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Full Length Article

# Spectral characteristics and white emission of $Dy^{3+}/Tm^{3+}$-$BaLaGa_3O_7$ phosphors

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ABSTRACT

$Tm^{3+}$-, $Dy^{3+}$-$BaLaGa_3O_7$ phosphors have been synthesized by solid-phase sintering. X-ray diffraction (XRD) and photoluminescence properties of the phosphors were investigated in detail. The sample $Tm^{3+}$ and $Dy^{3+}$ ions co-doped $BaLaGa_3O_7$ obtain white light emission by integrating a blue emission band located at 455 nm ($^1D_2 \rightarrow {}^3F_4$) and an orange one located at 573 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) attributed to $Tm^{3+}$ and $Dy^{3+}$ ions, respectively. The study on the luminescence mechanism showed that there is the energy transfer between $Tm^{3+}$ and $Dy^{3+}$ in $Tm^{3+}/Dy^{3+}$-$BaLaGa_3O_7$ phosphors.

## 1. Introduction

During the last decades the need for cheap, durable, and energy-saving illumination sources has pointed out those light-emitting diodes (LEDs) as the best candidates for future applications. Several materials and spectroscopic properties are investigated in order to succeed in optimizing white light devices. The first white light emitting diode (LED) became commercially available in 1997 [1–3]. Nowadays, many researchers are dedicated to develop new phosphor systems used as light-conversion phosphors for WLEDs. White light can be obtained by not only mixing the appropriate ratio of the three primary red, green, and blue colors, but also by creating the appropriate mixture of blue and yellow emissions [4–8]. Rare earth (RE) ions are often applied in various fields such as field-emission displays (FED), temperature sensor and solar cell ions for their promising applications in solid-state multicolor [9–12]. Among the RE ions, $Dy^{3+}$ ion has attracted much attention because of its white light emission [13,14].

It is well-known that a $Dy^{3+}$ ion with a $^4F_9$ electronic configuration generally has two dominant emission bands in visible range: the blue band (470–500 nm) due to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and the yellow band (570–600 nm) due to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. White light could be obtained with appropriate ratio of blue/yellow intensity in some special host lattices [15–17]. But $Dy^{3+}$ ions often emit yellow light because the ultra-sensitive transition dominated in the host lattice [18–20]. In such cases, the co-doped $Tm^{3+}$ ion is expected to effectively improve the blue emission portion and thus obtain the better color purity of white emission because the transition $^1D_2 \rightarrow {}^3F_4$ of $Tm^{3+}$ ions can emit blue emission (450 nm).

Because of the high chemical stability, good thermal quenching, and showing intense luminescence for WLEDs application when activated with rare earth ions $BaLaGa_3O_7$ (BLGO) is a good candidate as host structure. To our best knowledge, the luminescence properties of $Tm^{3+}$-, $Dy^{3+}$-$BaLaGa_3O_7$ have not been reported in the literature. In this paper, we have firstly demonstrated a white emitting $Tm^{3+}$-, $Dy^{3+}$-$BaLaGa_3O_7$ phosphors prepared by solid-state reaction method at high temperature.

## 2. Experimental

### 2.1. Preparation

The $Tm^{3+}$-, $Dy^{3+}$-$BaLaGa_3O_7$ and $Pr^{3+}$-$BaLaGa_3O_7$ samples were all prepared by solid-state reaction method at high temperature. The starting materials were $BaCO_3$ (AR grade), $La_2O_3$ (4N), $Ga_2O_3$ (5N), $Dy_2O_3$ (4N) and $Tm_2O_3$ (4N). The doping

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concentration varied from 0.5–5% in relation to $Tm^{3+}$, $Dy^{3+}$ ions in BLGO respectively.

The appropriate amounts of raw materials mentioned above were weighed according to the stoichiometric ratio, subsequently mixed and grounded together in an agate mortar. The powder mixtures were then transferred into corundum crucibles, and sintered in a muffle furnace at 1200 °C for 12 h to decompose the carbonate by a reaction-driven process and eliminate the water. The sintering temperature was then elevated to 1300 °C and kept for 8 h. After the temperature was cooled to room temperature in the muffle furnace and the samples were grounded and sintered again. The last grounded powder is used for subsequent measurement.

### 2.2. Characterization

All the samples were characterized by a MiniFlex2 X-ray powder diffractometer with Cu-Ka radiation (40 kV, 100 mA). The $2\theta$ scan range was 10–80° with a step size of 0.03°. The photoluminescence (PL) spectra were recorded with an Edinburgh Instruments FLS920 spectrofluorimeter equipped with a Xe light source and double excitation monochromators which the spectral resolution is 0.05–18 nm. The lifetime was measured by Edinburgh Instruments FSP920 spectrofluorimeter equipped with an OPO laser source double excitation monochromators which the spectral resolution is 0.05–18 nm. All the measurements were carried out at room temperature.

## 3. Results and discussion

The representative XRD patterns of $Dy^{3+}$-, $Tm^{3+}$-BLGO samples are shown in Fig. 1. All diffraction peaks of the samples coincide well with the literature values of BLGO (JCPDS No. 50-1800). No obvious shifting of peaks or other impurity phase can be detected at the current doping level, indicating that the $Tm^{3+}$, $Dy^{3+}$ ions are completely dissolved in the BLGO host lattice by replacing the $La^{3+}$ ions.

