Visible quantum cutting in BaF$_2$: Gd, Eu via downconversion

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Abstract

The visible quantum cutting in BaF$_2$: Gd, Eu via Downconversion has been observed. In the quantum cutting process, one VUV photon absorbed by Gd$^{3+}$ can be split into two visible photons emitting by Eu$^{3+}$ through cross-relaxation between Gd$^{3+}$ and Eu$^{3+}$. According to the calculation from the emission spectra under different wavelength excitation, we can obtain the two-step energy transfer process with a visible quantum efficiency up to 194%.

Keywords: BaF$_2$: Gd, Eu; Quantum cutting; VUV spectroscopy; Energy transfer; LiGdF$_4$: Eu; BaF$_2$: Ce

1. Introduction

Recently, a growing attention has focused on the quantum cutting process of rare earth doped compounds in the vacuum ultraviolet (VUV) region with energy higher than 50000 cm$^{-1}$ or wavelength shorter than 200 nm [1]. The development of new phosphors used for VUV excitation has become an important challenge in the field of luminescence materials research due to its theoretical significance and application. The well-known Dieke diagram which represents the energy levels of all trivalent lanthanide ions except for La$^{3+}$ and Lu$^{3+}$ in the energy range 0–40000 cm$^{-1}$ is the most useful tool to provide us the element energy level parameters in the research of rare earth ions (RE$^{3+}$) luminescence. The Dieke diagram has been extended to 50000 cm$^{-1}$ by a group of Argonne National Laboratory through theoretical calculation. The research of visible quantum cutting can also provide the higher energy level diagram (> 50000 cm$^{-1}$) of rare earth ions. Visible quantum cutting phosphors are required for application in mercury-free fluorescent tubes and in plasma display panels [2]. In both devices mentioned above, the VUV radiation is generated by a noble-gas discharge instead of the conventional mercury discharge. For example, the xenon dimer discharge yields a broad band in the VUV region with the maximum at 172 nm. The most phosphors currently widely used have less efficiencies under excitation of a noble-gas discharge than that of the conventional mercury discharge. In order to improve the quantum efficiency and energy efficiency, the concept of quantum cutting was proposed by Wegh et al. [3]. When a VUV photon
with energy more than twice the energy of a visible photon is absorbed, two visible photons are emitted by the phosphor. In order to realize the quantum cutting process, the band gap of host should be so wide that the high energy levels (>50000 cm⁻¹) can be located within the band gap. Fluoride can meet this requirement and is investigated extensively recently because its band gap is much wider than that of oxide. Wegh et al. has studied the visible quantum cutting of rare earth ions in fluoride. LiGdF₄:Eu³⁺ [1] and LiGdF₄:Er³⁺, Tb³⁺ [4] whose quantum cutting efficiency has reached 190% and 130%, respectively, when the absorption on other centers than Gd or Er is neglected. Meanwhile, the Dieke diagram of Gd³⁺ in VUV region has been extended to about 70000 cm⁻¹ by their research [5].

BaF₂ is a broad band gap crystal with $E_g = 10.9$ eV [6]. It is currently regarded as the fastest inorganic scintillator which has cross- luminescence bands peaked at 195 and 220 nm and a broad band peaking at about 300 nm due to self-trapped excitons. Much attention has been focused on the luminescent properties of rare earth ions activated BaF₂. The study of BaF₂: RE³⁺(Ce, Pr, Tb, Eu, Dy) [7–9] luminescence shows that not only the characteristic emission lines of rare earth ion are observed but also the scintillator light yield and scintillator time profiles are affected by these rare earth ions. In the previous research the main purpose of doping trivalent rare earth is to restrain the slow component at 300 nm of BaF₂ luminescence. The defects in BaF₂ host are also influenced from the thermoluminescence.

In this paper, we present the quantum cutting process via the combination of Gd,Eu in the host of BaF₂.

In fact, the energy transfer from the VUV emission in BaF₂ host to the RE³⁺ may be utilized to study the multi-photon emission process. The energy transfer from the very fast VUV emission in BaF₂ to Ce³⁺ has ever been reported in BaF₂:Ce³⁺ [10]. If the energy of the emission at 195 nm in BaF₂ host excited by 58 nm can be transferred to the Gd–Eu system, if it subsequently emits two red photons from the Eu³⁺ and if in the meanwhile the emission at 300 nm from BaF₂ host can also be transferred to another Eu³⁺, three-photon emission may occur. Although the possibility of such process may be rather remote and it is not beneficial to improve the energy efficiency in practice (the energy of the photon at 58 nm is much higher than that of three red light photons), the physics process and the idea for searching new way of quantum cutting materials may be useful.

2. Experimental

Powder samples of BaF₂: Eu³⁺, Gd³⁺ (both 1 mol% doping concentration) were prepared in a nitrogen atmosphere at 500°C for 5 h with 5N fluoride raw. The samples were checked by X-ray diffraction analysis and found to be single phase. Luminescence spectra and their excitation spectra were measured at VUV station of the 3B1B beam line of BSRF (Beijing). The wavelength range of the excitation monochromator ARC VM502 is 50–400 nm. The ARC SP308 monochromator whose wavelength range is from 380 to 850 nm was used for the emission spectra measurement. The signal was collected by Hamamalsu H7424-50 photon counter. The emission spectra were recorded from 500 to 710 nm. The excitation spectra were recorded at 50–200 nm.

