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Visible quantum cutting in $BaGd_2ZnO_5:Eu^{3+}$ phosphor

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Abstract

Eu^{3+} doped $BaGd_2ZnO_5$ phosphor was synthesized by a traditional solid-state reaction. The crystal structure of the product was characterized by means of X-ray diffraction (XRD). The ultraviolet (UV) and vacuum ultraviolet (VUV) photoluminescence properties of the phosphor were studied. Excitation spectra inferred that efficient energy transfer from Gd^{3+} to Eu^{3+} exists in the $BaGd_2ZnO_5:Eu^{3+}$. The visible quantum cutting process based on the Gd^{3+}–Eu^{3+} couple was observed in the $BaGd_2ZnO_5:Eu^{3+}$ phosphor. Two-step energy transfer process from Gd^{3+} to Eu^{3+}, viz. a cross-relaxation and a sequential transfer of the remaining excitation energy, is the mechanism responsible for visible quantum cutting in $BaGd_2ZnO_5:Eu^{3+}$ phosphor. Quantum cutting efficiency in $BaGd_2ZnO_5:Eu^{3+}$ was calculated to be around 133%.

Keywords: A. Powders: solid state reaction; B. Spectroscopy; C. Optical properties

1. Introduction

Nowadays, developing high efficient and environment-friendly lighting instrument to replace the traditional incandescent and fluorescent lamps is a significant subject. Non-mercury fluorescent lamp based on quantum cutting phosphors has been regarded as one of the promising candidates, owing to its facile preparation procedure, relatively low cost, fine illumination ability and environmental friendly characteristics [1,2]. However, to win higher quantum efficiency than the traditional mercury lamps, quantum cutting phosphors are required for mercury free lamps. Additionally, the quantum cutting phosphors could also find applications in the plasma display panels (PDP) [3,4]. Moreover, as a kind of light wavelength converting materials, the quantum cutting phosphors also interest the researchers in the attractive physical mechanisms of their luminescent processes [5,6]. Therefore, many efforts are devoted to the material and physical aspects of quantum cutting in rare earths doped materials [1–4].

To achieve high quantum cutting efficiency, both the luminescent centers and host matrixes are key factors which should be considered in the designs of quantum cutting materials. Usually, high quantum cutting efficiency can hardly be obtained from the materials with single-doping center due to the small inter-transition rates between excited states of rare earth ions. Thus, the rare earth co-doping is more preferable for the quantum cutting system in which the energy transfer rates can be controlled by adjusting the doping concentrations of donors and acceptors [1,5,6]. The most successful example with a quantum cutting efficiency of 190% was demonstrated by Wegh et al. in $LiGdF_4:Eu^{3+}$ using Gd^{3+}–Eu^{3+} couple [1]. To realize the quantum cutting from VUV to visible, the hosts, which should be transparent in VUV region or can transfer their absorbed energy to the quantum cutting centers, are required. At present, most of visible quantum cutting behaviors were observed in fluorides, but very less in some phosphates and borates [1,2,7–11]. It can be inferred that the host materials are also a bottleneck to the achievement of high efficiency quantum cutting. Exploring novel hosts is, therefore, important.

In comparison with fluorides, oxides can be more easily prepared via such as solid state reaction, co-precipitation,

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sol–gel and so on. On the other hand, oxides possess excellent chemical and physical stability which exhibits larger potential room for mercury free lamps or PDP. As one of oxide hosts, $BaGd_2ZnO_5$ has quite low phonon energy (about 360 cm^{-1}) and excellent stability, which may hold the probable multi-phonon relaxation back and favorite the cross-relaxation process [12]. Thus, $BaGd_2ZnO_5$ as a host material may be beneficial to quantum cutting. In this work, $BaGd_2ZnO_5:Eu^{3+}$ was studied as a quantum cutting phosphor for the first time and exhibits visible quantum efficiency around 133%.

2. Experimental

2.1. Samples preparation

$BaGd_2ZnO_5$:0.5 mol%Eu^{3+} phosphor was synthesized by a solid-state reaction using Gd_2O_3 (99.99%), Eu_2O_3 (99.99%), $BaCO_3$ (AR) and ZnO (AR) as starting materials. Stoichiometric homogenous mixture of the starting materials was obtained by ground thoroughly in an agate mortar. The mixture was calcined at 1200 °C in a muffle furnace for 4 h to obtain final products.

