y_4Al_2O_9$. On the other hand, tantalates have received attention, particularly with respect to the variety of crystal structure. In addition, the interesting luminescence properties of the rare earth polytantalates have been examined.[6] However, a little attention has been paid on the luminescence properties of Tm^{3+}-doped $YAlO_3$ and YTa_7O_{19} phosphors and their luminescence mechanism.[7]

The main purpose of this study is to prepare the blue phosphors of high color purity and strong emission intensity by the solid state reaction method. With this aim, the effect of Tm^{3+} doping on luminescence properties of $YAlO_3$ and YTa_7O_{19} was investigated by means of X-ray diffraction and photoluminescence analysis.

II. Experimental Procedure

1. Phosphor preparation

The schematic diagram of sample preparation of Tm^{3+}-doped $YAlO_3$ and YTa_7O_{19} phosphors by the solid state reaction method is shown in Fig. 1. Starting materials used in the preparation of them were high-purity powders of Y_2O_3 (99.99%), Al_2O_3 (99.999%), Ta_2O_5 (99.9%), and Tm_2O_3 (99.9%) from High Purity Chemicals Laboratory, Co. Ltd., Japan. The concentration of dopant Tm was ranged from 0 to 0.3 mol%. These materials were thoroughly mixed according to stoichiometric ratio of final phosphor in acetone with a mortar and pestle, and allowed to dry. The mixtures were calcined at 800°C for 6 hours in air. The calcination at this heat treatment produced a very friable powder that was easily ground with a mortar and pestle. The calcined powders were pressed into a disc-type pellet with 10 mm in diameter and 3 mm in thickness by a pressing device at 100 MPa. The pellet was sintered at 1500°C for 24 hours in air. The sintered body was ground and re-pelletized and re-sintered at the same conditions. This process was repeated

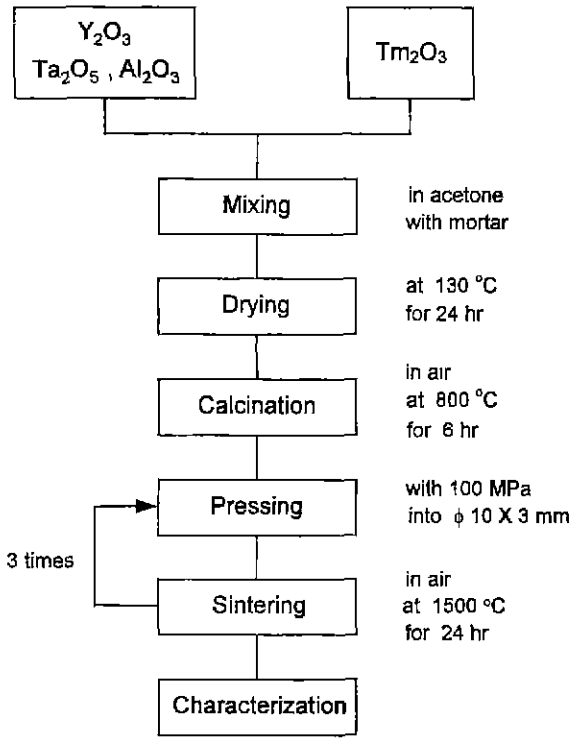

Fig. 1. Schematic diagram of the sample preparation of Tm^{3+}-doped $YAlO_3$ and YTa_7O_{19} phosphors.

once again.

2. Chracterization

The phases of samples were identified using a Rigaku DMAX-33 diffractometer system with Ni-filtered CuKα radiation. The photoluminescence (PL) emission and excitation spectra of the powder samples were obtained using a Perkin-Elmer LS50 luminescence spectrometer. The powder sample up to 0.3 gr was placed in a circular cell holder with a fused silica window. Powder samples were excited with 359 nm radiation from a pulsed xenon discharged lamp. The emission wavelength was scanned from 400 to 600 nm. at a scanning rate of 480 nm/min. For the measurements of excitation spectra the excitation wavelength was scanned from 300 to 400 nm at the same scanning rate, and emission monitored at 458 nm in the Tm^{3+}-doped $YAlO_3$ or at 455 nm in the Tm^{3+}-doped YTa_7O_{19}.

