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Photoluminescence properties of red emitting $BaGdB_9O_{16}$:Eu phosphor

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An investigation is reported of the photoluminescence properties of the $BaGdB_9O_{16}$:Eu phosphors. Under VUV excitation, $BaGdB_9O_{16}$:Eu exhibited a bright red luminescence with CIE chromaticity coordinates of (0.66, 0.34). The brightness was 80% of the commercial $(Y,Gd)BO_3$:Eu under identical excitation conditions. The PL spectrum showed a low field splitting of the ^7F_J levels of Eu, indicating the Eu ions experience local distortion. It also showed a vibrational mode associated with the Eu-O vibration. The physical mechanism responsible for Eu excitation was investigated by PLE and time-resolved spectroscopy. The PLE spectrum showed sharp lines due to the $^8S_{7/2} - {}^6I_J$ and ^6P_J transitions of Gd^{3+} in addition to the f-f transitions of Eu^{3+}. The charge transfer band of Eu was observed at 233 nm and the host absorption band was detected at 159 nm. The time-resolved spectroscopy showed that the Eu ions decay purely exponentially with a lifetime of 2.1 ms. Under excitation into the Gd ^6I_J level located below the fundamental absorption edge, the Eu luminescence was excited through the energy transfer process from Gd to Eu. The energy transfer rate was estimated to be 6000 s^{-1}. © *2002 Kluwer Academic Publishers*

1. Introduction

Interest in the development of efficient photonically driven phosphors has been greatly renewed by the emergence of plasma display technology, which uses short wavelength vacuum ultra-violet (VUV) radiation at 147 and 172 nm to excite visible emission from phosphors. Although a rich database of photoluminescent phosphors exists, most of these phosphors have been developed for fluorescent lamp application, and thus were optimized for the 254 nm radiation of the mercury discharge used in fluorescent lamps [1]. Thus, it is important both to reexamine existing materials and to investigate new materials for their potential to exhibit higher efficiency, superior maintenance, and higher absorption characteristics under the VUV excitation conditions. The borates have been shown to be excellent host materials, exhibiting efficient VUV absorption, good maintenance and excellent chromaticity when doped with rare earth ions. In fact, the borates are exceptional materials because they are not refractory and so can be prepared at relatively low temperatures (typically less than 1200°C), but nonetheless exhibit excellent maintenance [2]. This is contradictory to the commonly accepted wisdom that the high firing temperature (1400–1600°C) needed to prepare the refractory materials is essentially responsible for their good maintenance. This combination of good maintenance with low firing temperatures is additionally a significant economic advantage. Rare earth doped borates with high B_2O_3 contents are especially attractive, because of their excellent chemical and thermal stability, which is due to the small alkaline earth content and the rigid covalent boron-oxygen network [3]. In this paper, we report the synthesis and optical characterization of red emitting $BaGdB_9O_{16}$:Eu for potential application in plasma display panels.

2. Experimental procedures

$BaGdB_9O_{16}$:Eu was synthesized by the solid state reaction technique. First, the starting materials, $BaCO_3$, Gd_2O_3, Eu_2O_3 and H_3BO_3 were ball milled for 30 minutes to achieve uniform mixing and then the mixture was fired at 900–1000°C for 2 hours in air. The Eu concentration was varied between 1 and 10 at.%. The resulting powder samples were characterized by x-ray diffraction and photoluminescence (PL) and PL excitation (PLE) spectroscopy. For the PL measurements, a D_2 lamp enclosed within a vacuum spectrometer was used as the VUV excitation source between 110 and 350 nm and a Xe lamp was used for UV-visible excitation between 220 and 600 nm. For time-resolved PL spectroscopy, a tunable (220 nm–1.8 μm) OPO system pumped by a Nd:YAG laser was used to create sharp pulse excitation. The PL signal was dispersed by a 0.27 m single-pass monochromator and detected by a thermoelectrically cooled GaAs PMT operating in the photon counting mode. The measurement temperature was varied between 10 and 300 K.

