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Synthesis and photoluminescence properties of $(Y,Gd)SiO_5:Tb^{3+}$ under VUV excitation

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Abstract

Single phase of green-emitting $X_2-(Y,Gd)SiO5:Tb^{3+}$ phosphoqr was successfully prepared at 1250 °C by a co-precipitation process. The photoluminescence of as-prepared $Y_{1.9}SiO_5:0.1Tb^{3+}$ and $Y_{1.85}Gd_{0.05}SiO_5:0.1Tb^{3+}$ were investigated in vacuum ultraviolet region. Under 147 nm excitation, the phosphors showed main emission peak at 543 nm attributed to the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+}. According to the relative emission intensity of samples with different composition, the optimal substitution proportions of Tb and Gd for Y were determined to be 10% and 5%, respectively. Besides, $Y_{1.85}Gd_{0.05}SiO_5:0.1Tb^{3+}$ maintained the short decay time of $Y_2SiO_5:Tb^{3+}$ phosphor only 3.5 ms, which is much shorter than the commercial green-emitting phosphor $Zn_2SiO_4:Mn^{2+}$. As showed in the excitation spectrum, the 141 and 175 nm excitation bands were assigned to the charge transfer bands of Y–O and Gd–O, respectively. Compared to $Y_2SiO_5:Tb^{3+}$, Gd^{3+} provided another energy transfer channel from matrix to the luminescence center Tb^{3+}, thereby enhancing the photoluminescence efficiency. The projected density of states of Y_2SiO_5 and Gd_2SiO_5 were also discussed in this work trying to understand the charge transfer mechanics of this phosphor.

Keywords: A. Powders: chemical preparation; B. Spectroscopy; C. Optical properties

1. Introduction

Much attention has been paid to vacuum ultraviolet (VUV) phosphors due to the demands of plasma display panels (PDPs). Xe plasma discharge that generates VUV photons with the wavelength mainly at 147 and 172 nm is utilized as the excitation source. Phosphors that convert the VUV radiation into visible light are the main factor directly affecting the picture quality and the longevity of PDPs [1]. Most of the phosphors used in industry today are either silicate or sulfide based phosphors. Silicate-based phosphors have attracted much attention because of its low cost, high luminescent efficiency [2], and excellent stability and inertness against the degradation in chemical and thermal properties. Yttrium silicate (Y_2SiO_5) is an important luminescent host material for various rare-earth (RE) activators that has been synthesized by chemical method since 1964 [3]. Of the various RE ions, trivalent terbium (Tb^{3+}) displays efficient radiative recombination channels, mainly observed in the green region of the visible spectral range [4–7]. It is an important part of red green blue (RGB) panels since the maximum of the human eye sensibility falls in this region. Nowadays a representative green phosphor used for PDPs is $Zn_2SiO_4:Mn^{2+}$ (ZSM), but it is known to have a somewhat long decay time which is a significant shortcoming for exploiting the fast response of the PDPs especially the 3D PDPs [8]. As ZSM has been unable to meet the requirements of high quality display, a new kind of green phosphor with short decay time is in great need. Excitated by VUV light, Tb^{3+} activated yttrium silicate can emit green light and the decay time is 3.1 ms which is much shorter than the commercial ZSM 5.1 ms [9]. But considering the high energy of VUV light, the luminous efficiency of this phosphor is relatively low. It is a feasible method that co-doping with certain RE ions that can enhance the absorptivity and does not emit light to enhance the efficiency while

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maintain the purity of emitting light and the short decay time. It has been reported that the RE ion Gd^{3+} can play the role of intermediate energy transferor [10] in phosphors.

There is another property needed to be considered of Y_2SiO_5 that it exists in two phases, namely low-temperature phase X_1 and high-temperature phase X_2 with space groups of $P2_1/c$ and $B2/b$, respectively [11]. It has been proved that the X_2–Y_2SiO_5 is a better host lattice for the luminescence of lanthanide ions than the X_1–Y_2SiO_5 [12]. In this work, we try to get the X_2 phase Y_2SiO_5 in co-precipitation method and co-dope it with Tb and Gd.

2. Experimental section

All samples were prepared by co-precipitation method. The starting materials are Y_2O_3 (99.99%), Gd_2O_3 (99.99%), Tb_4O_7 (99.99%) and tetraethyl orthosilicate (TEOS) (analytical grade, AR). Stoichiometrically weighed Y_2O_3, Gd_2O_3 and Tb_4O_7 were dissolved in concentrated nitric acid (AR) and heated with stirring until the all the powders were dissolved. Distilled water / ethanol (AR) (1:1 in v/v) was added to the solution to adjust the pH value to about 1. Then 10% excess TEOS (considering of its volatility) and $(NH_4)_2CO_3$ (AR) in large excess were added into above solution under stirring at room temperature until the pH $\approx$ 8. After aging for 4 h, as no more precipitation could be observed, then the slurry was filtered, washed with distilled water and dried at 110 °C in air to obtain a white powder. The dried precursor was sintered at 1250 °C in ambient atmosphere for 4 h and the final sample was achieved.

The powder X-ray diffraction data were acquired by an advanced automatic diffractometer (XRD-7000, Shimadzu Limited) with Ni-filtered Cu Kα radiation (λ=0.15406 nm). The photoluminescence (PL) spectra were measured by a FLS920T spectrophotometer. The relative emission intensity under VUV excitation of these samples was recorded by a spectroscopic testing system provided by the Daiden Co. Ltd.

