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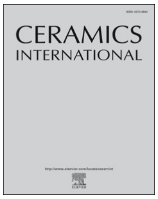

First observation of ^5D_J ($J=1, 2, 3$) emission transitions in Eu^{3+}-activated rare-earth antimony garnet $R_3Sb_5O_{12}$ (R = Y, Gd, La)

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ABSTRACT

$R_{2.9}Eu_{0.1}Sb_5O_{12}$ (R = Y, Gd, La) polycrystalline powders were prepared by solid-state reaction and characterized by X-ray powder diffraction (XRD), photoluminescence, decay lifetimes, and CIE color coordinates. The phosphors can be efficiently excited by UV-light and presents the emission covering the entire visible spectrum. Except for the commonly reported $^5D_0$–$^7F_{0,1,2,3,4}$ transitions of Eu^{3+} ions in $R_{2.9}Eu_{0.1}Sb_5O_{12}$ (R = Y, La), higher $^5D_{1,2,3}$ states present stronger emission lines. This produces white emission in the single-phased phosphor, whereas $R_{2.9}Eu_{0.1}Sb_5O_{12}$ (R = Gd) shows orange emission due to the absence of $^5D_{3,2}$ transitions. The emission mechanism from the high-energy levels of $^5D_{1,2,3}$ Eu^{3+} ion in $R_{2.9}Eu_{0.1}Sb_5O_{12}$ (R = Y, Gd, La) phosphors is also discussed.

1. Introduction

Trivalent Eu^{3+} is one of the most important activators, which often shows red emitting transitions (570–720 nm) due to its $^5D_0 \rightarrow {}^7F_J$ (J = 0–6) transitions. Eu^{3+}-activated phosphors have been applied in lighting, display, and X-ray detection. Many works reported the luminescence properties on $^5D_0 \rightarrow {}^7F_J$ (J = 0–6) transitions of Eu^{3+} ions in phosphors [1–6].

However, emission from high-energy $^5D_{3,2,1}$ levels of Eu^{3+} is not popular because it has strong dependence on Eu^{3+} concentration and phonon energy of the host [7]. Given that low Eu^{3+} doping level is **presented** in phosphor with soft lattice, the possible cross-relaxation and multiphonon relaxation will be prohibited. Thus, $^5D_{3,2,1}$ emission transitions will be produced in the blue and green regions. A proper host with low Eu^{3+} concentration can show $^5D_{3,2,1}$ together with $^5D_0$ emissions, producing white emission in Eu^{3+} singly activated phosphor [8]. In recent years, luminescence from high-energy ^5D_J levels ($^5D_1$, $^5D_2$, and $^5D_3$) in Eu^{3+}-activated phosphors, such as $Y_4Al_2O_9$ [8], $BaCa_2In_6O_{12}$ [9], $Ba_5Gd_8Zn_4O_{21}$ [10], $BaGd_2ZnO_5$ [11], $CaIn_2O_4$ [7], and $Bi_4O_3(BO_3)(PO_4)$ [12], have been reported.

Marcano and Rasines [10,13] firstly reported the garnet-like oxides $R_3Sb_5O_{12}$ (R = rare-earth ions) with space group I-43 m (No. 217) which strongly related to a fluorite defect structure. G. Blasse and Kiliaan [14] investigated the luminescence of $Gd_3Sb_5O_{12}$, which showed an orange emission below 100 K under UV excitation with independence of doping. The orange luminescence was ascribed to Sb^{3+} ion in $Gd_3Sb_5O_{12}$. 1 mol Eu^{3+} or Tb^{3+} activated $Gd_3Sb_5O_{12}$ showed weak emission lines in this host. However, accommodation for activator ions and the luminescence properties of $R_3Sb_5O_{12}$ are still unclear. Compared with the well-known garnet host of $Y_3Al_5O_{12}$, $R_3Sb_5O_{12}$ could have more rigid framework because Sb^{5+} (2.05) has a higher electronegativity than that of Al^{3+} (1.61). Accordingly, the higher thermal stability of rare-earth-activated $R_3Sb_5O_{12}$ could be expected. In this work, transitions from high-energy $^5D_{3,2,1}$ levels in $R_3Sb_5O_{12}$ (R = Y, Gd, La):Eu^{3+} were reported. The emission mechanism was briefly discussed.

2. Experimental

Eu^{3+}-activated $R_3Sb_5O_{12}$ (R = Y, Gd, La) polycrystalline powders were synthesized via solid-state reaction methods. In this work, $R_{2.9}Eu_{0.1}Sb_5O_{12}$ (R = Y, Gd, La) was introduced because the optimal white-light could be obtained via adjusting the doping Eu^{3+} concentration. The elements diffusion takes place in the interfaces of raw particles; then final products could be produced after nucleation and crystal growth. This method has some advantages such as facile production process, low costs, and high efficiencies etc. The mixture stoichiometric chemicals of R_2O_3 (R = Y, Gd, La) and Sb_2O_3 were firstly heated at 700 °C for 5 h to release the moisture and got a chance for mixture. Then the mixtures were heated at 800 °C for 10 h to get the final products after the solid-state reaction.