3. Results and discussion

Under 147 nm excitation, $BaGdB_9O_{16}$:Eu was found to exhibited a strong red emission, characteristic of Eu^{3+} ions, with CIE chromaticity coordinates of (0.66, 0.34). To further enhance the optical quality and light output the effect of firing temperature and stoichiometry were investigated. To investigate the effect of firing temperature, the powder samples were prepared at 900 and 1000°C while keeping all other preparation conditions constant. Although the x-ray diffraction patterns were similar, the relative brightness was increased by about 60% for all Eu concentrations investigated, as shown in Fig. 1, when the firing temperature was increased from 900 to 1000°C. Also to compensate for the loss of B_2O_3 at high temperatures, 10% excess H_3BO_3 was added to the originally stoichiometric starting material mixture for the samples fired at 1000°C. As a result of the addition of the excess H_3BO_3, the PL intensity more than doubled, while the x-ray diffraction pattern was once again hardly changed. The fact that the x-ray diffraction pattern was not affected indicated that all of the samples were crystallized in the same structure. These results suggest that the lower firing temperatures and stoichiometric mixtures of the starting material produce higher defect densities, which significantly reduced the luminescence efficiency. At the current stage of development, the best sample had a Eu concentration of 7.5 at.%, exhibiting a brightness of approximately 80% compared to the commercial $(Y,Gd)BO_3$:Eu phosphor. Further improvement will be possible by adjusting the firing temperature and the addition of excess H_3BO_3 to suppress the formation of non-radiative defects.

Fig. 2 shows the PL spectrum obtained for $BaGdB_9O_{16}$:Eu (5.0 at.%) under 274 nm UV excitation. The spectrum was observed to be dominated by the main line at 613 nm due to the $^5D_0 - {}^7F_2$ transition of Eu^{3+}, which is typical of Eu^{3+} ions occupying sites with no inversion symmetry. The spectrum also showed many additional lines due to the spinorbit split ground states, ^7F_J $(J = 0-6)$, each of which is further split by the crystal field. In order to more clearly present the smaller features, the logarithmic of the PL spectrum is shown in the inset of Fig. 2. This presentation of the data shows an emission peak at 575 nm that is attributed to the $^5D_0 - {}^7F_0$ transition. This transition is strictly forbidden when the crystal field is small and consequently there is no mixing between different J levels. The observation of this transition, therefore, indicates that the crystal field in $BaGdB_9O_{16}$:Eu is strong enough to cause significant mixing between the ^7F_J multiplets, thereby relaxing the J selection rule. The $^5D_0 - {}^7F_0$ emission was accompanied by two phonon replicas separated by 15 meV. This phonon energy was also observed for the $^5D_0 - {}^7F_1$ and $^7F_2$ transitions. Because this energy is much smaller than the phonon energies reported for the BO_3^{-3} group, which are of the order of 100 meV, it was assigned to Eu-O vibration, in good agreement with the previous observation reported for $Ca_4GdO(BO_3)_3$:Eu [4]. A high-resolution examination of the emission spectrum revealed that the $^5D_0 - {}^7F_1$ and $^7F_2$ transitions were composed of 3 and 5 split levels, respectively, in addition to the phonon replicas arising from coupling to the Eu-O vibrational modes. From x-ray diffraction studies, Tian *et al.* reported that $BaGdB_9O_{16}$ crystallized in a hexagonal structure, [3] for which the symmetry