2.2. Characterization

The phase identification was performed by X-ray powder diffraction (Shimadzu XRD-6000) with $CuK\alpha_1$ radiation ($\lambda = 0.15406$ nm). The XRD data were collected by using a scanning mode in the 2θ ranging from 10° to 70° with a scanning step size of 0.02° and a scanning rate of 4.0° min^{-1}. The photoluminescence excitation and emission spectra were measured by a Hitachi F-4600 spectrophotometer equipped with a 150 W xenon lamp as an excitation source. The VUV excitation and emission spectra were measured by vacuum ultra-violet spectrophotometer manufactured by Changchun Institute of Optical, Fine Mechanics and Physics, Chinese Academy of Science (CIOMP, CAS, China), equipped with an excitation source of D_2 lamp. All the spectra were recorded at room temperature.

3. Results and discussion

The crystal structure and phase purity of the prepared sample was identified by XRD. The pattern of $BaGd_2ZnO_5$:0.5 mol% Eu^{3+} is shown in Fig. 1 together with the pattern plotted by using the data reported in JCPDS card No. 49-0518 for $BaGd_2ZnO_5$ powder. The XRD pattern of the studied sample agrees well with the pure $BaGd_2ZnO_5$, and no additional diffraction peaks were found, indicating that the sample is single-phased at the purity level that XRD can identify. Moreover, the diffraction peaks are sharp and intense, suggesting that the product is well crystallized, which may be in favor of an ideal luminescent efficiency.

The excitation ($\lambda_{em} = 628$ nm, $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}) and emission ($\lambda_{ex} = 275$ nm, $^8S_{7/2} \rightarrow {}^6I_J$ of Gd^{3+}) spectra for $BaGd_2ZnO_5$:0.5 mol% Eu^{3+} are shown in Fig. 2(a) and (b), respectively. In the excitation spectra, the broad band comes from both the contributions of O^2-Eu^{3+} charge transfer transition and the f–f transitions of Gd^{3+} from $^8S_{7/2}$ to ^6I_J, ^6D_J and ^6P_J. The weak lines ranging from 350 to 500 nm can be assigned to the intrinsic f–f transitions of Eu^{3+} from $^7F_0$ to $^5L_6$

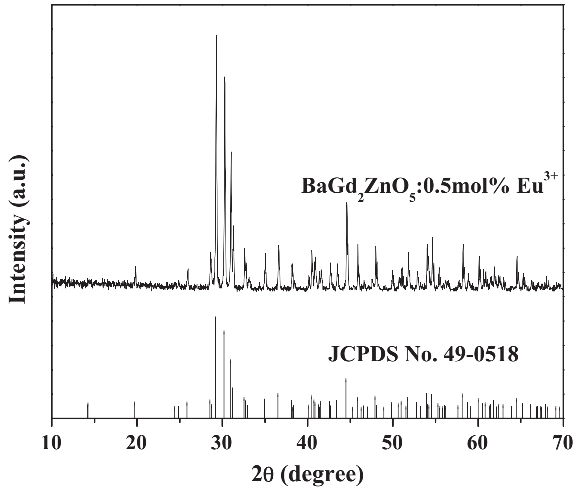

Fig. 1. XRD pattern for the prepared $BaGd_2ZnO_5$:0.5 mol% Eu^{3+} phosphor and the standard data for $BaGd_2ZnO_5$.

