High color purity phosphors of LaAlGe$_2$O$_7$ doped with Tm$^{3+}$ and Er$^{3+}$

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(Received 8 March 2006; accepted 29 June 2006; published online 23 August 2006)

Phosphors of LaAlGe$_2$O$_7$ doped with Tm$^{3+}$ and Er$^{3+}$ of high color purity, exhibiting a narrow band emission in the blue and green regions, were obtained. (La$_{1-x}$Ln$_x$)AlGe$_2$O$_7$ (Ln=Tm,Er) powders are bright emitters, with chromaticity color coordinates that are comparable to or better than those of standard phosphors for display or lighting devices. The blue emission of the Tm$^{3+}$-doped phosphor had CIE chromaticity coordinates (0.151, 0.033) with a dominant wavelength of 455 nm and a color purity of 94%. The Er$^{3+}$-doped phosphor had color coordinates (0.249, 0.718), a dominant wavelength of 542 nm, and 92% purity. © 2006 American Institute of Physics.

DOI: 10.1063/1.2337275

Rare-earth-ion-doped crystalline has attracted considerable research interest owing to its excellent luminescent properties. The use of rare-earth element-based phosphor, based on “line-type” f-f transitions, can narrow the emissions to the visible range, resulting in high efficiency and a high luminescent equivalent. Thulium-doped phosphors have attracted substantial attention in recent years because Tm$^{3+}$ ions provide blue luminescence with potential applications in screens and displays, such as cathode-ray tube screens, field-emission displays, and electroluminescent devices. Conventional blue phosphors (ZnS: Ag, ZnS: Tm, F) are the most efficient blue light emitters. However, using sulfide-based materials has such disadvantages as chemical instability during operation, corrosion of the emitter cathode in field-emission displays induced by sulfur-related contaminant gases, and luminescence saturation at high excitation density. Hence, the use of oxide-based phosphors as a source of radiation is an emerging field. Certainly, oxides such as Y$_2$O$_3$; Tm, SrHfO$_3$; Tm, and Y$_3$GaO$_6$; Tm are serviceable alternatives to the presently used sulfides.

Erbium-doped materials have been widely adopted in optical telecommunications systems because of their particular emission band around 1.53 $\mu$m in the IR region. More recently, however, Er-activated materials have been studied as a light source because of their green emissions. In this study, LaAlGe$_2$O$_7$ activated with Tm$^{3+}$ and Er$^{3+}$ was prepared, and its photoluminescence (PL) characteristics were investigated.

Tm$^{3+}$- and Er$^{3+}$-doped LaAlGe$_2$O$_7$ were synthesized by a vibrating milled solid state reaction. The starting materials were La$_2$O$_3$, GeO$_2$, Al$_2$O$_3$, Tm$_2$O$_3$, and Er$_2$O$_3$. After they had been mechanically activated by grinding in a high energy vibromill, the mixtures were calcined at 1250 °C in air for 12 h. Conventional x-ray diffraction technique was employed to identify the phase. The data of all the samples reveal a single phase without any impurity and indicate that the Tm$^{3+}$ and Er$^{3+}$ ions were satisfactorily substituted for the La$^{3+}$ ions.