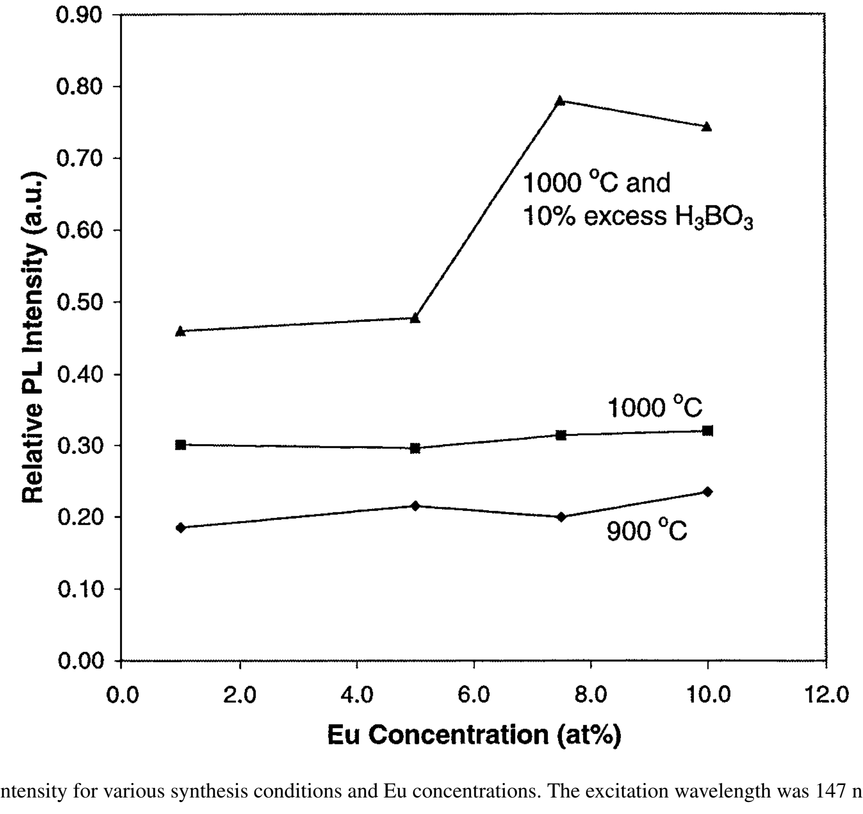

Figure 1 Relative PL intensity for various synthesis conditions and Eu concentrations. The excitation wavelength was 147 nm.

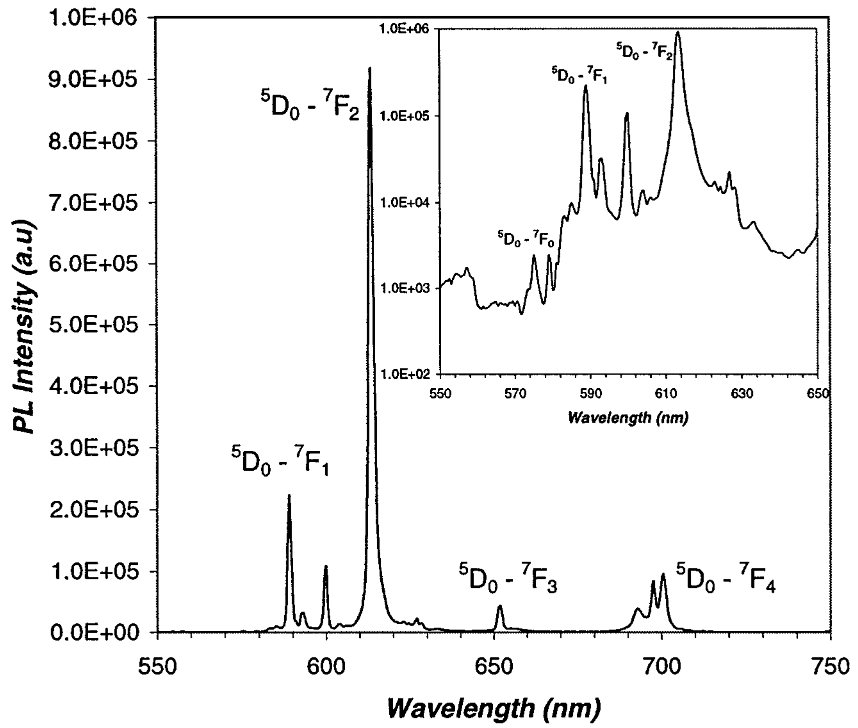

Figure 2 Room temperature photoluminescence spectrum of $BaGdB_9O_{16}$:Eu with an excitation wavelength of 274 nm. Inset: PL spectrum in logarithmic scale.

consideration predicts that the crystal field should split the $^7F_1$ and $^7F_2$ levels into only 2 and 3 Stark components, respectively. The fact that 3 and 5 split components were observed for the $^7F_1$ and $^7F_2$ levels indicates the presence of a local lattice distortion that lowers the site symmetry experienced by the Eu ions.

