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Persistent luminescence of RE^{3+} co-doped $Sr_3B_2O_6$:Eu^{2+} yellow phosphors (RE = Nd, Gd, Dy)

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ABSTRACT

Bright and persistent luminescence in the yellow to reddish region was observed in newly developed $Sr_{3-x-y}B_2O_6$:xEu^{2+},yRE^{3+} (RE = Nd, Gd, Dy) phosphors. The effects of a series of RE^{3+} co-dopants (RE = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, or Yb) on achieving persistent luminescence were evaluated by varying the reducing conditions and laser illumination time. The Eu^{2+} single-doped and Eu^{2+}/Dy^{3+} co-doped samples showed a large red-shift in phosphorescence emission. The persistent luminescence intensity increased with increasing illumination time of a 355 nm laser, which is unique to these persistent phosphors. The PL decay rates were well fitted to either the bi- or tri-exponential forms. The PL decay modes were discussed in relation to the ionization potential of RE^{3+} ions and oxygen vacancies. The covalent characters of the B-O and Sr-O bonds for both the reduced and oxidized samples were calculated and compared with the electron density distribution map obtained using the maximum entropy method. The electron density contours around the O^{2-} apices of the BO_3 triangle was relaxed outwardly in the reduced sample. This relaxation could reinforce the nephaulexetic effect in Sr (Eu^{2+})-O coordination.

1. Introduction

Persistent phosphors emitting in the orange to red region are very limited in number and their luminescent performances are very low compared to those of blue-green phosphors [1–3]. The present study examined the persistent luminescence properties in RE^{3+}-co-doped $Sr_3B_2O_6$: Eu^{2+} phosphors. To the best of the authors' knowledge, persistent luminescence in strontium borate has not been reported. After the initial investigation by Machida et al., the photoluminescence (PL) properties of Eu-doped strontium borates were investigated in several host materials, such as SrB_6O_{10}, SrB_4O_7, SrB_2O_4, $Sr_2B_2O_5$, and $Sr_3B_2O_6$ [4–6].

The Eu ions in the SrB_2O_4 and $Sr_2B_2O_5$ cannot be reduced to the divalent state (Eu^{2+}), even under a prolonged reduction treatment and they remain in the trivalent state (Eu^{3+}). On the other hand, Eu ions in SrB_6O_{10} and SrB_4O_7 can be reduced easily to the divalent state but these materials show very low luminescence efficiency [4]. $Sr_3B_2O_6$:Eu has intermediate character between the two aforementioned borate groups; it can be reduced under strong reducing conditions and prolonged heat treatment times, and emits enhanced yellow light. [7,8]

$Sr_3B_2O_6$ has attracted considerable interest because of its tunable optical properties over a wide color range by doping or co-doping. Eu^{2+}/Ce^{3+} co-doping produces a range of hues from blue to yellow orange emission according to the Eu^{2+}/Ce^{3+} ratio under UV excitation [9]. Lihan et al. [10] reported that Dy^{3+} single doping rendered white light comprised of a blue emission centered at 479 nm and a yellow emission centered at 574 nm under 349 nm-UV excitation.

A few strontium borates, such as SrB_4O_7:Dy^{3+} and $Sr_3B_2O_6$:Sm^{3+}, show thermally stimulated luminescence (TL) [11–13]. The SrB_4O_7:Dy^{3+} polycrystalline sample irradiated by β–rays showed a TL glow peak at 497 K, which was attributed to the f-f transitions of Dy^{3+} ions. The TL fading rate of this tetraborate was so slow that the TL intensity remained relatively constant after 30 days at RT. $Sr_3B_2O_6$:Sm^{3+} nano-phosphors irradiated by γ–rays (high-dose of 1000–5000 Gy) also showed a TL glow peak at 400 K. These TL phenomena observed in Sr-borates led us to examine $Sr_3B_2O_6$:Eu^{2+} as a potential candidate yellow-reddish persistent phosphor.

