Photoluminescence Properties of Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$ under VUV / UV excitation

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Abstract

A series of phosphors Li$_6$Gd$_{1-x}$(BO$_3$)$_3$:xTb$^{3+}$ (0≤x≤1) was prepared by a conventional solid-state reaction method and their photoluminescence properties under VUV/UV excitation were demonstrated. For the excitation spectrum, the host-related absorption band, $f$-$f$ and $f$-$d$ transitions of Gd$^{3+}$ and Tb$^{3+}$, charge transfer of O$^2-/g$Gd$^{3+}$ and O$^2-/g$Tb$^{3+}$ were assigned. In Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$, visible quantum cutting through downconversion was observed upon Tb$^{3+}$ 4f$^8$-4f$^7$5d$^1$ excitation and host excitation. The quantum cutting process was demonstrated combining a possible model.

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Keywords: photoluminescence; downconversion; Li$_6$Gd(BO$_3$)$_3$

1. Introduction

The photoluminescence properties of rare earth ions in different oxysalt hosts in the VUV/UV range have attracted much attention due to their practical application [1-5]. When excited at VUV/UV light, few oxide phosphors have shown the potential application due to their weak absorption in the VUV/UV range or low energy transfer efficiency from VUV/UV photon to visible photon. To obtain high quantum conversion efficiency, an efficient method is via quantum cutting. It was reported that quantum cutting could be realized in an oxide with the band gap large enough [6].

The optical gap (Eg) of Li$_6$Gd(BO$_3$)$_3$ is large [7] to accommodate levels of rare earth ions. Li$_6$Gd(BO$_3$)$_3$ belongs to the monoclinic crystal system with P2$_1$/c (Z=4) as the space group. [8] The structure unit of Li$_6$Gd(BO$_3$)$_3$ consist of BO$_3$ triangle panels, distorted GdO$_8$, LiO$_4$, and LiO$_5$ polyhedra. The Gd-O tetragonal prisms, connecting to one another by common edges along the direction oblique to the c axis, distribute in different layers in two-dimensional chains, which is shown in the insert of Fig.1. The smallest Gd-Gd distance in the same chain is 3.912 Å and that between different chains in the same layer is 8.846 Å. The Gd-Gd intrachain distance is rather short, while the corresponding interchain distance is about twice as large leading to the one-dimensional character of the crystal structure. Tb$^{3+}$-activated phosphors are usually excellent emitters of green light due to an effective excitation through the 4f-5d transitions covering a broad range of wavelengths and effective 5D$_4$-7F$^j$ transitions. [9] The ionic radii of Tb$^{3+}$ (r$_{Tb^{3+}}$=1.04 Å) is close to Gd$^{3+}$ (r$_{Gd^{3+}}$=1.06 Å) of Li$_6$Gd(BO$_3$)$_3$ host with eight-fold coordination environment [10]. The similar ionic radii values of Gd$^{3+}$ and Tb$^{3+}$ as well as the one-dimensional character of Li$_6$Gd(BO$_3$)$_3$ could permit the high-doping levels of Tb$^{3+}$.

In this study, we investigated the photoluminescence properties of Tb$^{3+}$ activated Li$_6$Gd(BO$_3$)$_3$ which has a large band gap under VUV/UV light

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excitation. The results demonstrate that visible quantum cutting occurs in Li$_6$Gd(BO$_3$)$_2$:Tb$^{3+}$.

Fig. 1 Gd-O tetragonal prisms distributing in different layers in two-dimensional chains of Li$_6$Gd(BO$_3$)$_3$.

2. Experimental details

The compounds Li$_6$Gd$_{1-x}$BO$_3$:xTb$^{3+}$ (0 ≤ x ≤ 1) were prepared using mixtures of Li$_2$CO$_3$ (98%), HBO$_3$ (99.5%), Gd$_2$O$_3$ (99.99%), and Tb$_2$O$_3$ (99.99%), and fired in reducing mixtures at 660 °C for 6 h. The phase identification of samples was carried out by a Rigaku D/Max-2400 X-ray diffractometer with Ni-filter Cu Kα radiation.

