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Luminescence studies of Sm^{3+} single-doped and Sm^{3+}, Dy^{3+} co-doped $NaGdTiO_4$ phosphors

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ABSTRACT

Sm^{3+} single-doped and Sm^{3+}, Dy^{3+} co-doped $NaGdTiO_4$ phosphors were synthesized via a traditional high temperature solid-state reaction method. The crystal structure was characterized by means of x-ray diffraction. The luminescence properties and energy transfer in Sm^{3+} single-doped and Sm^{3+}, Dy^{3+} co-doped $NaGdTiO_4$ phosphors were systematically studied. The electric dipole-dipole interaction between Sm^{3+} ions was identified as the main mechanism for the concentration dependent fluorescence quenching in Sm^{3+} single-doped samples. It is confirmed that there is almost no energy transfer between Sm^{3+} and Dy^{3+} in Sm^{3+}, Dy^{3+} co-doped samples. The introduction of Sm^{3+} can compensate the red emission component and adjust the colorimetric performance of Dy^{3+}-doped $NaGdTiO_4$ phosphors. Moreover, different emitting colors can be obtained from Sm^{3+}, Dy^{3+} co-doped $NaGdTiO_4$ phosphor by changing the excitation pathway.

1. Introduction

Recently, rare earth (RE) doped luminescence materials have received great interest for their potential applications in the fields of lighting, display devices, solid-state laser, and optoelectronic devices, etc. [1–4]. In the field of solid-state lighting, white light emitting diodes (WLEDs), as a more preferable replacement for the conventional incandescent lamps and fluorescent lamps have attracted much attention owing to their many advantages such as high luminous efficiency, low power consumption, environmental friendliness, and long serving lifetime [5–8]. Nowadays, phosphor-conversion is the most common method for achieving white light emission. The mainstreamed commercial WLEDs are just obtained by combining the GaN-based blue LED chip with a yellow-emitting YAG: Ce^{3+} phosphor. However, such WLEDs have several drawbacks in practical applications, for example lower color rendering index and higher color temperature due to the deficiency of red emission [9–11]. It has been reported that trivalent dysprosium ion (Dy^{3+}) might be used as a promising activator for white light emission since its peculiar blue (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$) and yellow (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$) emissions [12–14]. However, Dy^{3+} single-doped sample has the same problem of lack of red component emission as the above-mentioned commercial WLEDs. Therefore, exploring a suitable red phosphor to compensate the red component is of great significance for obtaining WLEDs with high performance. Typically, fixed-color emission independent from excitation wavelength is obtained in one luminescence material. However, in practical applications the phosphors with varied-color emissions are also required in some fields, for example, optical anti-fake and neon sign. Therefore, developing novel phosphors emitting various colors upon adjusting the excitation wavelength is also significant.

As is well known, the host material plays an important role in RE-doped phosphors. Among various kinds of host materials, titanates have attracted particular interest due to its easy preparation, low cost, and excellent physical and chemical stabilities [13–16]. Moreover, the TiO_4^{4-} group has intense and broad absorption band in the near ultraviolet region and the absorbed energy can be effectively transferred to the luminescence centers. Therefore, in the present study $NaGdTiO_4$ was chosen as host matrix to examine the spectral properties of RE ions.

In this work, we studied on the luminescence properties and energy transfer of Sm^{3+} single-doped and Sm^{3+}, Dy^{3+} co-doped $NaGdTiO_4$ phosphors with various Sm^{3+} concentrations synthesized via a simple high temperature solid-state reaction route. The x-ray diffraction (XRD) and fluorescence spectroscopy were used to characterize the samples. The luminescence properties and energy transfer of Sm^{3+} single-doped and Sm^{3+}, Dy^{3+} co-doped samples are systematically discussed. The chromatic features of the phosphors are also investigated.