3. Result and discussion

The emission spectra under excitation 273 and 202 nm are shown in Fig 1. The emission lines of Eu³⁺ peaked at 527, 556 nm correspond to $^5D_1 \rightarrow ^7F_{1,2}$ transitions, and the lines at 594, 620, 656, 702 nm are due to $^5D_0 \rightarrow ^7F_{1,2,3,4}$ transitions. The excitation spectrum with emission wavelength of 595 nm is shown in Fig. 2. There are excitation lines of Eu³⁺ ions peaking at about 202, 245 and 274 nm responsible for $^8S_{7/2} \rightarrow ^6G_J$, $^6D_J$, $^6I_J$, respectively. Compared with the excitation spectrum of LiGdF₄: Eu [1], the charge transfer band of Eu³⁺–F⁻ about 155 nm is absent in BaF₂: Gd,Eu, but a band peaked at 125 nm
appears. Additionally, the higher energy $4f^7-4f^7$ transitions (wavelength region 160–190 nm) are missing. It may result from the errors of the calibration during the excitation spectrum measure.

The schematic process of quantum cutting is shown in Fig. 3 (see Ref. [1]). The quantum cutting process can occur through the combination of Gd$^{3+}$ and Eu$^{3+}$ in which Gd$^{3+}$ plays the role of absorbing a VUV photon (corresponding to $^8S_{7/2} \rightarrow ^6G_J$) and cutting into two visible photons (two red light photons in this paper) emitted by two Eu$^{3+}$ ions. The energy of transitions $^6G_J \rightarrow ^6P_J$ on Gd$^{3+}$ just matches the $^7F_J \rightarrow ^5D_0$ transitions energy on Eu$^{3+}$. Upon excitation in the $^6G_J$ levels of Gd$^{3+}$, as the first step, energy is transferred by cross-relaxation between Gd$^{3+}$ and Eu$^{3+}$ which makes Gd$^{3+}$ fall into the $^6P_J$ state and Eu$^{3+}$ is
Excited into the $^5D_0$ state. In the second step the remaining excitation energy of Gd$^{3+}$ in the $^6P_J$ state is transferred to another Eu$^{3+}$ ion, i.e. exciting the Eu$^{3+}$ ion into a high excited state. Then a fast relaxation from a high excited state to $^5D_J$ states will occur. After the first step, because the Eu$^{3+}$ ion only excited into $^5D_0$ state, only the emissions of $^5D_0$–$^7F_J$ transitions are expected. Nevertheless after the second step, all levels of $^5D_{3,2,1,0}$ of Eu$^{3+}$ are probably occupied, so the emission wavelength consists of all of the $^5D_J (J = 0, 1, 2, 3)$–$^7F_J$ transitions.

In order to calculate the quantum cutting efficiency, some premises must be proposed. The absorption efficiency of VUV photon cannot be taken into account. Some nonradiative losses at defects and impurities are ignored. In the experiment, different excitations are adopted including the excitation of Gd$^{3+}$–$^6G_J$ with 202 nm and the excitation of Gd$^{3+}$–$^6I_J$ with 273 nm. Upon excitation in $^6I_J$ level with 273 nm, the quantum cutting never occurs because no cross-relaxation exists, so the $^5D_J$–$^7F_J$ transitions emission of Eu$^{3+}$ has a normal branching ratio between $^5D_0$ and $^5D_{1,2,3}$. Upon excitation in $^6G_J$ level with 202 nm, the quantum cutting can occur through a two-step energy transfer. In the second step, the emission of Eu$^{3+}$ has a normal branching ratio. The first step will lead to the increase of $^5D_0$ emission. So the ratio of $^5D_0$ and $^5D_{1,2,3}$ emission is expected to increase. To determine the efficiency of the cross-relaxation, the formula proposed by Wegh [1] was adopted as follows:

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

where $P_{CR}$ is the probability for cross-relaxation, $P_{DT}$ is the probability for the direct transfer from Gd$^{3+}$ to Eu$^{3+}$. $R(5D_0/5D_{1,2,3})$ is the ratio of the $^5D_0$ and $^5D_{1,2,3}$ emission integral intensities. The subscript ($^6G_J$ or $^6I_J$) represents the excitation level for which the ratio is observed.

From the emission spectra, the value of $R(5D_0/5D_{1,2,3})_{5G_J}$ and $R(5D_0/5D_{1,2,3})_{5I_J}$ can be calculated to be 26.1 and 13.0, respectively. Therefore, the value of $P_{CR}/P_{CR} + P_{DT}$ is 0.94. It means that there are 94% Gd$^{3+}$ ions in the $^6G_J$ excited state relax via a two-step energy transfer emitting two visible photons. So the quantum cutting efficiency of 194% can be obtained.
Quantum cutting in the Gd–Eu system requires energy migration over the Gd sublattice to Eu. So if we expect to observe the effective quantum cutting, the concentration of Gd as an absorber or donor of energy should be more than that of Eu and make sure to transfer their energy to Eu$^{3+}$ ions efficiently. But in the experiment the concentrations of the Gd and Eu are both 1%, the quantum cutting still occurs effectively because trivalent ions tend to cluster in BaF$_2$, which induces a local high concentration of Gd and Eu in host. Meanwhile, the distance between Eu and Gd ions will decrease due to their clustering so the energy transfer of Gd–Eu can become more efficient.

4. Conclusion

The visible quantum cutting through down-conversion utilizing the two-step energy transfer between Gd$^{3+}$ and Eu$^{3+}$ is realized in BaF$_2$:Eu$^{3+}$, Gd$^{3+}$. Here the Gd$^{3+}$ ions play the role of quantum cutting. An absolute quantum efficiency of the material under VUV excitation has not been determined. We can obtain the two-step energy transfer process with a visible quantum cutting efficiency to 194%.

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References