Diffuse reflectance spectra were obtained by a BaSO$_4$ powder calibrated UV-VIS spectrophotometer (PE lambda 950). The UV luminescence spectra were measured by FLS920T fluorescence spectrophotometer. The VUV spectra were recorded at Beamline 4B8 in Beijing Synchrotron Radiation Facilities (BSRF) under dedicated synchrotron mode (2.5 GeV, 150-60 mA). All measurements were carried out at room temperature.

3. Results and discussion

3.1 Structural characterization

The XRD patterns of all the samples referred in this work were measured. The result indicates they are of a single phase. For representative, the patterns Li$_6$Gd$_{1-x}$BO$_3$:xTb$^{3+}$ (x=0, 0.2, 0.4, 0.6, 0.8, 1) are presented in Fig. 2. It is observed that the exhibited patterns can be well indexed based on the simulated pattern, showing they share the same phase.

Fig. 2 The XRD patterns of Li$_6$Gd$_{1-x}$BO$_3$:xTb$^{3+}$ (x=0, 0.2, 0.4, 0.6, 0.8, 1) and the simulated XRD pattern.
3.2 UV-Vis diffuse reflectance spectra

Fig. 3 indicates the diffuse reflection spectrum of Li₆Gd(BO₃)₃, from which a drop trend from longer wavelength to shorter wavelength can be observed. In addition, two sharp absorption peaks at 274 and 312 nm are presented, which are due to the transitions from ground state level of Gd³⁺ (⁸S₇/₂) to ⁶I₇ and ⁶P₆ levels, respectively. The large-range optical absorption in Li₆Gd(BO₃)₃ may be caused by some uncertain defects produced in the synthesis process.

3.3 Spectroscopic properties of Li₆Gd(BO₃)₃:Tb³⁺

The excitation spectrum of Li₆Gd₀.₉(BO₃)₃:₀.₁Tb³⁺ in the UV-VUV region was measured, which is indicated in Fig. 4. It can be observed that the spectrum is consisted of broad bands below 300 nm and some sharp lines around 253, 274 and 312 nm. The sharp lines around 253, 274 and 312 nm can be assigned to the Gd³⁺ transitions from the ground level ⁸S₇/₂ to the excited state level ⁶D₅/₂, ⁶I₇, ⁶P₆, respectively. Many BO₃³⁻-containing borates exhibit absorption around 140-180 nm [11-12], thus the broad band around 176 nm is determined to be host-related absorption band. Usually, O²⁻→Tb³⁺ charge transfer band (CTB) and O²⁻→Gd³⁺ CTB appear in the high energy region. Based on the Jørgensen empirical formula

\[ E_{\sigma}(cm^{-1}) = [\chi_{opt}(X) - \chi_{opt}(M)] \times 30,000cm^{-1} \]  

(1)

[\chi_{opt}(X) and \chi_{opt}(M) are the optical electronegativities of the anion X and central metal cation M, respectively] [13]. Using \chi_{opt}(O)=3.1 [14], \chi_{opt}(Gd)= 0.91 and \chi_{opt}(Tb)=0.95 [15] into the formula above, the CTB of O²⁻→Gd³⁺ and
O$_2^-$→Tb$^{3+}$ can be calculated to be 152 nm and 155 nm respectively. Thus, we consider the CTBs of O$_2^-$→Gd$^{3+}$ and O$_2^-$→Tb$^{3+}$ can be also included in the band at 176 nm. The spin-allowed (SA) $^7$F$_6$→$^7$D$_J$ transitions (with higher energies and intensities) and spin-forbidden (SF) $^7$F$_6$→$^7$D$_J$ transitions (with lower energies and intensities) will occur when one electron is promoted from the ground states $4^f^8$ ($^7$F$_6$) to $4^f^5d^1$ excitation levels [16], and the $^7$D$_J$/$^9$D$_J$ levels will be splitted due to the effect of crystal field. Thus, the transitions from $^7$F$_6$ to the $^7$D$_J$/$^9$D$_J$ sublevels will probably exist in the excitation spectrum, which results in the complicated f-d transitions of Tb$^{3+}$. Therefore, these additional bands at wavelength above 190 nm are related to the f-d transitions of Tb$^{3+}$. In order to assign the bands regioning from 190 nm to 290 nm, we adopt the following expression which was proposed by Dorenbos [17]:

$$D(A) = E(\text{Ce, free}) - E(Ln, A) + \Delta E_{Ln,Ce} \quad (2)$$

Here, $E(\text{Ce, free})$, which has been determined to be 49340 cm$^{-1}$, is defined as the energy of the first f-d transition of Ce$^{3+}$ as a free (gaseous) ion. $E(Ln, A)$ is the f-d energy difference of the lanthanide ions Ln$^{3+}$ doped in compound A and $\Delta E_{Ln,Ce}$ is defined as the difference of f-d energy of Ln$^{3+}$ with that of the first electric dipole allowed transition in Ce$^{3+}$. Using the value of $D(A)$ in Li$_5$Gd(BO$_3$)$_3$, via, 20559 cm$^{-1}$ [18], the position of f-d transitions Gd$^{3+}$ is determined to be 134 nm which could be overlapped with band H, and the position of the lowest SA f-d transitions and SF f-d transitions of Tb$^{3+}$ ions can be predicated to be 238±5 nm and 285±6 nm respectively, which are coincidence with the positions of the bands at 234 and 281 nm.

**Fig. 5 (a)** Emission spectra of the sample Li$_6$Gd$_{0.99}$(BO$_3$)$_3$:0.01Tb$^{3+}$ and Li$_6$Gd$_{0.9}$(BO$_3$)$_3$:0.1Tb$^{3+}$ upon 172 nm excitation, (b) the relationship between relative intensity of 543 nm and Tb$^{3+}$-doped concentration upon 274 and 172 nm excitation.

Upon 274 and 172 nm light excitation, the characteristic emission of Tb$^{3+}$ from $^5$D$_{4}$→$^7$F$_J$ transitions can be observed (shown as Fig. 5 (a)). It can be observed that the emission intensity at 543 nm increases with increasing Tb$^{3+}$ content to $x=0.6$ (shown in the inset of Fig. 5 (b)), and then decreases excited at 274 nm. A possible reason for this high quenching concentration is the special structure of Li$_6$Gd(BO$_3$)$_3$, which supports zigzag chains for Tb$^{3+}$ restricting the energy migration to one dimension. Thus, the probability that the migrating excitation encounters one of the randomly distributed killer sites is reduced. Thus, the quenching concentration is determined to be 0.6 for excitation at 274 nm. When excited at 172 nm, the quenching concentration is considered to be 0.3. It has been reported that the high quenching concentration under VUV excitation has been related to the weak interaction between Tb$^{3+}$ ion and host lattice [19], however, no direct evidence has been given. The reasons for the high quenching concentration need to be further studied. The different quenching properties under 274 and 147 nm light excitations imply that the quenching mechanisms mechanism under UV excitation is different from that under VUV excitation.

### 3.4 Quantum cutting and possible models in Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$

To determine whether visible quantum cutting occurs in Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$, we investigate the emission spectra of Li$_6$Gd$_{0.9}$(BO$_3$)$_3$:0.1Tb$^{3+}$ excited at 274 nm (the $^9$I$_1$ level of Gd$^{3+}$), 217 nm (the $^4$F$^5$5d$^1$ level of Tb$^{3+}$) and 172 nm (the host absorption) as a representation shown in Fig. 6. By scaling the spectra on the emission intensity for the
$^5\text{D}_3 \rightarrow ^7\text{F}_3$ transition of Tb$^{3+}$. The emission intensity from level $^5\text{D}_2$ of Tb$^{3+}$ excited at 217 and 172 nm is stronger than that excited at 274 nm. This result indicates that the quantum cutting indeed occurs in Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$ excited at 217 and 172 nm.