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2. Experimental

2.1. Sample synthesis

Two sets of $NaGdTiO_4$: *x* mol% Sm^{3+} ($x=0.2$, 0.5, 1, 3, 5, 7 and 9) and $NaGdTiO_4$: 3 mol% Dy^{3+}, *y* mol% Sm^{3+} ($y=0$, 1, 2, 3, 4, 5) phosphors were synthesized via a traditional high temperature solid-state reaction method in air atmosphere. In a typical synthesis, stoichiometric amounts of Gd_2O_3 (99.99%), Sm_2O_3 (99.99%), Dy_2O_3 (99.99%), TiO_2, and Na_2CO_3 powders were weighed firstly. Here excessive Na_2CO_3 (50 mol%) were used as a flux to improve the chemical reaction. The weighed starting materials were then well mixed in an agate mortar and calcined at 1000 °C for 4 h. A detailed preparation procedure could be found in Ref. [14].

2.2. Sample characterization

XRD were performed on a SHIMADZU XRD-6000 diffractometer with CuKα ($\lambda=1.5406$ Å) radiation. The fluorescence spectra and fluorescence decay curves of the phosphors were obtained by a Hitachi F-4600 fluorospectrophotometer with a 150 W xenon lamp as the excitation source. This fluorospectrophotometer was well intensity-calibrated for the excitation and emission spectra. The temperatures of the studied samples were controlled by a sample temperature controlling system DMU-TC 450 assembled in our lab.

3. Results and discussion

3.1. Crystal structure

In order to identify the crystal structure of the obtained samples, XRD measurements were performed for all the obtained $NaGdTiO_4$ phosphors. It is found that all the samples exhibit very similar diffraction patterns and coincide with the standard diffraction data in JCPDS card no. 86-0830 for orthorhombic $NaGdTiO_4$. Fig. 1 shows the normalized XRD patterns of the as-synthesized $NaGdTiO_4$ phosphors single-doped with 5 mol% Sm^{3+} (top) and co-doped with 3 mol% Dy^{3+} and 5 mol% Sm^{3+} (middle) as representatives, together with the standard pattern of the orthorhombic structure $NaGdTiO_4$ (bottom) for comparison. It can be found that all of the observed diffraction peaks from the as-synthesized samples are in good agreement with those appearing in the JCPDS card no. 86-0830. No extraneous diffraction peaks emerge in these patterns, indicating Sm^{3+} and Dy^{3+} doping does not obviously affect the crystal structure of $NaGdTiO_4$ in the studied concentration range. Meanwhile, the well-defined peaks demonstrate that Sm^{3+} and Dy^{3+} have been substituted into the host lattice of $NaGdTiO_4$.

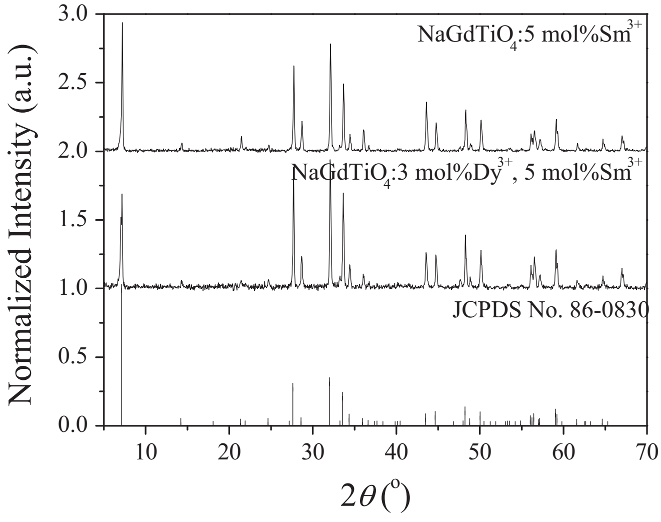

Fig. 1. Normalized XRD patterns for the phosphors $NaGdTiO_4$: 5 mol% Sm^{3+} (top), $NaGdTiO_4$: 3 mol% Dy^{3+}, 5 mol% Sm^{3+} (middle) and for the standard data reported in JCPDS card No. 86-0830 (bottom).

