Blue-Emitting Phosphor of YInGe2O7 Doped with Tm3+ Ions

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YInGe2O7/Tm samples, with \( x = 0–7 \) mol %, exhibit an emission in the blue region with a dominant wavelength of \( \Delta_2 \rightarrow \Phi_2 \) at 453 nm. The energy is absorbed by the Tm\(^{3+}\) ion to the \( \Delta_2 \) emitting level, then transferred to a lower state via radiative transition. A single exponential decay behavior was observed for diluted samples, and a nonexponential decay behavior occurred when YInGe2O7 was doped with a higher Tm\(^{3+}\) ion concentration. The saturation of emission intensity excited by intra-4f transitions occurred at a concentration of \( x = 0.04 \), indicating that the concentration quenching is active when \( x > 0.04 \).


Oxide phosphors have recently gained much attention for applications such as screens in plasma display panels and field-emission displays and for white color light-emitting diodes because of their higher chemical stability and resistance to moisture relative to that of sulfide/phosphors.\textsuperscript{1–3} Yttrium indium germanate have the thortveite structure with a symmetry described by the space group \( C2/m \) (no. 12). This crystallizes in the monoclinic system, with cell parameters \( a = 6.8286 \) Å, \( b = 8.8836 \) Å, and \( c = 4.9045 \) Å. The In\(^{3+}\) and Y\(^{3+}\) cations occupy the same octahedral site, forming a hexagonal arrangement on the \( ab \) planes.\textsuperscript{4} It has been suggested that the YInGe\(_2\)O\(_7\) possesses excellent optical properties.

Rare-earth ions have been extensively employed as activators for various phosphors. It is well known that Tm\(^{3+}\) ions doped into various oxide host materials exhibit a blue emission with excellent color coordinates for use in full-color emissive displays utilizing photoluminescence (PL) and cathodoluminescence.\textsuperscript{5,6} Many studies have been done on Tm-activated orthovanadate blue phosphors such as YVO\(_4/Tm\) and GdVO\(_4/Tm\), because of their stability under high excitation density, appropriate lifetimes, and color-rendering properties.\textsuperscript{6,7} However, the role of the rare-earth Tm\(^{3+}\) ions doped in YInGe\(_2\)O\(_7\) has not yet been studied.

In this study, the Tm\(^{3+}\)-ion-doped yttrium indium germanate phosphors were synthesized using the vibrating milled solid-state reaction. The structure and the PL properties of YInGe\(_2\)O\(_7/Tm\)\(^{3+}\) phosphors were also investigated.

**Experimental**

**Preparation of samples.**—The Tm\(^{3+}\)-doped YInGe\(_2\)O\(_7\) was prepared by the vibrating milled solid-state reaction using Y\(_2\)O\(_3\), In\(_2\)O\(_3\), GeO\(_2\), and Tm\(_2\)O\(_3\) powders. The starting materials, with a purity of 99.99%, were supplied by the Aldrich Chemical Company and Alfa Aesar. After being mechanically activated by grinding in a high-energy vibro-mill for 15 min with zirconia balls in a polyethylene jar, the mixtures were calcined at 1200°C in air for 10 h.

**Characterization.**—The effects of Tm\(^{3+}\) doping and thermal treatment on the structure were carefully studied by X-ray powder diffractometry (XRD, Rigaku Dmax-33 X-ray diffractometer) using Cu K\(_\alpha\) radiation with a source power of 30 kV and a current of 20 mA to identify the possible phases formed after heat treatment. Both the excitation and luminescence spectra of these phosphors were recorded on a Hitachi F-4500 fluorescence spectrophotometer using a 150 W xenon arc lamp as the excitation source at room temperature. Lifetime measurements of samples were carried out by Edinburgh Instrument FLP920.

**Results and Discussion**

The rare-earth ions can easily replace the yttrium ion because the properties of yttrium and other rare-earth ions are similar. Figure 1 shows the XRD pattern of YInGe\(_2\)O\(_7\) doped with various concentrations of Tm\(^{3+}\) calcined at 1200°C in air for 10 h. All of the peaks can be attributed to the single-phase thortveite structure. The full width at half-maximum (fwhm) of these peaks does not show any obvious differences and indicates that the crystallinity of YInGe\(_2\)O\(_7/Tm\) seems to be the same with an increase in Tm\(^{3+}\) concentrations as the trivalent thulium ions (0.880 Å)\textsuperscript{3} are introduced to substitute the trivalent yttrium ions (0.9 Å)\textsuperscript{3} in the (Y\(_1\)\textsubscript{x}Tm\(_x\))InGe\(_2\)O\(_7\) system. The differences are almost the same between Tm\(^{3+}\) and Y\(^{3+}\) ion radii and they form a solid solution in doped concentrations from 0 to 7 mol %. This indicates that the grain sizes do not change significantly with the increase in Tm\(^{3+}\) concentrations. Additionally, there are no change compensation issues for the Tm\(^{3+}\) ions substituting the Y\(^{3+}\) ions in the YInGe\(_2\)O\(_7\) lattice, as both have the same valence.

Figure 2 depicts the PL excitation spectra of YInGe\(_2\)O\(_7\) doped with 4 mol % Tm\(^{3+}\) ion phosphors calcined at 1200°C in air for 10 h (\( \lambda_{ex} = 453 \) nm). The spectrum of YInGe\(_2\)O\(_7/Tm\)\(^{3+}\) exhibits a wide band in the UV region, and several groups of sharp lines between 200 and 300 nm are assigned to \( \Delta_2 \rightarrow \Phi_2 \) transitions. The small peaks located between 260 and 300 nm are assigned to the typical 4f\(^{15}\) → 4f\(^{14}\) intra-configuration forbidden transition of Tm\(^{3+}\) ions. In Fig. 2, the small peaks located between 260 and 300 nm are assigned to \( \Delta_2 \rightarrow \Phi_2 \) transitions. The sharp peak at 355 nm corresponds to the \( \Delta_2 \rightarrow \Phi_2 \) transition. Tm\(^{3+}\) has complicated energy levels and various possible transitions because of a strong deviation from R-S coupling in the 4f configuration. More-
over, the excited states of Tm$^{3+}$ ions may relax via many paths, giving rise to UV, visible, and infrared emission with moderate intensity.