Fig. 6 Emission spectra of Li$_6$Gd$_{0.9}$(BO$_3$)$_3$:0.1Tb$^{3+}$ under 172, 217 and 274 nm light excitation. The spectra are scaled on the emission intensity for the $^5\text{D}_3 \rightarrow ^7\text{F}_3$ transition of Tb$^{3+}$.

Fig. 7 Energy-level diagrams of visible quantum cutting through two-step energy transfer in Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$ excited at (a) 274 nm, (b) 217 nm and (c) 172 nm. ① represents cross relaxation and ② represents direct energy transfer.

Fig. 7 gives the possible energy level diagrams for Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$ upon different excitation wavelengths. When Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$ is excited at 274 nm, Gd$^{3+}$ is pumped to $^6\text{I}_7$ level and then consume the energy via two ways shown in Fig. 7 (a). One is from $^6\text{I}_1$ level relaxed to $^6\text{P}_{3/2}$ state nonradiatively when direct energy transfer from $^6\text{P}_{7/2}$ to the neighboring Tb$^{3+}$ ion. The other way is radiative relaxation of Gd$^{3+}$ from $^6\text{P}_{7/2}$ to $^8\text{S}_{7/2}$. No visible QC occurs in this process. While upon excitation of $4f^8$-$4f^75d^1$ transition of Tb$^{3+}$ at 217 nm, two possible cases take place (Fig. 7 (b)): in the first case, Tb$^{3+}$ ion in Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$ is excited from ground state to $4f^75d^1$ state, and then relaxes to an intermediated level $^5\text{D}_3$, then the released energy is transferred to a neighboring Tb$^{3+}$ by cross relaxation resulting the excitation of Tb$^{3+}$ to the level $^5\text{D}_4$ (process ②). This process results the extra green photons. The second way is that Tb$^{3+}$ is relaxed from $4f^75d^1$ state to levels $^5\text{D}_3$ and $^5\text{D}_4$, the released energy is transferred to the neighboring Gd$^{3+}$. 
176 nm is determined to be host-related absorption, thus it is considered that when Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$ is excited at 176 nm, the energy is first absorbed by host and then is transferred from the host to a higher 4f$^7$5d$^1$ state of Tb$^{3+}$. Subsequently, three cases could occur: (1) the energy relaxes to a proper intermediated level of Tb$^{3+}$, and then the released energy is transferred to a neighboring Tb$^{3+}$ by cross relaxation as observed in Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$ upon excitation at 217 nm; (2) the energy relaxes to a proper intermediated level of Gd$^{3+}$, then energy transfer occurs from the intermediated level of Gd$^{3+}$ to a higher 4f$^7$5d$^1$ state of Tb$^{3+}$, then occurs as case 1. The rest is relaxed to 6P$^7/2$ state nonradiatively and radiative relaxation of Gd$^{3+}$ from 6P$^7/2$ to 8S$^7/2$ takes place; (3) the energy relaxes to a proper intermediated level of Tb$^{3+}$, and then relaxed from 4f$^7$5d$^1$ state to levels 5D$^3$ and 5D$^4$, the released energy is transferred to the neighboring Gd$^{3+}$.

4. Conclusion

The photoluminescence properties of a series of phosphors Li$_{6}$Gd$_{1-x}$BO$_3$:xTb$^{3+}$ (0≤x≤1) under VUV/UV excitation were demonstrated. The host-related absorption band of Li$_{6}$Gd$_{1-x}$BO$_3$:xTb$^{3+}$ (0.5≤x≤1) was determined to be 176 nm, and the f-f and f-d transitions of Gd$^{3+}$ and Tb$^{3+}$, charge transfer of O$_2^-$-Gd$^{3+}$ and O$_2^-$-Tb$^{3+}$ were also assigned in the excitation spectrum. In Li$_6$Gd(BO$_3$)$_3$:Tb$^{3+}$, visible quantum cutting through downconversion was observed upon both Tb$^{3+}$ 4f$^8$-4f$^7$5d$^1$ and host excitation.

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6. References

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