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Effect of codopants on enhanced luminescence of $GdTaO_4:Eu^{3+}$ phosphors

Xiaolin Liu, Kun Han, Mu Gu*, Lihong Xiao, Chen Ni, Shiming Huang, Bo Liu

Laboratory of Waves & Microstructure Materials, Pohl Institute of Solid State Physics, Tongji University, Shanghai 200092, People's Republic of China

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Abstract

$(Gd_{0.92-x}M_x)TaO_4:Eu_{0.08}$ ($M = Li^+, Na^+, K^+, Mg^{2+}, Zn^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}$) phosphors were synthesized by conventional solid-state reaction. The effect of codoping M ions on enhanced photoluminescence (PL) of $GdTaO_4:Eu^{3+}$ was investigated. It was found that the improvement of PL intensity was closely related to the effective ionic radius of codopant and the mismatch in Pauling's electronegativity between codopant and Gd. The PL intensity of $GdTaO_4:Eu^{3+}$ phosphor was improved evidently by codoping with Li^+, Mg^{2+}, Zn^{2+}, or Al^{3+} whose radius is less than that of Gd^{3+}, and hardly with Na^+, K^+, Ca^{2+}, or Ba^{2+} whose radius is larger than that of Gd^{3+}. Meanwhile, the intensity increased with the electronegativity mismatch for codoping with Li^+, Mg^{2+}, Zn^{2+}, or Al^{3+}. It was proposed that the effect of codopants on enhanced luminescence was mainly regarded as the result of a suitable local distortion of crystal field surrounding the Eu^{3+} activator. These results will play an important role in seeking some more effective codopants.

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1. Introduction

Rare-earth tantalate is one of the promising materials for applications in X-ray imaging systems because of its excellent scintillation performance [1]. For instance, Eu^{3+} activated $GdTaO_4$ phosphors possess the advantages of high density ($8.84\ g\ cm^{-3}$), stable chemical properties, strong irradiation hardness, good X-ray absorption and red emission of Eu^{3+} ion coinciding with the maximum efficiency of CCD detector [2]. Many researchers have reported the inspiring luminescent properties of rare-earth tantalate phosphors [3–6]. Certainly, it will be very beneficial to further improve their luminescent intensities for practical applications.

In many cases the luminescent efficiency of phosphors can be enhanced by modifying their compositions. It has been reported that sometimes even very small quantities of codopants can lead to a great improvement of luminescent efficiency of phosphors [7–9]. In our prior work, the enhanced luminescence of $GdTaO_4:Eu^{3+}$phosphors by codoping with Zn^{2+} ions were also reported [10]. All of these results indicated that various codopants might exhibit different effects. Some ions may directly act as a flux [7,8] or sensitizer [9], and the others could enter into the host lattice, creating oxygen vacancies or altering the crystal field surrounding the activator, then affecting the luminescence performances of the phosphors [8,11]. However, there is a lack of knowledge on the intercommunication between codopants. It is very important to inquire into the characteristics of codopants so as to further understand the mechanism of enhanced luminescence, and also help us to look for some more effective codoping ions. To the best of our knowledge, this problem has been seldom studied.

In this paper, various M ions ($M = Li^+, Na^+, K^+, Mg^{2+}, Zn^{2+}, Ca^{2+}, Ba^{2+}$, and Al^{3+}) were doped individually into $GdTaO_4:Eu^{3+}$ phosphors. The influence of codopants on the photoluminescence (PL) of the phosphors was investigated primarily. The results indicated that enhanced luminescence was closely related not only to the effective radius of codopant, but also to the mismatch in the electronegativity between codopant and Gd.

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* Corresponding author. Tel.: +86 021 65980219; fax: +86 021 65980219.
E-mail address: muguk@online.sh.cn (M. Gu).

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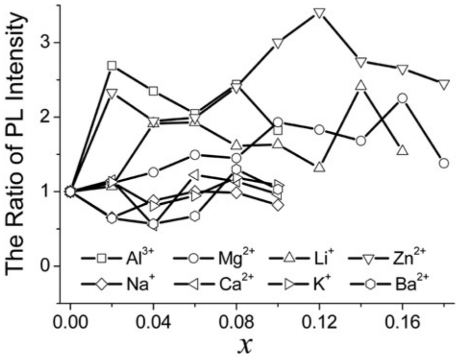

Fig. 1. The PL intensity ratio of $(Gd_{0.92-x}M_x)TaO_4:Eu_{0.08}$ to $Gd_{0.92}TaO_4:Eu_{0.08}$ phosphors fired at 1200 °C, $\lambda_{ex} = 250$ nm, where M denotes $Li^+, Na^+, K^+, Mg^{2+}, Zn^{2+}, Ca^{2+}, Ba^{2+}$ and Al^{3+}.

2. Experimental

$(Gd_{0.92-x}M_x)TaO_4:Eu_{008}$ ($M = Li^+, Na^+, K^+, Mg^{2+}, Zn^{2+}, Ca^{2+}, Ba^{2+}$, or Al^{3+}) phosphors were synthesized by conventional solid-state reaction. The raw materials were $Gd_2O_3, Ta_2O_5, Eu_2O_3$ (all of 99.99% purity), which were prefired first at 900 °C to eliminate any contained moisture and undecomposed oxalates, then weighed at the stoichiometric molar ratio of $Gd^{3+}:Ta^{5+}:Eu^{3+}:M = (0.92 - x):1:0.08:x$ ($x = 0$–0.18) with sequential mixing and grinding. M ions were added in the form of nitrate or carbonate. The blend was heated up to 1200 °C from room temperature at a rate of 4 °C/min and remained there for 3 h. Finally, it was naturally cooled to room temperature again, followed by careful grinding.