Figure 1 presents PL excitation and emission spectra associated with Tm$^{3+}$ ions in LaAlGe$_2$O$_7$. The sharp excitation peaks between 200 and 400 nm are assigned to the typical 4$f^5$→4$f^6$ intraconfiguration forbidden transitions of Tm$^{3+}$. Tm$^{3+}$ has complicated energy levels and various possible transitions because of a strong deviation from R-S coupling in the 4f configuration. Accordingly, the excited states of Tm$^{3+}$ ions may relax via a large number of paths, giving rise to ultraviolet, visible, and infrared emission with moderate intensity. The major emission peak of Tm$^{3+}$ was at 543 nm and a very weak peak was observed at 512 nm, corresponding to the transitions $^3D_2→^3F_4$ and $^1D_2→^3H_6$, respectively. Compared to conventional Tm-doped phosphors, particularly noteworthy is that the transitions from $^1G_4$ to $^3H_6$ manifold do not appear in LaAlGe$_2$O$_7$, such as $^1G_4→^3H_6$ ($\sim$475 nm). Reisfeld has noted that nonradiative relaxation between various J states of rare-earth ions may occur by the simultaneous emission of several phonons which conserve...
the energy of the transitions, and these multiphonon processes arise from the interaction of the electronic levels of the rare earth with the vibrations of the host lattice. Therefore, it may be expected that very efficient nonradiative relaxation for the $^1G_4$ level would occur in LaAlGe$_2$O$_7$ lattice. The blue $^1D_2 \rightarrow ^3F_4$ emission is quite sharp, with a full width at half maximum of about 6 nm. This spectral feature reveals high color purity and excellent chromaticity coordinate characteristics. A series of La$_{1-x}$Tm$_x$AlGe$_2$O$_7$ samples was synthesized as the dopant concentration ranged from 0.1 to 30 mol %. The most efficient PL intensities occurred when the Tm$^{3+}$ content increased, revealing that more than one decay channel, which changes the decay curves.

The effect of Tm$^{3+}$ content on the $^1D_2 \rightarrow ^3F_4$ transition decay curves is shown in Fig. 2. A single exponential decay was observed in the diluted samples. At higher concentrations, however, the observed decay curves were nonexponential, and the nonexponential change becomes more prominent as Tm$^{3+}$ content increases, revealing that more than one relaxation process exists. When the luminescent centers have different local environments, the associated ions will relax at different rates. If the rates are dramatically different, then diverse decay curves are likely to be observed. Nevertheless, the low-doped samples yield single exponential decay curves with a long lifetime, eliminating this possibility. Additionally, it is unlikely that only one site with the shorter lifetime is populated for higher concentration. The energy transfer over ion-ion interaction between two neighboring activator ions would be beneficial to resolve this issue. The distance between Tm$^{3+}$ ions decreases as the Tm$^{3+}$ concentration increases; subsequently, the energy transfer process between Tm$^{3+}$ ions becomes more frequent, providing an extra decay channel which changes the decay curves.

Samples with low Tm$^{3+}$ content would minimize the effects of the interactions between optically active ions. The monoeponential decay curve fit indicates that the LaAlGe$_2$O$_7$ contains a unique crystallographic site available for the activator (Tm$^{3+}$ instead La$^{3+}$), so that only one luminescent mechanism applies. This result is inconsistent with preliminary investigations of the LnAlGe$_2$O$_7$-type (Ln: trivalent rare-earth ions) structure, where Ln$^{3+}$ ions are incorporated into single-centered hosts until all rare-earth sites have been substituted.

Trivalent erbium with the $4f^{11}$ configuration has complex energy levels with various possible transitions between $4f$ levels. The transitions between these $4f$ levels are highly selective and are associated with sharp lines in the spectra. Figure 3 shows PL excitation and emission spectra of LaAlGe$_2$O$_7$: Er. The excitation spectrum consists of a series of sharp intra-$4f$-shell transitions from the ground state $^4I_{15/2}$ to higher energy levels. For all samples, only green emission was observed and attributed to the transition from the $^2H_{11/2}$ and $^4S_{3/2}$ states to the $^4I_{15/2}$ ground state. In particular, the emission peaks were centered in the green region, so its color coordinates were desirable. Such partial emission in only the green region with favorable color coordinates is unusual for Er$^{3+}$ other inorganic oxide host, where Er$^{3+}$ ions are incorporated into single-centered hosts until all rare-earth sites have been substituted.