In the present study, the effects of lanthanide co-dopants (RE = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Yb) on persistent luminescence were explored in the $Sr_3B_2O_6$: Eu^{2+} phosphor. The combinations of Eu^{2+}/Nd^{3+} and Eu^{2+}/Dy^{3+} ions produced a very bright afterglow in the yellow-reddish color range with a long decay life time. To achieve persistent luminescence from this phosphor, laser excitation with sufficient time and a prolonged reduction treatment were necessary. The

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persistent luminescence mechanism will be discussed in relation to the ionization potential of RE^{3+} and energy trap levels of oxygen vacancies (V_O). The covalent character of the Sr-O and B-O polyhedral was assessed in $Sr_3B_2O_6$:Eu^{2+},RE^{3+} samples and compared with the electron density distribution map calculated using XRD data.

2. Experimental

The chemical formulae of the synthesized samples were $Sr_{3-x-y}B_2O_6$:xEu^{2+},yRE^{3+} (RE = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Yb). x and y were varied in the range of 0.005 ~ 0.015 mol. The samples were prepared using a normal solid state reaction method with high purity $SrCO_3$, B_2O_3, and RE_2O_3 powders as the starting materials. The raw materials were weighed according to the stoichiometric ratio, mixed thoroughly in a mortar with ethyl alcohol, and calcined in air at 1000 °C for 5 h. The calcined powders were pulverized and reduced under a gas mixture of 5%H_2-95N_2 at 1280–1310 °C for 5–20 h. Some of the calcined samples were annealed in air at 1280 °C for 10hr. and their photoluminescence (PL) properties were measured and compared with those of the reduced samples.

The PL and PL decay rate of the prepared samples were characterized. The PL spectra were recorded using an ultraviolet-visible PL measurement system (Scinco S-4100 UV–vis Spectrophotometer) at room temperature. The decay rate was measured using a different PL measuring system. A frequency-tripled pulsed laser (Laser-export LCM-DTL-374QT) emitting 355 nm UV-light was used as the excitation source for measuring the PL decay rate. The time-averaged power supplied to the samples was ca. 0.5 mW from the 355 nm pulsed laser. The size of the beam focused on the samples was ca. 0.1 mm. PL was measured in a back-scattering configuration and was dispersed by a 50 cm single grating monochromator (ARC SpectraPro-500) after passing through a long-pass filter to remove elastically scattered laser light. PL spectra were recorded using a thermoelectrically cooled CCD camera (Andor DV420-OE). When measuring the decay rate of a sample, the collection of a persistent PL spectrum began immediately after blocking the excitation source and was continued with a time interval of 10 s between consecutive PL measurements. The exposure time of the excitation laser source on the sample was varied from 10 s to 10 min for each sample.

The non-uniform spectral response of the equipment was not corrected for the analysis of the persistent PL property. The crystal structures were analyzed by X-ray diffraction (Shimadzu X-ray Diffractometer XRD-6100) and the Rietveld refinement method. The electron density distribution was calculated using the maximum entropy method implemented in the VENUS software package.

3. Results

Since the doping concentration of the RE (RE = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, or Yb) including Eu ion is very low that it is very difficult to measure the valence state of the RE ion in the reduced phosphor samples. The valence change of Eu from trivalent to divalent could be easily confirmed by comparing the PL spectra of the phosphor samples before and after the reduction treatment. The PL spectrum before the reduction should consist of the characteristic sharp lines corresponding to the f-f transitions of Eu^{3+}. Spectroscopic lines from other RE^{3+} ions could not be observed under the PL(E) measurement conditions adopted in our study. On the other hand the PL spectrum of the reduced sample would consist of a broad band of f-d transition of Eu^{2+} ion. The valence state of other RE ion, such as Nd, Sm, Gd, Tb, Dy, Ho, or Yb remains trivalent after the reduction treatment because trivalent state of these lanthanide ions are thermodynamically very stable.[1,2] These trivalent co-dopants can be electron trap sites for the persistent luminescence.