Fig. 3 shows the VUV-visible PLE spectrum for $BaGdB_9O_{16}$ with an Eu concentration of 7.5 at.%. In order to cover the complete spectral range, both the D_2 and Xe lamp excited spectra are plotted together. Close examination of the spectra revealed features due to both Gd and Eu. The spectrum was dominated by an intense excitation peak at 394 nm due to the $^7F_0 - 5L_6$ transition. Strong features due to the $^7F_0 - {}^5D_1$ and $^5D_2$ transitions were also observed at 534 and 465 nm, respectively, in addition to many other sharp lines due to the various f-f transitions of Eu^{3+}. The intense excitation lines at 274 and 310 nm were assigned to the $^8S_{7/2} - {}^6I_J$ and ^6P_J transitions of Gd^{3+}, respectively, and strongly suggested an efficient energy transfer from Gd to Eu. The broad excitation band observed at shorter wavelength was assigned to charge transfer transition between Eu and the neighboring oxygen anions. Since the position of this band was close to the tuning edge of the Xe lamp, a more accurate determination was made by taking the PLE spectrum with the VUV spectroscopy system, as shown in Fig. 3. Three excitation bands at 153, 233 and 274 nm were clearly identified. The sharp line at 274 nm was assigned to the $^8S_{7/2} - {}^6I_J$ transition of Gd^{3+} and the broad band centered at 233 nm was attributed to charge transfer between Eu and O. However, the charge transfer band was located at a smaller wavelength than the previously reported value of 249 nm [5]. Also, the peak wavelength of the charge transfer band was shorter than most other Eu doped borates, for which the change transfer bands were typically found to be between 250–300 nm. Finally, the broad excitation band at 153 nm was attributed to host absorption, because of its similar position to the host absorption of $Gd(BO_3)_3$ (159 nm) [6]. The excitation process is believed to be similar to that reported for $Gd(BO_3)_3$. That is, the host excitation is mediated by the excitation of the Gd sublattice, which allows efficient exciton migration through the lattice until a Eu activator ion is located to transfer energy and produce luminescence.

To further investigate the interaction mechanism between the Gd and Eu ions, time-resolved spectroscopy was performed. Fig. 4 shows the luminescence decay of the Eu^{3+} emission at 10 K. When the charge transfer band of Eu was directly pumped by 260 nm excitation, the luminescence showed a sharp rise followed by an ideal exponential decay. The decay time was calculated to be 2.1 ms by numerically fitting the decay curve with an exponential function. When the excitation wavelength was changed to 274 nm, the position of the Gd^{3+} $^8S_{7/2} - {}^6P_J$ transition, the Eu luminescence showed a slow rise followed by a decay with the same decay time as the 260 nm excitation. The initial slow rise was attributed to the finite transfer time involved in the Gd-Eu energy transfer process, as schematically shown in the inset of Fig. 4. The position of the maximum was shifted by 450 μs compared to the charge transfer excitation at 260 nm. The rate equations governing the decay of Gd and Eu ions are

$$\frac{dN_G(t)}{dt} = -W_G N_G(t) - W_{ET} N_G(t)$$

$$\frac{dN_E(t)}{dt} = W_{ET} N_E(t) - W_E N_E(t)$$

where N_G and N_E are the density of excited Gd and Eu ions, W_G and W_E are the intrinsic decay rates of Gd