3. Results and discussion

3.1. Phase Characterizations and XRD analysis

Fig. 1 (*a*) and (*b*) present the powder X-ray diffraction patterns of $Y_{2-x}SiO_5{:}xTb^{3+}$ with x=0, 0.01, 0.04, 0.1, 0.15, 0.2 and $Y_{1.9-y}Gd_ySiO_5$: $0.1Tb^{3+}$ with y=0, 0.005, 0.01, 0.05, 0.1, 0.2. The formula $Y_{2-x-y}Gd_ySiO_5{:}xTb^{3+}$ is used to represent the sample composition. All the patterns are well in agreement with the standard JCPDS 36-1476, indicating that a single phase of X_2–Y_2SiO_5 crystallized completely at 1250 °C. No shifting of diffraction features was observed with increasing the doped Tb^{3+} and Gd^{3+} proportion attributed to the low doping levels and the similarity of ionic radii of Y^{3+} with Tb^{3+} and Gd^{3+} [13].

3.2. Analysis of VUV spectra

Shown in Fig. 2 are the emission spectra of $Y_{1.9}SiO_5{:}0.1Tb^{3+}$, $Y_{1.85}Gd_{0.05}SiO_5{:}0.1Tb^{3+}$ and commercial $Zn_2SiO_4{:}Mn^{2+}$ under VUV excitation of 147 nm. The emission intensity of $Y_{1.85}Gd_{0.05}SiO_5{:}0.1Tb^{3+}$ and $Y_{1.9}SiO_5$: $0.1Tb^{3+}$ is much higher than commercial $Zn_2SiO_4{:}Mn^{2+}$. Both of the emission spectra of $Y_{1.9}SiO_5{:}0.1Tb^{3+}$ and $Y_{1.85}Gd_{0.05}SiO_5{:}0.1Tb^{3+}$ exhibit characteristic emissions of Tb^{3+} which are located around 488, 543, 591 and 618 nm corresponding to $^5D_4\rightarrow{}^7F_6$, $^5D_4\rightarrow{}^7F_5$, $^5D_4\rightarrow{}^7F_4$, and $^5D_4\rightarrow{}^7F_3$ transitions, respectively. It exhibits green-emitting color due to the strongest emission peak at 543 nm ($^5D_4\rightarrow{}^7F_5$). As shown in Fig. 2, the intensity of electric-dipole allowed transitions $^5D_4\rightarrow{}^7F_{5,6}$ was much stronger than that of magnetic-dipole allowed transitions $^5D_4\rightarrow{}^7F_{3,4}$. For the absence of inversion symmetry at the Tb^{3+} (or Y^{3+}) lattice site, the electric-dipole transition would dominate. Moreover, it is found that the Gd–Tb co-doped sample emission intensity is higher than the Tb singly doped sample. No emission spectrum of Gd^{3+} is founded indicating that the doped Gd^{3+} played as a sensitizer which transferred the energy to the luminescence center Tb^{3+}, but itself does not emit light thereby maintaining the color purity of the emitting light.

To optimize the activator content doped in the host lattice, the relative emission intensity is measured as a function of Tb^{3+} concentration relative to Y^{3+}. As shown in Fig. 3, the relative intensity ($^5D_4\rightarrow{}^7F_5$, 543 nm) of $Y_{2-x}SiO_5{:}xTb^{3+}$ is found to increase with increasing Tb^{3+} concentration and reaches a maximum when x=0.1. Attributed to concentration-quenching effect, the relative intensity is found to decrease with the concentration of doped Tb^{3+} greater than 10%. As the wavelength of excitation light altering from 147 to 172 nm, the emission spectrum resembles those excitated at 147 nm both in shape and trend. So the doped Tb^{3+} content is maintained at 10% for all phosphor samples discussed in the following.

As the X_2–$Y_2SiO_5{:}Tb^{3+}$ is reported to emit green light in the VUV range [9], we attempt to design a PDP phosphor with great PL efficiency by doping Gd into the Y site of $Y_{1.9}SiO_5{:}0.1Tb^{3+}$ which composition has been previously optimized to form $Y_{1.9-y}Gd_ySiO_5{:}0.1Tb^{3+}$ phosphors in a series with varied y value. The emission spectra of $Y_{1.9-y}Gd_ySiO_5{:}0.1Tb^{3+}$ is similar with $Y_{1.9}SiO_5{:}0.1Tb^{3+}$, as $Y_{1.85}Gd_{0.05}Tb_{0.1}SiO_5$ is showed in fig. 2 as an example.

Shown in Fig. 4 is the dependence of doped Gd content on the relative intensity of $^5D_4\rightarrow{}^7F_5$ (543 nm) emission observed for $Y_{1.9-y}Gd_ySiO_5{:}0.1Tb^{3+}$ phosphors with y=0.005, 0.01, 0.05, 0.1 and 0.2. The relative emission intensity increases abruptly as Gd doped at a small proportion (i.e., y=0.01). According to the results presented in Fig. 4, concentration-quenching is attributed to excessive doping of Gd (i.e., $y>0.05$) that gradually imposes a detrimental effect on the VUV PL intensity. The result is same when the wavelength of excitation was altered from 147 to 172 nm. The optimal doping proportion of Gd^{3+} is thus selected as 0.05 forming a composition $Y_{1.85}Gd_{0.05}SiO_5{:}0.1Tb^{3+}$ that was adopted for the following spectral and optical investigations.