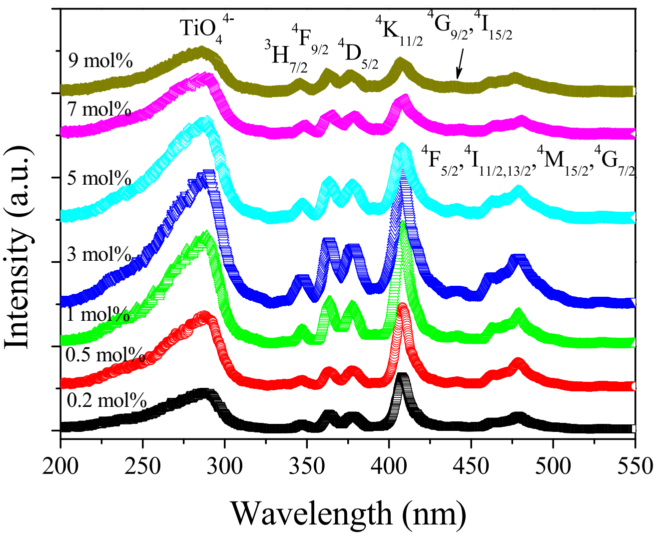

Fig. 2. Excitation spectra of $NaGdTiO_4$: *x* mol% Sm^{3+} ($x=0.2$, 0.5, 1, 3, 5, 7 and 9) measured by monitoring 605 nm emission of Sm^{3+}.

3.2. Luminescence properties and energy transfer of Sm^{3+}

Excitation spectra of all the Sm^{3+} single-doped samples with various Sm^{3+} concentrations were measured under the same conditions and are shown in Fig. 2. The monitored wavelength is the dominant emission at 605 nm corresponding to the $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition of Sm^{3+}. It can be seen that all the samples have a similar spectral profile in addition to the intensity. Each excitation spectrum is composed of two parts. One is a broad band ranging from 200 to 300 nm with a maximum value at around 288 nm corresponding to the absorption of TiO_4^{4-} group [14,17], indicating an energy transfer from $NaGdTiO_4$ host to Sm^{3+}. Another is consisting of a series of sharp peaks located at 300–500 nm, which can be assigned to the intrinsic *f–f* transitions of Sm^{3+} from the ground state $^6H_{5/2}$ to the excited states $^3H_{7/2}$, $^4F_{9/2}$, $^4D_{5/2}$, $^4K_{11/2}$, $^4G_{9/2}$, $^4I_{15/2}$, $^4F_{5/2}$, $^4I_{13/2}$, $^4I_{11/2}$, $^4M_{15/2}$, and $^4G_{7/2}$, respectively. It can also be found that the absorption intensity of TiO_4^{4-} group is almost equivalent with that of the strongest *f–f* transition $^6H_{5/2}\rightarrow{}^4K_{11/2}$ of Sm^{3+}, implying an efficient energy transfer from $NaGdTiO_4$ host to Sm^{3+}.

Fig. 3 shows the emission spectra for the samples single-doped with various Sm^{3+} concentrations upon 288 nm and 408 nm excitations measured at the same experimental conditions. It can be seen that all of the spectra excited by 288 nm almost have the same spectral profile, including a weak broad band emission and four sharp lines. The weak broad band emission originates from the $NaGdTiO_4$ host, while the four sharp lines centered at 566, 605, 651 and 714 nm being the characteristic emissions of Sm^{3+} correspond to the transitions from $^4G_{5/2}$ level to $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ levels, respectively [18,19]. Under 408 nm excitation corresponding to the absorption of $^6H_{5/2}\rightarrow{}^4K_{11/2}$ transition of Sm^{3+}, only those four characteristic emissions of Sm^{3+} can be detected. From Fig. 3, it can also be found that the intensities of all of the spectra follow the same change trend with increasing Sm^{3+} concentration in both excitation cases. The intensity of the broad band