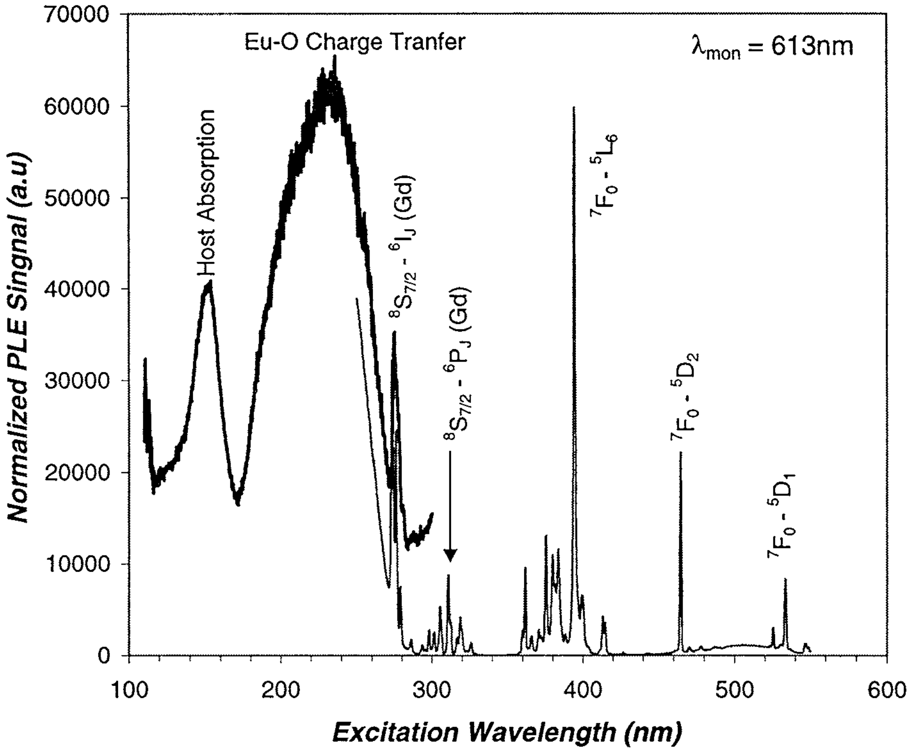

Figure 3 Photoluminescence excitation spectra of $BaGdB_9O_{16}$:Eu. A D_2 lamp was used for the VUV region and an Xe lamp for the UV-visible region. The main emission band at 613 nm was monitored for both spectra.

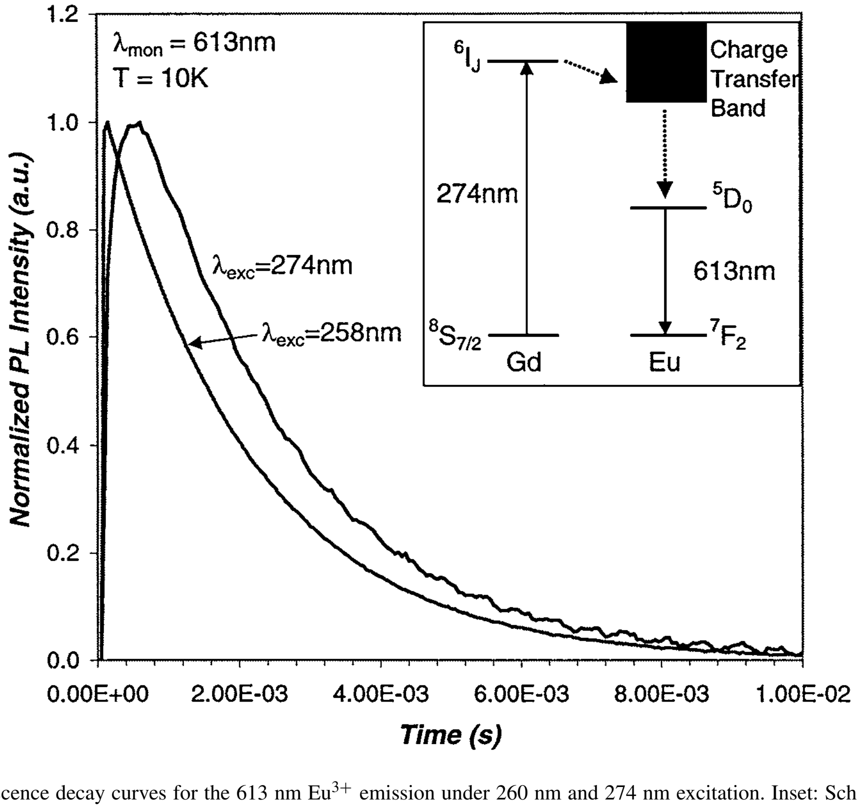

Figure 4 10 K luminescence decay curves for the 613 nm Eu^{3+} emission under 260 nm and 274 nm excitation. Inset: Schematic of the excitation process for the Eu ions through the energy transfer from Gd ions.

