A combinatorial approach to the discovery and optimization of YCa$_4$O(BO$_3$)$_3$-based luminescent materials

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Abstract

Thin films of YCa$_4$O(BO$_3$)$_3$ (YCOB)-based new luminescent materials were explored by the combinatorial pulsed laser deposition (PLD) method which enabled us to fabricate continuous composition spread film libraries. Strong red and green luminescence were found in the Y$_{1-x}$Eu$_x$COB (0 ≤ x ≤ 1), (YEuCOB) and Y$_{1-y}$Tb$_y$COB (0 ≤ y ≤ 1) (YTbCOB) films, respectively. The film libraries were characterized by photoluminescence (PL), PL decay, an electron-probe microanalyzer and an electron diffraction analysis. The luminescent intensities in the amorphous film libraries strongly depended on the chemical composition of each rare-earth (RE) ion. The optimum concentration of rare-earth ions in YEuCOB and YTbCOB were experimentally determined to be Eu = 7.5% and Tb = 20–30%, respectively.

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1. Introduction

Recently, there is a considerable interest in the development of advanced luminescent materials for a variety of applications, such as flat panel displays, lighting and X-ray imaging systems. To enhance their
luminescence properties, many phosphors for practical use are composed of multi-compound systems. However, the present reliable theories are inadequate to predict the relation between composition and luminescent color and efficiency. Many commercial phosphor materials have been discovered through one-by-one serial synthesis and testing so far [1,2].

The combinatorial approach is well suited for the investigation of ternary and more components materials with unpredictable properties [3]. Recently, many research groups started to apply the combinatorial method for high-throughput discovery and optimization of luminescent materials [4–6].

We focused attention on the rare-earth (RE) calcium oxyborate family, with general composition RECa$_4$O(BO$_3$)$_3$ (RECOB) (RE = La–Lu, Y) as new phosphor materials [7,8]. The advantages of this system are as follows: (1) they have rare-earth ions in crystal structure which act as a luminescence center and (2) they have good thermal- and chemical-stability for UV light irradiation [9]. YCOB has a monoclinic acentric structure without inversion symmetry and the space group is $C_{mn}$. Although electric dipole f–f transitions in free rare-earth (4f) ions are strictly forbidden, in case of an asymmetric crystal, electric dipole transition is strongly induced. On the other hand, magnetic dipole transitions are allowed between the f$^n$ configuration states [10,11]. Therefore, in YCOB-based phosphors without inversion symmetry, the emission intensity will be enhanced due to both electric dipole transitions and magnetic dipole transitions.

In this paper, we show YCOB-based thin films as new luminescent materials screened by the combinatorial method where the optimum compositions as well as the luminescence mechanism were quantitatively evaluated by time-integrated and time-resolved photoluminescence (PL) spectra measurements.

2. Experiment

YCOB–EuCOB (YEuCOB) and YCOB–TbCOB (YTbCOB) binary composition spread films were fabricated on SiO$_2$ substrates by the combinatorial pulsed laser deposition (PLD) method with a specially designed mask scheme, which enabled us to fabricate continuous composition spread film libraries. The detailed process is described elsewhere [12]. A pulsed KrF excimer laser ($\lambda = 248$ nm) with a laser fluence of 2 J/cm$^2$ was focused on sintered RECOB targets in $1.3 \times 10^{-4}$ Pa oxygen at a 5 Hz repetition rate. The substrate temperature was kept at 500 °C by an infrared lamp.

Chemical composition of the films was determined using an electron-probe microanalyzer. Structural analyses of the films was performed by an electron diffraction analysis. Photoluminescence properties of the entire film libraries were investigated by taking color photographs under excitation with an ultraviolet (254 nm) lamp. To clarify the luminescent mechanism, especially the concentration-quenching behavior [13], time-integrated PL spectra at room temperature were measured using a He–Cd laser (325 nm, 1.5 mW) for excitation, and time-resolved PL spectra at room temperature were measured using the fourth harmonics of a Q-switched pulse yttrium aluminum garnet (YAG) laser for excitation (266 nm, 1 mJ, pulse duration of 8 ns and a repetition rate of 10 Hz).