The XRD patterns from 10° to 120° were measured on a Rigaku D/Max diffractometer with Cu Kα radiation (λ = 1.5405 Å). Photoluminescence was tested using a spectrometer (Perkin-Elmer-LS-

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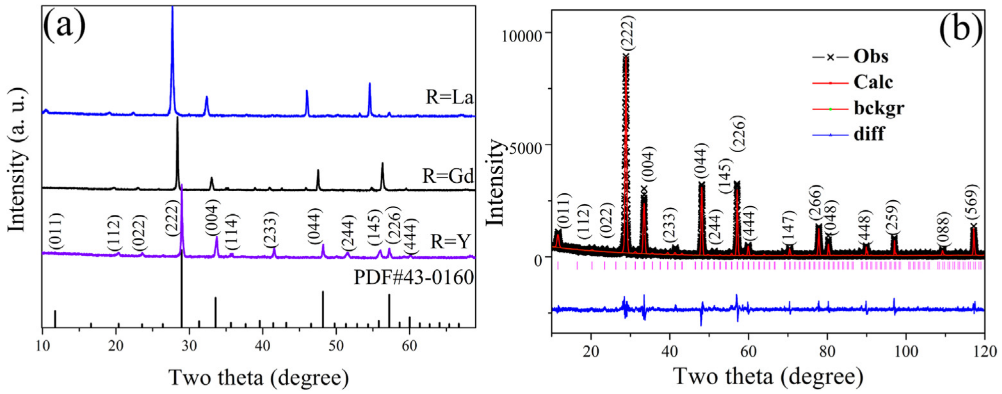

Fig. 1. XRD patterns of $R_{2.9}Eu_{0.1}Sb_5O_{12}$ (R = Y, Gd, La) (a) and the representative Rietveld refinement for $Gd_{2.9}Eu_{0.1}Sb_5O_{12}$ (b).

50B). The luminescence decay curve was tested via the excitation of forth harmonic wavelength of YAG:Nd laser (Spectron Laser Sys. SL802G, with a pulse width of 5 ns and a repetition rate of 10 Hz). Excitation is a pulsed UV light with the wavelength of 266 nm generated by an Nd: YAG laser (Spectron Laser System SL802G). Luminescence signals were dispersed by a 75 cm monochrometer (ActonResearch Corp., Pro-750) and multiplied by a PMT (Hamamatsu R928). The decay signals were recorded using a digital oscilloscope (LeCloy 9301). Raman spectra were recorded at room temperature using a Jobin Yvon T64000 spectrometer. The available excitation wavelength provided by an argon ion laser was 514.53 nm.

3. Results

The typical XRD patterns of $R_{2.9}Eu_{0.1}Sb_5O_{12}$ (R = Y, Gd, La) phosphors are displayed in Fig. 1(a). These XRD patterns are in excellent agreement with the PDF standard card PDF#43-0160. These samples are in single phase and **crystallize** in the garnet-type framework. No impurities are observed. There is a shift to small two theta angle with the sequence of Y, Ga and La indicating the expansion of the lattices. This is attributed to the increase of the ionic radius from Y^{3+} (0.9 Å) to Gd^{3+} (0.938 Å) and La^{3+} (1.032 Å). The crystal structures are investigated by Rietveld refinements. The typical result is displayed in Fig. 1(b) for $R = Gd$. The refined structural parameters and atom positions are shown in Table 1. The parameters of R_p = 7.52%, R_{wp} = 9.3221, X^2 = 8.258% indicate the high reliability in the structural refinement. Gd^{3+} only occupies one cation site (12d) in the lattices, which is available for the substitution of Eu^{3+} ion. The single-phased $Gd_{\mathbf{2.9}}\mathbf{Eu_{0.1}Sb_5O_{12}}$ sample crystallizes in the cubic space group I-43 m (217) with cell parameters of a = 10.8745 Å, V = 1285.961 Å^3, and Z = 4.

Structure according to the crystallographic data is shown in Fig. 2(a, b), which adopts the garnet lattices in a space group of I-43 m (No. 217). Two kinds of Sb, i.e., Sb(1) and Sb(2) with coordination numbers of four and three are observed, respectively. R^{3+} ions are located in a quasicubic environment of oxygen atoms in a S_4 point symmetry, and GdO_8 polyhedra connected with each other by edge-sharing. The distance of two neighboring Gd ions is 3.896 Å [15].

Table 1
Crystallographic data for $Gd_{2.9}Eu_{0.1}Sb_5O_{12}$ based on Rietveld refinement.