The corresponding chromaticity Commission Internationale de l’Eclairage (CIE) coordinates are illustrated in Fig. 4. With the $(x, y)$ chromaticity coordinates, the dominant wavelength and the color purity compared to CIE Standard Source C [illuminant C $(x=0.3101, y=0.3162)$] for Tm$^{3+}$- and Er$^{3+}$-doped phosphors are listed in Table I. For Tm-doped LaAlGe$_2$O$_7$, the values obtained (0.151, 0.033), with a color purity of 94%, are superior (high color purity) to those reported for currently available commercial blue phosphors, such as Y$_2$O$_3$: Tm (0.158, 0.150), $^5$Sr$_2$B$_5$O$_9$:Cl: Tm (0.166, 0.379). The dominant wavelength color of the Tm-doped LaAlGe$_2$O$_7$ is 453 nm. For Tm$^{3+}$-doped phosphors, the dominant wavelength color of the Tm$^{3+}$-doped phosphors is at 541 nm.
0.115,\textsuperscript{17} Ba\textsubscript{2}B\textsubscript{2}O\textsubscript{4}:Cl: Tm (0.172, 0.088),\textsuperscript{18} ZnS: Ag (0.145, 0.081),\textsuperscript{19} and BaMgAl\textsubscript{10}O\textsubscript{17}: Eu (0.147, 0.067).\textsuperscript{20} In comparison with green phosphors Y\textsubscript{2}O\textsubscript{3}: Tb (0.319, 0.597),\textsuperscript{2} Zn\textsubscript{2}SiO\textsubscript{4}: Tb (0.287, 0.554),\textsuperscript{21} ZnS: Cu, Al (0.284, 0.605),\textsuperscript{22} and Y\textsubscript{2}O\textsubscript{3}: Er (0.32, 0.62),\textsuperscript{12} the Er-doped LaAlGe\textsubscript{2}O\textsubscript{7} had preferable CIE (0.249, 0.718) and color purity (92\%). These information provide evidence that the Tm\textsuperscript{3+}- and Er\textsuperscript{3+}-doped LaAlGe\textsubscript{2}O\textsubscript{7} phosphors exhibit vivid blue and green emissions with CIE color coordinates and color purity that are comparable to or better than those reported for the most-used phosphors. Furthermore, the Tm\textsuperscript{3+} and Er\textsuperscript{3+} phosphors allow a wide color gamut that is much wider than that recommended by the European Broadcasting Union (EBU) and the National Television System Committee (NTSC) primary system colors [EBU illuminant blue=(0.15, 0.06), green =(0.29, 0.60); NTSC illuminant blue=(0.14, 0.08), green = (0.21, 0.71)]. Phosphors with such high color purity emit primarily blue and green, from which a wide spectrum of colors is generated by appropriate mixing.

In summary, the emission spectra of the Tm\textsuperscript{3+}- and Er\textsuperscript{3+}-doped LaAlGe\textsubscript{2}O\textsubscript{7} samples corresponded to vivid blue and green emissions. The presence of a single optically active site in LaAlGe\textsubscript{2}O\textsubscript{7} may explain the monoexponential decay curves for samples with low activator concentrations, where the energy transfer between activator ions is negligible. The lanthanide germinates in the system (La\textsubscript{1-x}Ln\textsubscript{x})AlGe\textsubscript{2}O\textsubscript{7} (Ln=Tm, Er) samples clearly exhibit excellent chromaticity coordinates of (0.151, 0.033) with a color purity of 94\% and (0.249, 0.718) with a color purity of 92\% when doped with Tm and Er, respectively.

The authors would like to thank the National Science Council of Taiwan, Republic of China, for financially supporting this research under Contract No. NSC94-2216-E-006-017.

\begin{table}[h]
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\begin{tabular}{|c|c|c|}
\hline
Phosphor & CIE (x, y) & Dominant wavelength (nm) & Purity (\%)
\hline
LaAlGe\textsubscript{2}O\textsubscript{7}: Tm & (0.151, 0.033) & 455 & 94
LaAlGe\textsubscript{2}O\textsubscript{7}: Er & (0.249, 0.718) & 542 & 92
\hline
\end{tabular}
\caption{Chromaticity coordinate, dominant wavelength, and color purity for blue and green phosphors.}
\end{table}