3. Results and discussion

Strong red and green luminescence was found in the YEuCOB and YTbCOB system, respectively. The film libraries showed strong dependence of luminescence intensities on the chemical composition. Fig. 1(a and b) show photographs of the ultraviolet-excited (254 nm) PL of the entire film libraries (a)Y$_{1-x}$Eu$_x$COB and (b)Y$_{1-y}$Tb$_y$COB, revealing the emission intensity as a function of (a) Eu and (b) Tb ion concentration (%), respectively. The photographs show that (a) red and (b) green emission intensity drastically increased and remained at constant brightness, then gradually decreased with increasing Eu and Tb ion concentration, respectively. Therefore, the libraries clearly revealed the optimum order of Eu and Tb ion concentration of those systems.

Fig. 1(c) shows an electron diffraction pattern of the YTbCOB film as a typical example of YCOB-based thin films, which showed halo pattern. YCOB-based thin films grown at 500 °C became amorphous. This temperature range is well suited for use with inexpensive soda-lime glass substrates.

The PL emission spectra of (a) YEuCOB and (b) YTbCOB are illustrated in Fig. 2, and the excitation spectra are inserted in Fig. 2. In the emission spectrum
of YEuCOB, typical Eu\(^{3+}\) emission peaks were
observed at 577, 590, 615, 655 and 705 nm, which
were assigned to the \(5D_0 \rightarrow 7F_j\) \((j = 0, 1, 2, 3, 4)\)
transitions. While, in the emission spectrum of
YTbCOB, typical Tb\(^{3+}\) emission peaks were observed
at 488, 542, 586 and 622 nm, which were assigned to
the \(5D_0 \rightarrow 7F_j\) \((j = 6, 5, 4, 3)\) transitions.

Using the combinatorial method to change Eu
composition \((x)\) and Tb composition \((y)\), we observed
the \(z\)-dependent \((z = x \text{ or } y)\) behavior of PL intensity
(solid circles in Fig. 3(a and b)). In case of YEuCOB,
comparison of the \(5D_0 \rightarrow 7F_2\) transition for each \(x\)
reveals this concentration-quenching behavior; the PL
intensity of \(5D_0 \rightarrow 7F_2\) transition increased with
increasing \(x\) up to 7.5%, and then gradually decreased
with further increase in \(x\). In case of YTbCOB, the PL
intensity of \(5D_4 \rightarrow 7F_5\) transition increased with
increasing \(y\) up to 20% and remained till 30%, and
then gradually decreased with further increase in \(y\).

The decay curves for \(z\) were measured at an
emission wavelength of 615 nm (YEuCOB) and
540 nm (YTbCOB), which corresponds to the
\(5D_0 \rightarrow 7F_2\) transition and the \(5D_4 \rightarrow 7F_5\) transition,
respectively. Both the decay rate of \(5D_0 \rightarrow 7F_2\) and
\(5D_4 \rightarrow 7F_5\) transition increased with increasing \(z\) (the
solid circles in inset of Fig. 3(a and b)).

The \(z\)-dependence of PL decay behavior indicates a
nonradiative recombination process occurring in the
energy transfer between Eu or Tb ions via the radiative
recombination process at the 4f\(^8\) configuration. When
\(z\) is increased, the energy transfer between Eu or Tb
ions becomes more frequent, thus accelerating the PL
decay. To explain both the magnitude of PL intensity
and the decay rate as a function of $z$, here we consider the nonradiative relaxation rate occurring in the resonant energy transfer between the Eu or Tb states in addition to the radiative relaxation rate in the radiative $^{5}\text{D} \rightarrow ^{7}\text{F}$ transition. By solving the rate equation for the two decay rates [8], both the dependence of on $z$ and a theoretical time-integrated PL intensity as a function of $z$ can be obtained (solid lines in Fig. 3(a and b)). The agreement between the measured and theoretical curves strongly implies that the emission process of YCOB-based systems is significantly affected by the nonradiative decay process occurring in the energy transfer between activator ions.

4. Conclusions

Thin films of YCOB-based luminescent materials were fabricated on a SiO$_2$ substrate by a combinatorial pulsed laser deposition technique. The film compositions changed continuously in a full-range from YCOB to EuCOB and from YCOB to TbCOB on a single substrate, respectively. Each composition spread film library quickly reveals the optimum Eu and Tb concentration range. The optimum concentrations of rare-earth ions in YEuCOB and YTbCOB for highest luminescent intensity were experimentally determined to be Eu = 7.5% and Tb = 20–30%, respectively. Noteworthy fact is that the thin films of these phosphors are grown at 500 °C, which extends a range of options to substrate material.

References