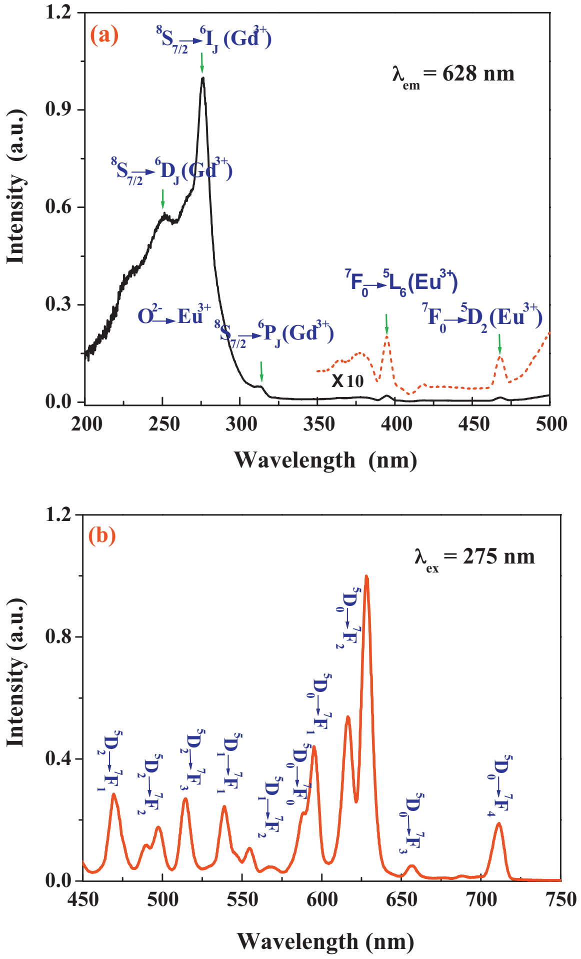

Fig. 2. UV excitation (a) and emission (b) spectra of $BaGd_2ZnO_5$:0.5 mol% Eu^{3+}phosphor.

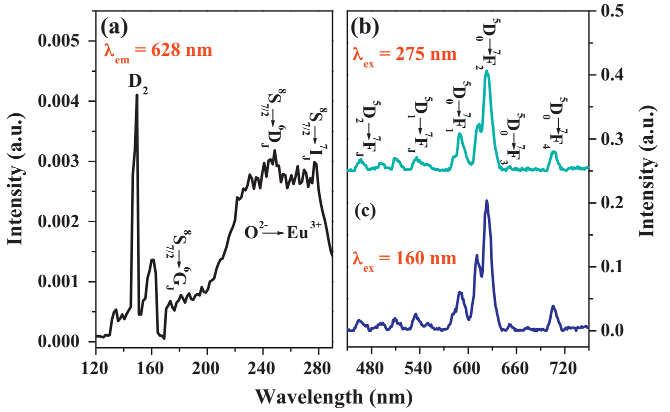

Fig. 3. VUV excitation (a) and emission (b and c) spectra of $BaGd_2ZnO_5$:0.5 mol% Eu^{3+} phosphor.

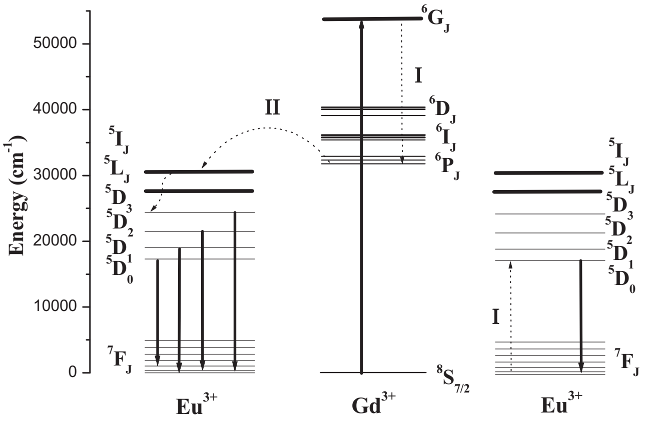

Fig. 4. Visible quantum cutting processes based on the Gd^{3+}–Eu^{3+} couple in the $BaGd_2ZnO_5$:Eu^{3+} phosphor.

and $^5D_2$, which can be seen as the dash curve enlarged by 10 times in Fig. 2(a) [7]. The existence of the transitions of Gd^{3+} in the excitation spectrum suggests that efficient energy transfer takes place from Gd^{3+} to Eu^{3+}. Under 275 nm excitation, the characteristic emissions from $^5D_2$, $^5D_1$ and $^5D_0$ levels to ^7F_J (J = 1–4) levels of Eu^{3+} are observed as labeled in Fig. 2(b) [13]. The $^5D_2 \rightarrow {}^7F_J$ and $^5D_1 \rightarrow {}^7F_J$ emission peaks are strong, which can be explained by the low phonon energy of the host lattice. Moreover, the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition is dominant in the emission spectrum, which indicates that the sites occupied by Eu^{3+} ions in the $BaGd_2ZnO_5$ phosphor deviates from the symmetric center [14].