It is well known that luminescence of Tm-activated oxides is caused by the intramolecular energy transfer from the host to thulium ions. The efficiency of this energy transfer depends on the efficiency of the host absorption and the host-to-Tm energy transformation. Figure 3 is the PL emission spectra measured from 200 to 900 nm for YInGe$_2$O$_7$:4%Tm phosphors calcined at 1200°C in air for 10 h under the excitation wavelength at 355 nm. The emission wavelengths are all in the blue-light region. The major emission peak of Tm$^{3+}$ was at 453 nm and two very weak peaks were observed at about 474 nm, corresponding to the transition of $^1D_2 \rightarrow ^3F_4$ and $^1G_4 \rightarrow ^3H_6$, respectively. Compared to some Tm-doped phosphors, it is noteworthy that the transition from $^1G_4$ to $^3H_6$ is predominant in the emission spectra for the Tm-doped phosphor. It has been suggested that the Tm$^{3+}$ has three emitting levels, including $^3P_0$ (35,000 cm$^{-1}$), $^1D_2$ (27,770 cm$^{-1}$), and $^1G_4$ (21,200 cm$^{-1}$). In YInGe$_2$O$_7$:Tm phosphors, the excited energy level of Tm$^{3+}$ ion is at $^3P_0$ (28,172 cm$^{-1}$), and the host lattice only has enough energy to populate the $^1D_2$ (27,770 cm$^{-1}$) or $^1G_4$ (21,200 cm$^{-1}$) emitting levels. As can be seen in the emission spectrum, the middle emitting level $^1D_2$ is predominant, and there is a weak transition of $^1G_4 \rightarrow ^3H_6$ presented at 474 nm. It can be supposed that the energy is first absorbed by the Tm$^{3+}$ ion to the $^1D_2$ emitting level and then transferred to a lower state via radiative transition. Simultaneously, a little energy of $^1D_2$ relaxed rapidly to the lowest emitting level $^1G_4$ via nonradiative transition, finally transiting from $^1G_4$ to the ground state. The mechanism of the energy absorbed and transferred by the Tm$^{3+}$ ions is shown in Fig. 4.

When the luminescent centers have different local environments, the association ions will relax at different rates. Figure 5 shows the decay curve of the $^1D_2 \rightarrow ^3F_4$ emission for YInGe$_2$O$_7$ doped with different Tm$^{3+}$ concentrations. In general, the Tm$^{3+}$-doped phosphors showed a short decay time (~20 μs). The decay curves show that the effect on YInGe$_2$O$_7$ doped with different Tm$^{3+}$ ion concentrations on the $^1D_2 \rightarrow ^3F_4$ transition is a single exponential decay observed in the diluted samples (3 mol % Tm). Additionally, the results also show that for YInGe$_2$O$_7$ doped with a higher Tm$^{3+}$ ion concentration, the observed decay curves were nonexponential, and the nonexponential change becomes more prominent as the Tm$^{3+}$ concentration increases, revealing that more than one relaxation process exists. The probability of an energy transfer among Tm$^{3+}$ ions becomes more frequent because the distances between Tm$^{3+}$ ions decreases as the Tm$^{3+}$ concentration increases, which provides an extra decay channel and changes the decay curves.

The luminescence intensities of phosphor materials always de-
pend on the doped concentrations. The emission intensity of the 1D2 → 3F4 transition with different Tm3+ concentrations under excitation at 355 nm is shown in Fig. 6. In the current study, the concentration quenching effect was observed. The emission intensity of the 1D2 → 3F4 transition increases with increasing Tm3+ concentrations in the lower Tm3+ concentration region until the saturated PL intensity is reached and then diminishes. It reached a maximum when the Tm3+ concentration was 4 mol % and decreased with increasing Tm3+ concentrations, which indicates that the concentration quenching is active when x > 0.04.

In YInGe2O7/Tm3+, different concentrations of Tm3+ ions did not change the shape of curves but did change the intensities of the emission spectra. Figure 7 shows the CIE color coordinates of YInGe2O7:4 mol %Tm, which is in the blue region with CIE color coordinates of x = 0.120 and y = 0.159.

Conclusions

A new blue-emitting phosphor, Tm3+-doped YInGe2O7, was synthesized by a vibrating milled solid-state reaction, and its luminescence properties have been investigated. The phosphor presents a
blue emission at 453 nm under excitation at 355 nm, which belongs to the \( ^1D_2 \rightarrow ^3F_4 \) transition, indicating that the energy is first absorbed by the Tm\(^{3+}\) ion to the \(^1D_2\) emitting level and then transferred to a lower state via radiative transition. The decay curves show a single exponential decay behavior in the diluted samples. A nonexponential decay behavior was observed when YInGe\(_2\)O\(_7\) was doped with a higher Tm\(^{3+}\) ion concentration. The XRD diffraction pattern indicates that all of the peaks can be attributed to the single-phase thortveitite structure. The saturation of the emission intensity excited by intra-4f transitions occurs when the Tm\(^{3+}\) concentration is 4 mol \% with a CIE color coordinate of \( x = 0.252 \) and \( y = 0.595 \). Concentration quenching is active when \( x > 0.04 \).

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