and Eu, respectively, and W_{ET} is the energy transfer rate between Gd and Eu. If W_{ET} does not possess any time dependence, the general solution for $N_E(t)$ is

$$N_E(t) = W_{ET}\,e^{-W_E t}\int_0^t e^{W_E x} N_G(x)\,dx$$

An analytical solution can be obtained if the Gd decay, $N_G(t)$, is assumed to be purely exponential.

$$N_E(t) = \frac{N_G(0)W_{ET}}{W_G + W_{ET} - W_E}\left(e^{-W_E t} - e^{-(W_G+W_{ET})t}\right)$$

This result clearly predicts that the Eu luminescence should show a slow rise, reach a maximum, and then decay with either its own intrinsic lifetime or the Gd decay rate, whichever is the smaller. The condition for maximum can be found by differentiating the above equation with respect to t and setting it equal to zero, which gives,

$$W_E\, e^{-W_E t_{max}} = (W_G + W_{ET})\, e^{-(W_G+W_{ET})t_{max}}$$

where t_{max} is the time that the Eu luminescence reaches a maximum.

From the experimental results shown in Fig. 4, we obtain $W_E = 480\ s^{-1}$ and $t_{max} = 450\ \mu s$. Then, from the above equation, we found that $W_G + W_{ET} = 6170\ s^{-1}$. Considering that the Gd^{3+} luminescence usually exhibit decay times on the order of a few milliseconds due to the forbidden nature of f-f transitions, it is expected that $W_G \sim 400\ s^{-1}$ and thus $W_G \ll W_{ET}$. Then, the energy transfer rate from Gd to Eu in $BaGdB_9O_{16}$:Eu was estimated to be approximately 6000 s^{-1}, which corresponds to an energy transfer time of 170 μs. This value of W_{ET} was smaller than that observed for $GdAlO_3$:Eu which was on the order of $10^6\ s^{-1}$ [7]. This difference was attributed to the smaller overlap between the Eu charge transfer band (233 nm) and the Gd ^6I_J level (274 nm) in $BaGdB_9O_{16}$:Eu whereas the charge transfer band of Eu is centered at 265 nm in $GdAlO_3$:Eu, providing a strong spectral overlap with the Gd ^6I_J level at 274 nm [8].

4. Conclusion

In summary, a spectroscopic study on $BaGdB_9O_{16}$:Eu was reported. The solid state reaction technique was found to produce highly efficient powder samples. The PL spectrum was shown to be dominated by a main line at 613 nm, indicating that the Eu ions occupied the Ba sites with no inversion symmetry. The fine structure observed in the emission bands exhibited low symmetry splitting, suggesting that the Eu sites experienced local distortion. The mechanism of the excitation process was investigated by PLE. The spectra measured at the 613 nm $^5D_0 - {}^7F_2$ transition of Eu^{3+} showed sharp line excitation bands due to the f-f transitions of both Eu^{3+} and Gd^{3+} ions. The charge transfer band of Eu was observed at 233 nm, which was at considerably shorter wavelengths than most other Eu doped borates. The excitation band due to the host absorption was also observed at 153 nm. The observation of Gd^{3+} bands indicated the presence of efficient energy transfer from Gd to Eu. Similarly to other borates, the host excitation occurs through the creation of excitons in the Gd sublattice which migrate until they find and recombine at Eu activators. The energy transfer process between Gd and Eu ions were studied by time-resolved spectroscopy. The Eu luminescence showed a purely exponential decay with a lifetime of 2.1 ms. When excited through the Gd ^6I_J level, the Eu luminescence exhibited a slow buildup, from which the Gd-Eu transfer rate was estimated to be 6000 s^{-1}. The transfer rate is smaller than the $GdAlO_3$:Eu system because the overlap between the Eu charge transfer band and the Gd ^6I_J level was smaller. The full optimization of this phosphor that can increase the VUV absorption and improve the overlap between Gd and Eu should make it a viable candidate for use in plasma display panels.

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