III. Results and Discussion

1. Preparation

All the powder samples prepared in this work appeared to be white in color. Figure 2 shows the X-ray diffraction patterns of $Y_{0.984}Tm_{0.016}AlO_3$ and $Y_{0.880}Tm_{0.120}Ta_7O_{19}$ powder samples prepared by the solid state reaction method. The diffraction patterns of $YAlO_3$ and YTa_7O_{19} included in the sintered samples agreed well with those of the JCPDS cards 11-662 and 30-1465. As shown in this figure, most of

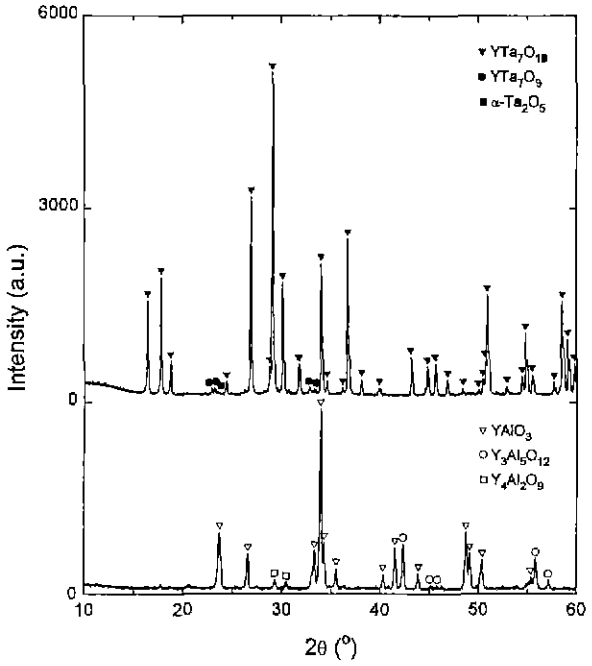

Fig. 2. X-ray diffraction patterns of $Y_{0.984}Tm_{0.016}AlO_3$ and $Y_{0.880}Tm_{0.120}Ta_7O_{19}$.

the peaks in $Y_{0.984}Tm_{0.016}AlO_3$ and $Y_{0.880}Tm_{0.120}Ta_7O_{19}$ powder samples were readily indexed as having perovskite and hexagonal symmetry, respectively. This implied that the product was mainly composed of stoichiometric $YAlO_3$ or YTa_7O_{19}. On the other hand, a little amount of impurity phases, e.g., α-Ta_2O_5 were included in the host materials. Such supplementary peaks were perhaps due to the incomplete solid state reaction. In fact the intensity of such peaks tends to decrease with increasing sintering temperature and time. As reported by many researchers,[4,5,8] the formation of $YAlO_3$ and YTa_7O_{19} was found to be realized only within a narrow temperature range.

2. Optical properties

Figure 3 shows the excitation and emission spectra of $Y_{0.984}Tm_{0.016}AlO_3$ powder. The Tm^{3+}-doped $YAlO_3$ phosphor showed a narrow band emission spectrum with the strongest line corresponding to the $^1G_4 \rightarrow {}^3H_6$ transition,[7,9] as observed around 458 nm under the 359 nm excitation condition. This wavelength is located within the blue light range. The excitation spectrum of $Y_{0.984}Tm_{0.016}AlO_3$ monitored at 458 nm exhibited a narrow band with a peak at 359 nm. The highest emission intensity of the Tm^{3+}-doped $YAlO_3$ phosphors was observed at the 0.016 mol% doped sample. However, the spectrum showed a weak shoulder at the shorter wavelength side, suggesting the presence of another emission band with a maximum around 458 nm.