Fig. 1 shows the PL excitation (PLE) and PL spectra of the $Sr_{3-x-y}B_2O_6$:xEu^{3+} yRE^{3+} (RE = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, or Yb) samples before the reduction treatment: annealed in air at 1280 °C. The PL spectral lines were typical of Eu^{3+} centers. In the PLE spectra, the broad band centered at ca. 280 nm is the charge transfer state (CTS) band of the Eu-O bonds. The sharp lines between 323 and 480 nm correspond to the f-f transitions from the ^7F_o ground state: ^7F_o -$^5D_{2–4}$, ^7F_o-$^5G_{2–3}$, and ^7F_o -$^5L_{6–10}$. In the PL spectra, the dominant peak at ca. 610 nm was assigned to the electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) and the small peak at ca. 590 nm originates from the magnetic dipole transition ($^5D_0 \rightarrow {}^7F_1$).[14]

The PL spectra of the co-doped samples after reduction treatment are presented in Figs. 2 and 3. The Eu^{2+}/Dy^{3+} co-doped ($Sr_{3-x-y}B_2O_6$:xEu^{3+},yDy^{3+}) and Eu^{2+}/RE^{3+} co-doped ($Sr_{3-x-y}B_2O_6$:xEu^{3+} yRE^{3+}) samples are presented in Figs. 2 and 3, respectively. The samples reduced at 1310 °C for 10 ~ 20 h showed very broad PLE and PL spectra. These samples showed similar PLE and PL spectral shapes with peak wavelengths of ca. 610 and 398 nm, respectively. The broad band observed in PL and PLE spectra are characteristic of Eu^{2+} center. On the other hand, the sharp lines in the PL(E) spectra before the reduction treatment (Fig. 1) are characteristic of f-f transition of Eu^{3+} centers. Generally the 5d wave function of Eu^{2+} strongly interacts with surrounding ligands and cations. Hence the crystal field around the Eu^{2+} has drastic effect on the excitation and emission spectrum. The $4f^65d^1$ electronic levels of Eu^{2+} are split into several energy states due to a strong and asymmetric crystal field. This non-cubic splitting produces a broad emission and excitation spectra. Hence the broad spectral shape indicates that the valence state of Eu ion has changed to divalent by the reduction treatment. The PLE spectra in Fig. 2 show a few small

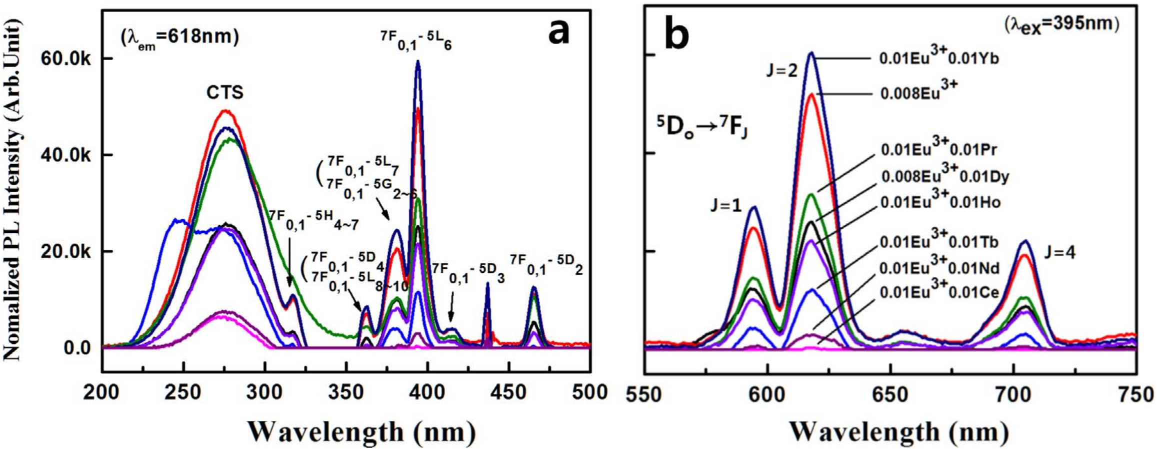

Fig. 1. PL and PLE spectra of the $Sr_3B_2O_6$:xEu^{3+},yRE^{3+} phosphors synthesized in air at 1280 °C.