Formula	$Gd_{2.9}Eu_{0.1}Sb_5O_{12}$
Space group	Cubic, I-43 m (217)
Cell parameters	a = 10.8745 Å, α = 90°, V = 1285.961 Å^3, Z = 4
Reliability factors	R_p = 7.52%, R_{wp} = 9.3221, X^2 = 8.258%,

Atom	Wyck.	x	y	z	Occ.
Sb2	8c	0.2544(19)	0.2544(19)	0.2544(19)	1
Gd1	12d	1/4	1/2	0	0.967
Eu1	12d	1/4	1/2	0	0.033
Sb1	12e	0.2694(14)	0	0	1
O2	24 g	0.34700	0.34700	0.14000	1
O1	24 g	0.11200	0.11200	0.39700	1

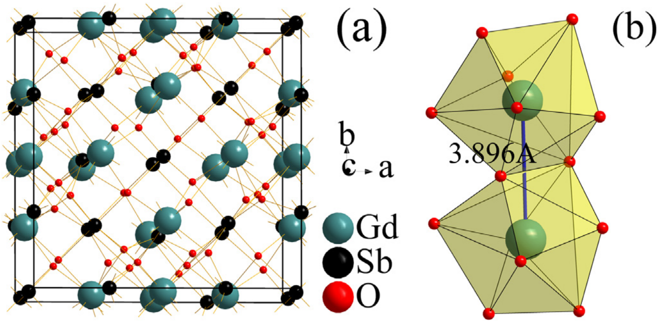

Fig. 2. Structure project (a) and connection between of RO_8 polyhedra (b) of $Gd_{2.9}Eu_{0.1}Sb_5O_{12}$.

The SEM pictures of the final phosphor products are shown in Fig. 3a and b, which show grains with size of 2–5 μm. EDX analysis shown in Fig. 3c and d indicates that the pure sample only shows signals from Gd, Sb, and O. Meanwhile, the signals from Eu^{3+} are clearly detected in Eu-doped samples. The quantitative analyses are consistent with the atom ratio in the formula as shown in the figures.

Fig. 4a shows the emission of $R_{2.9}Eu_{0.1}Sb_5O_{12}$ (R = Y, Gd, La) under 254 nm. The complicated emission peaks are $^5D_{3,2,1,0} \rightarrow {}^7F_J$ (J = 0–4) transitions, including 418 nm ($^5D_3 \rightarrow {}^7F_1$), 429 nm ($^5D_3 \rightarrow {}^7F_2$), 447 nm ($^5D_3 \rightarrow {}^7F_3$), 468 nm ($^5D_3 \rightarrow {}^7F_4$), 476 nm ($^5D_2 \rightarrow {}^7F_1$), 499 nm ($^5D_2 \rightarrow {}^7F_2$), 516 nm ($^5D_2 \rightarrow {}^7F_3$), 541 nm ($^5D_1 \rightarrow {}^7F_1$), 556 nm ($^5D_1 \rightarrow {}^7F_2$), 570 nm ($^5D_1 \rightarrow {}^7F_3$), 589 nm ($^5D_0 \rightarrow {}^7F_1$), 627 nm ($^5D_0 \rightarrow {}^7F_2$), 660 nm ($^5D_0 \rightarrow {}^7F_3$), and 705 nm ($^5D_0 \rightarrow {}^7F_4$). Some differences are observed for the phosphors with R = Gd and R = Y, La. The $^5D_3$, $^5D_2$, $^5D_1$ to ^7F_J emission peaks are strong in $R_{2.9}Eu_{0.1}Sb_5O_{12}$ (R = Y, La) phosphors. However, $^5D_3$ and $^5D_2$ transitions are nearly quenched in $R_{2.9}Eu_{0.1}Sb_5O_{12}$ (R = Gd). The mechanism is not clear at the present stage. The possible cause could be that Y^{3+} and La^{3+} are optically inert ions, while, Gd^{3+} is optically active with the excited state ($^8S_{7/2} \rightarrow {}^6G_J$) and emission level ($^6P_J \rightarrow {}^8S_{7/2}$) at around 254 nm and 311 nm, respectively. The excitation light at 254 nm in Fig. 4a could directly excite the Gd^{3+} sub-lattices and gave the subsequent energy relaxation or energy transfer to Eu^{3+} ions. This indicates the excitation and emission mechanisms have some differences between the phosphors with R = Gd and the R = Y, La. The non-radiative transitions could happen and inhibit the emission from $^5D_{1,2,3}$ high energy levels.

The excitation of $R_{2.9}Eu_{0.1}Sb_5O_{12}$ (R = Y, Gd, La) (Fig. 4b) is detected by monitoring emission from $^5D_{1,2,3}$ and $^5D_0$ emission. All spectra have similar profile consisting of broad bands at 220–300 nm