Figure 4 shows the excitation and emission spectra of the $Y_{0.880}Tm_{0.120}Ta_7O_{19}$ powder. In YTa_7O_{19} host material the Tm^{3+} ion showed very sharply defined luminescent levels. Consequently, it was found that both the ex-

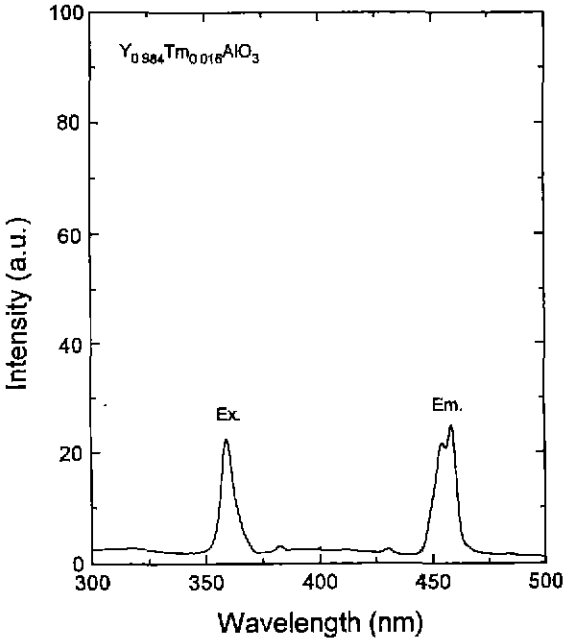

Fig. 3. Excitation and emission spectra of $Y_{0.984}Tm_{0.016}AlO_3$

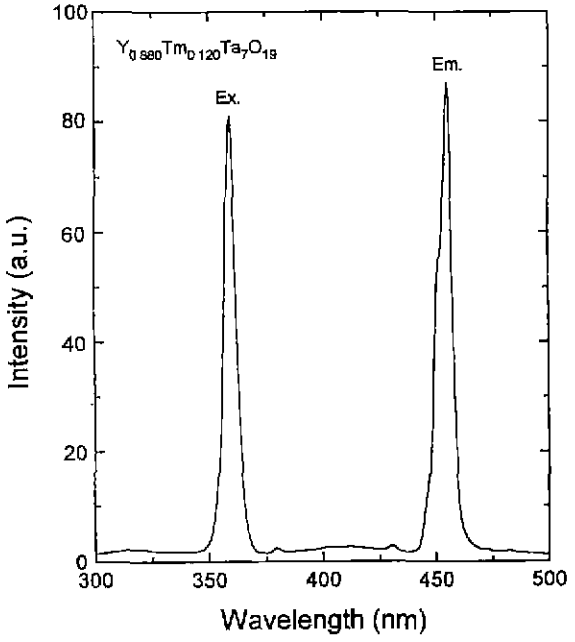

Fig. 4. Excitation and emission spectra of $Y_{0.880}Tm_{0.120}Ta_7O_{19}$.

citation and emission spectra were confined to a narrower region of the spectrum. The excitation spectrum consisted with a typical Tm^{3+} band at 359 nm, corresponding to transition from the ground state $^3H_6$ to the excited state $^1D_2$. The emission band had its peak at about 455 nm, which was attributed to the $^1G_4 \rightarrow {}^3H_6$ transition[7,9] characteristics of Tm^{3+}. This wavelength means very high purity of blue color. Color centers in host materials were induced by the thulium ions. According to the excitation and emission spectra in Figs. 3 and 4, the Tm^{3+} emission intensity near 455~460 nm of Tm^{3+}-doped