### 3.1. Spectra properties of $Dy^{3+}$ doped BLGO

The photoluminescence excitation spectrum and the emission spectrum of $Dy^{3+}$: BLGO sample are shown in Fig. 2. Fig. 2(a) shows the peaks located at 344, 383, 422, 451, 471 nm are attributed to the transition of the $Dy^{3+}$ ions from $^6H_{15/2}$ level to the $^6P_{7/2}$, $^4K_{17/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$ levels, respectively [21]. The emission spectra of BLGO: 1.0% $Dy^{3+}$ excited at 344 nm is shown in Fig. 2(b). The emission intensity of $Dy^{3+}$ ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) as a function of its doping concentration in BLGO samples which was excited at the 344 nm is shown in Fig. 3. The main stronger emission peak centered at 476, 573, 661 attributes to the transition $^4F_{9/2}\rightarrow{}^6H_{15/2}$, $^4F_{9/2}\rightarrow{}^6H_{13/2}$, $^4F_{9/2}\rightarrow{}^6H_{11/2}$ respectively and that with the increasing of the doping concentration, the luminous intensity ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) of $Dy^{3+}$ ions becomes stronger and reaches the maximum when the doping concentration is 2.0%. With the doping concentration continues to increase, the luminous intensity of $Dy^{3+}$ ions becomes weaker, which shows the typical concentration quenching effect. The emission spectra also show that the intensity of the yellow emission is significantly stronger than that of the blue emission. The chromaticity coordinates of the samples all fall on the yellow which was identified in Fig. 4(a).

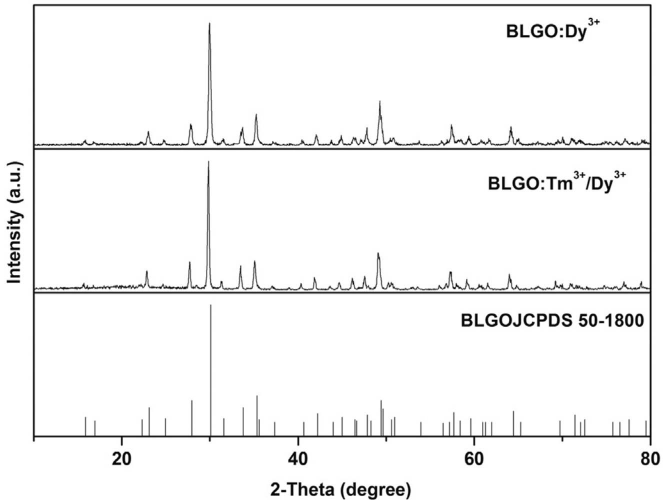

**Fig. 1.** The representative XRD patterns of $Dy^{3+}$, $Tm^{3+}$: BLGO samples.

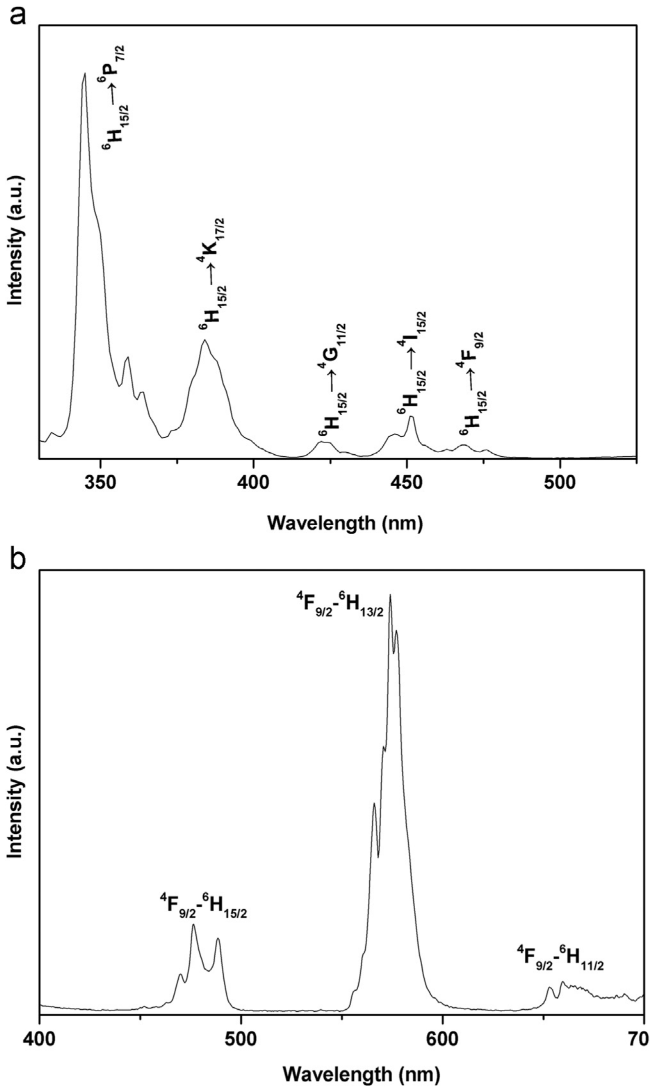

**Fig. 2.** (a) Excitation spectrum ($\lambda_{em}$=573 nm) of the BLGO: 1.0% $Dy^{3+}$. (b) Emission spectrum ($\lambda_{ex}$=344 nm) of the BLGO: 1.0% $Dy^{3+}$.

### 3.2. Spectra properties of $Tm^{3+}$/$Dy^{3+}$ doped BLGO

As we know the $Tm^{3+}$/$Dy^{3+}$-codoped phosphors are effective on improving the blue light emission portion and white light with good color purity have been obtained [22,23]. The excitation and emission spectra of $Tm^{3+}$: BLGO sample are shown in Fig. 5. The excitation peak at 347 nm attributes to the absorption transition of $^3H_6\rightarrow{}^1D_2$ of $Tm^{3+}$ [24]. The emission peak at 454 nm attributes to the transition $^1D_2\rightarrow{}^3F_4$ of $Tm^{3+}$ ions. Fig. 6 presents the emission spectra of