Fig. 3(a) shows the VUV–UV excitation spectrum by monitoring 628 nm emission corresponding to $^5D_0 \rightarrow {}^7F_2$ transition. In this excitation spectrum, the $^8S_{7/2} \rightarrow {}^6G_J$ transitions of Gd^{3+}, which is of benefit to quantum cutting in Gd^{3+}–Eu^{3+} couple system, can be observed in the VUV region [8]. Fig. 3(b) and (c) exhibits the emission spectra of $BaGd_2ZnO_5$:0.5 mol% Eu^{3+} excited by 275 and 160 nm corresponding to the transitions of Gd^{3+} from $^8S_{7/2}$ to ^6I_J and ^6G_J, respectively. In the emission spectra, peaks at 590, 623, 651 and 705 nm can be attributed to the $^5D_0 \rightarrow^7 F_J$ (J = 1, 2, 3, 4) transitions of Eu^{3+}, and those ranging from 450 to 570 nm are attributed to the $^5D_{1,2} \rightarrow {}^7F_J$ transitions [15].

Gd^{3+}–Eu^{3+} couple is known as the most promising cutter couple for achieving visible quantum cutting by far [1,5]. The visible quantum cutting process can be achieved via a two-step energy transfer process as illustrated in Fig. 4. In the first energy transfer step (process I in Fig. 4), since there is a large spectral overlap between the $^6G_J \rightarrow {}^6P_J$ transition of Gd^{3+} and the $^7F_J \rightarrow {}^5D_0$ transitions of Eu^{3+}, the cross-relaxation process can take place efficiently through the channel of $^6G_J + {}^7F_J \rightarrow {}^6P_J + {}^5D_0$, which will result in a visible photon emission from $^5D_0 \rightarrow {}^7F_J$ transitions of Eu^{3+} and the population of ^6P_J levels of Gd^{3+}. In the second energy transfer step (process II in Fig. 4), the population of ^6P_J levels can be transferred further to the ^5I_J level of Eu^{3+}, and then the electrons at ^5I_J states relax rapidly to ^5D_J via cascade multiphonon nonradiative process. This process produces another visible photon emission, which is derived from ^5D_J to ^7F_J transitions of Eu^{3+}. In this way, the emissions of two visible photons by absorbing one VUV photon can be achieved via down-conversion in the Gd^{3+}–Eu^{3+} couple.

Wegh et al. have proposed the following equation to estimate the efficiency of the cross-relaxation in Gd^{3+}–Eu^{3+} systems [1]:

$$\frac{P_{CR}}{P_{CR}+P_{DT}} = \frac{R(^5D_0/^5D_{1,2,3})_{^6G_J} - R(^5D_0/^5D_{1,2,3})_{^6I_J}}{1 + R(^5D_0/^5D_{1,2,3})_{^6I_J}} \tag{1}$$

where P_{CR} and P_{DT} are the probabilities of cross-relaxation and direct energy transfer from Gd^{3+} to Eu^{3+}, respectively. $R(^5D_0/^5D_{1,2,3})_{^6G_J}$ and $R(^5D_0/^5D_{1,2,3})_{^6I_J}$ are the emission intensity ratios of $^5D_0$ to $^5D_{1,2,3}$ upon ^6G_J and ^6I_J excitation, respectively. The integrated intensities for $^5D_0$ and $^5D_{1,2}$ emissions were calculated from the emission spectra in Fig. 3(b) and (c), so that we can get the integrated emission intensity ratios $^5D_0/^5D_{1,2,3}$ upon ^6G_J and ^6I_J excitations to be 6.51 and 4.64, respectively. If we assume that there are no nonradiative losses in the direct energy transfer process (II), the quantum efficiency of $BaGd_2ZnO_5$:0.5 mol% Eu^{3+} can be calculated to be about 133%.

4. Conclusion

$BaGd_2ZnO_5$:Eu^{3+} phosphor has been prepared via a facile solid state reaction, and characterized by means of XRD, UV and VUV spectra. The XRD results showed that the obtained sample is well-crystallized $BaGd_2ZnO_5$. The energy transfers from Gd^{3+} to Eu^{3+} were observed by inspecting the excitation spectra when 628 nm emission of Eu^{3+} was monitored. Under 160 nm VUV excitation, the phenomenon of visible quantum cutting for Gd^{3+}–Eu^{3+} couple in $BaGd_2ZnO_5$:Eu^{3+} was observed through downconversion. The mechanism for visible quantum cutting was studied and quantum efficiency of $BaGd_2ZnO_5$:0.5 mol% Eu^{3+} was calculated to be around 133%.

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