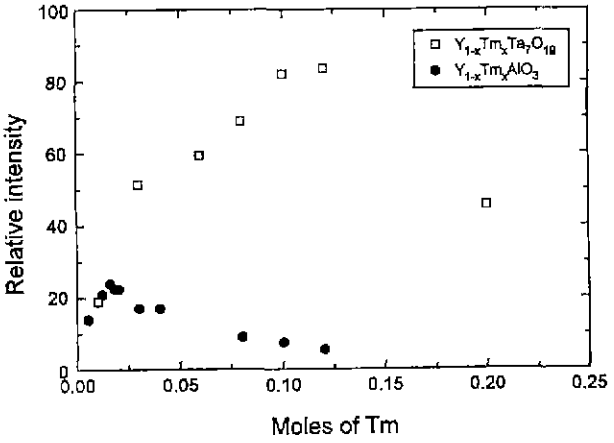

Fig. 5. Concentration dependence of emission intensity of Tm^{3+} in $Y_{1-x}Tm_xAlO_3$ and $Y_{1-x}Tm_xTa_7O_{19}$.

YTa_7O_{19} revealed very strong, compared with that of Tm^{3+}-doped $YAlO_3$. As can be seen in the emission spectra of Figs. 3 and 4, the Tm^{3+} luminescence band of YTa_7O_{19} was almost the same as that of $YAlO_3$ in shape. The band evidently shifted towards a little shorter wavelength than that of $YAlO_3$. The electrons of the 4f orbital in Tm^{3+} are generally shielded from the crystal field by the filled 5s and 5p orbitals. Hence, the difference in emission wavelength might suggest that altogether, the energy levels corresponding to 4f electrons were subjected to the crystal-field perturbation, in particular, due to the lattice energy. However, it was confirmed that the four-fold splitting of the band was due to no change in magnitude of the crystal field components and reflected no change in site symmetry, despite the different crystal structure.[7]

The relative emission intensity of photoluminescence from $Y_{1-x}Tm_xAlO_3$ and $Y_{1-x}Tm_xTa_7O_{19}$ samples are displayed against Tm^{3+} concentration (x) in Fig. 5. These emission intensities compared in this figure were attributed to the $^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+}. The spectra of Tm^{3+}-doped YTa_7O_{19} were very similar to those of the corresponding Tm^{3+}-doped $YAlO_3$; only the absolute energies are much higher. In addition, a unique profile of the Tm^{3+} concentration dependence of the emission intensity was observed in $Y_{1-x}Tm_xAlO_3$ and $Y_{1-x}Tm_xTa_7O_{19}$. As can be seen in Fig. 5, the emission intensity of Tm^{3+}-doped YTa_7O_{19} was comparable to that of Tm^{3+}-doped $YAlO_3$. This figure shows that the emission intensity of Tm^{3+}-doped YTa_7O_{19} increases by approximately a few times that of Tm^{3+}-doped $YAlO_3$. In addition, it follows that the concentration quenching of emission has taken place near x=0.016 in $Y_{1-x}Tm_xAlO_3$ and x=0.12 in $Y_{1-x}Tm_xTa_7O_{19}$

IV. Concluding Remarks

The luminescence properties of Tm^{3+}-doped $YAlO_3$ and YTa_7O_{19} phosphors prepared by the solid state reaction method were studied by mainly photoluminescence spec-

trometer and X-ray diffractometer. The following concluding remarks could be made:

1. Most of the peaks in $Y_{0.984}Tm_{0.016}AlO_3$ and $Y_{0.880}Tm_{0.120}Ta_7O_{19}$ powder samples were readily indexed as having perovskite and hexagonal symmetry, respectively.

2. Under 359 nm excitation, Tm^{3+}-doped $YAlO_3$ and YTa_7O_{19} phosphors exhibited a very narrow-band emission, peaking at 458 nm and 455 nm, respectively. The intense blue emission of $Y_{1-x}Tm_xAlO_3$ and $Y_{1-x}Tm_xTa_7O_{19}$ was quenched above x=0.016 and 0.120, respectively.

3. The blue emission intensity of Tm^{3+}-doped YTa_7O_{19} was much stronger than that of Tm^{3+}-doped $YAlO_3$.

Acknolegedgments

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