The excitation and emission spectra were recorded with a Perkin-Elmer LS-55 luminescence spectrometer. The structure of phosphor was examined by a Rigaku D/max-2550 X-ray powder diffractometer with Cu Kα radiation ($\lambda = 1.5405$ Å) operated at 40 kV and 100 mA. All measurements were carried out at room temperature.

3. Results and discussion

To determine the optimal concentration of codopant, PL intensity at 611 nm, which is the strongest emission peak of the Eu^{3+} activator, was recorded, and the PL intensity ratio of $(Gd_{0.92-x}M_x)TaO_4:Eu_{0.08}$ to $Gd_{0.92}TaO_4:Eu_{0.08}$ is illustrated in Fig. 1. The intensity is associated with the codopant contents, and the optimal x values for $Li^+, Na^+, K^+, Mg^{2+}, Zn^{2+}, Ca^{2+}, Ba^{2+}$, and Al^{3+} are 0.14, 0.06, 0.08, 0.16, 0.12, 0.06, 0.08, and 0.02 respectively. The following discussions will mainly focus on the samples with optimal concentration.

The PL spectra of $(Gd_{0.92-x}M_x)TaO_4:Eu_{0.08}$ ($M = Li^+, Na^+, K^+, Mg^{2+}, Zn^{2+}, Ca^{2+}, Ba^{2+}$, and Al^{3+}) phosphors are shown in Fig. 2. Narrow emission peaks are expected due to the shielding effect of 4f electrons by 5s and 5p electrons in the outer shells of the Eu^{3+} activator. The strongest emission peak located at 611 nm is assigned to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions, and the peaks around 591 and 705 nm are related to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively. It is obvious that different codopants have different contributions on PL intensity of $GdTaO_4:Eu^{3+}$ phosphor. And the intensity is improved remarkably by codoping with Li^+, Mg^{2+}, Zn^{2+}, or Al^{3+}, and hardly with Na^+, K^+, Ca^{2+}, or Ba^{2+}.

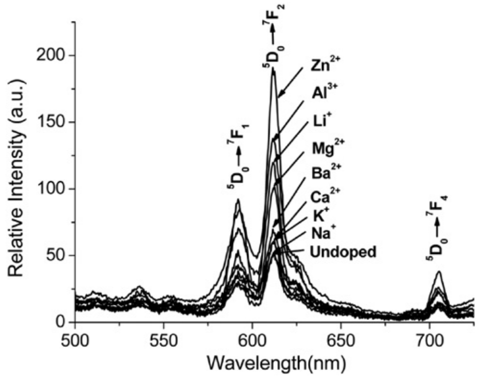

Fig. 2. Emission spectra of $(Gd_{0.92-x}M_x)TaO_4:Eu_{0.08}$ phosphors fired at 1200 °C, $\lambda_{ex} = 250$ nm, where M denotes $Li^+, Na^+, K^+, Mg^{2+}, Zn^{2+}, Ca^{2+}, Ba^{2+}$ and Al^{3+}, and the optimal x values for them are 0.14, 0.06, 0.08, 0.16, 0.12, 0.06, 0.08, and 0.02, respectively.

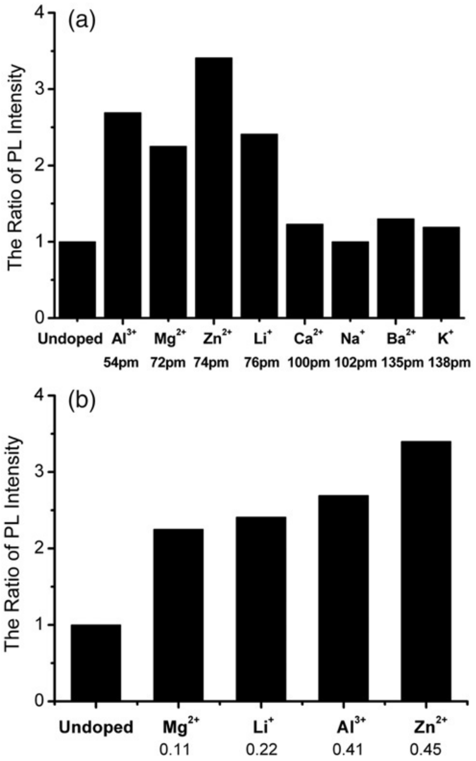

Fig. 3. The dependence of PL intensity ratio of $(Gd_{0.92-x}M_x)TaO_4:Eu_{0.08}$ to $Gd_{0.92}TaO_4:Eu_{0.08}$ phosphors fired at 1200 °C ($\lambda_{ex} = 250$ nm) on (a) effective ionic radius and (b) the electronegativity mismatch, where M denotes $Li^+, Na^+, K^+, Mg^{2+}, Zn^{2+}, Ca^{2+}, Ba^{2+}$ and Al^{3+}, and the optimal x values for them are 0.14, 0.06, 0.08, 0.16, 0.12, 0.06, 0.08, and 0.02, respectively.

The incorporation of codoping ions in the host lattice is associated with the mismatches in size and electronegativity between codopant and host cation. The effective ionic radii and Pauling's electronegativities of codopants are given in Table 1 [12]. To understand the influence of the size on