Luminescent properties of trivalent praseodymium-doped lanthanum aluminum germanate LaAlGe$_2$O$_7$

Yu-Chun Li$^a$, Yen-Hwei Chang$^{a,*}$, Yu-Feng Lin$^a$, Yee-Shin Chang$^b$, Yi-Jing Lin$^a$

$^a$Department of Materials Science and Engineering, National Cheng Kung University, No. 1, Ta-Hsueh Road, Tainan 70101, Taiwan

$^b$Institute of Electro-Optical and Materials Science, National Formosa University Huwei, Yunlin 632, Taiwan

Received 4 September 2006; received in revised form 25 February 2007; accepted 4 June 2007

Abstract

The luminescent characteristics of Pr$^{3+}$-activated LaAlGe$_2$O$_7$ were investigated. In response to excitation using 448 nm blue light, the emission spectra involved most of the $^3P_0$-$^3H_J$ transitions. The dominant emission came from the $^3P_0$-$^3H_4$ transition at 487 nm. $^1D_2$ fluorescence quenching was observed in highly doped samples and is related to the cross-relaxation processes among neighboring Pr$^{3+}$ ions. In contrast with conventional Pr$^{3+}$-activated phosphors, the extraordinary excitation spectra showed only intense $f$–$f$ transition of Pr$^{3+}$ ions, while the 4$f$–5$d$ transition was eliminated. This is ascribed to photoionization. By analyzing absorption and excitation spectra, it is recognized that no efficient energy transfer occurs between Pr$^{3+}$ and the host lattice in LaAlGe$_2$O$_7$.

Keywords: D. Luminescence

1. Introduction

Rare-earth-ion-doped crystallite has attracted considerable research interest owing to its excellent luminescent properties. The rare-earth ions are characterized by a partially filled 4$f$ shell that is well shielded by 5$s^2$ and 5$p^6$ orbitals. Therefore, emission transitions yield sharp lines in the optical spectra [1]. 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-lumen equivalence. Pr$^{3+}$-doped phosphor materials with full color luminescence have received substantial interest because the Pr$^{3+}$ ions show a number of different emissions depending on the host lattice in which they are incorporated, for example red (from the $^1D_2$ level), green (from the $^3P_0$ level), blue (from the $^1S_0$ level) and ultraviolet (from the 4$f$–5$d$ state) [2].

The phases composed by the elements with smaller differences of electronegativity ($\Delta X$) correspond to a narrower band gap of compounds, leading to higher conductivity. The difference between the electronegativities of Si and O ($\Delta X = 1.54$) exceeds that between Ge and O ($\Delta X = 1.43$) [3]. Therefore, germanates are the host candidate in the search for phosphors with reasonable conductivity. The stoichiometric formula of germanates M$\text{RGe}_2\text{O}_7$ (where M = Al$^{3+}$, Ga$^{3+}$ or Fe$^{3+}$ and R = rare-earth ion) was reported in the early 1980s to belong to the monoclinic AlNdGe$_2$O$_7$ structure type [4–6], space group $P2_1/c$ (no. 14). These kinds of compounds are of great interest in laser crystal physics; for instance, the incorporation of R$^{3+}$ activators into single-centered hosts up to full substitution of all cations gives the possibility of obtaining the so-called self-activated crystals, and the oxygen coordination around rare-earth cations is only ninefold (CN9). The luminescence study of a series of such compounds provides a lot of valuable information for optical applications. We have found the Tb$^{3+}$ and Tm$^{3+}$ ions in LaAlGe$_2$O$_7$ present intense green and blue light emissions, respectively [7,8]. In this investigation, the Pr$^{3+}$-doped LaAlGe$_2$O$_7$ samples were prepared using a solid-state reaction. The phases, the morphologies and the photoluminescent properties of LaAlGe$_2$O$_7$: Pr$^{3+}$ were studied.
2. Experimental

Trivalent Pr-doped LaAlGe2O7 samples were synthesized by a vibrating milled solid-state reaction. The starting materials were La2O3, GeO2, Al2O3, and Pr6O11 (purity $\geq$99.99%). After they had been mechanically activated by grinding in a high-energy vibro-mill, the mixtures were calcined at 1250°C in air for 12 h. The heat treatment powders were then fired under a reducing atmosphere (4% H2/96% Ar) at 800°C for 2 h to convert Pr4+ to Pr3+ in order to obtain higher emission intensity. This reduction process improved the emission intensity by about 20%.

Conventional X-ray diffraction (XRD) techniques were employed to identify the phases. Both excitation and luminescence spectra of these phosphors were recorded on a Hitachi F-4500 fluorescence spectrophotometer using a 150 W Xe lamp as a source at room temperature. The surface morphology was examined by high-resolution scanning electron microscopy (HR-SEM, S4200, Hitachi). Optical absorption spectra were measured at room temperature using a Hitachi U-3010 UV-visible spectrophotometer. An integrating sphere is suitable for absorbance measurement of a turbid sample and reflection measurement of a solid sample surface. The integrating sphere attachment is used for measuring our samples.

3. Results and discussion

The XRD data of the samples reveals a single-phase without any impurity; all of the peaks were identified to be the monoclinic LaAlGe2O7 phase (space group $P2_1/c$). The lattice parameters of the extensive substitution of Pr3+ for La3+ in (La1-xPrx)AlGe2O7 (0 $\leq$ x $\leq$ 0.3) estimated from the XRD data are shown in Fig. 1. Clearly, the structure shrinks gradually along the a, b and c axes as the Pr3+ concentrations increase. It was recognized that a slight difference in the ionic radius between La3+ ($r_{\text{La}} = 1.216$ Å) and Pr3+ ($r_{\text{Pr}} = 1.179$ Å) ions resulted in a small difference in the lattice parameter of the solid solution. A linear relationship holds between the lattice constants of the monoclinic structure and the amount of Pr3+ ions. This is direct experimental evidence of the fact that the crystal can be assigned to the structural nature of the LaAlGe2O7 phase, and an indication that the Pr3+ ions were satisfactorily substituted for the La3+ ions in the lattice.

The LaAlGe2O7 powders doped with Pr3+ ions at concentrations from 0.05 to 30 mol% do not significantly affect morphology. The SEM images reveal that the particles are irregularly shaped, with sizes between 1 and 6 μm.

Fig. 2 shows the emission spectra obtained by excitation with a wavelength of around 448 nm. For all samples under investigation, the spectrum mainly consists of manifolds arising from the emission of the $^3P_0$ state to the $^3H_{4,5,6}$ and $^3F_2$ states, in the visible region near 487, 530, 610 and 644 nm, respectively. Additionally, a very weak peak was observed around 600 nm, corresponding to the transition $^{1}D_{2} \rightarrow ^{3}H_{4}$. Emission from the $^{1}D_{2}$ level was more difficult to obtain, because the multi-phonon relaxation is not very efficient. The energy gap of about 4000 cm$^{-1}$ between the $^{1}P_{0}$ and the next lower lying level, the $^{1}D_{2}$, is larger than the low-phonon energy of the host lattice. The approximate frequencies of the highest-energy phonons in germanate
and aluminate are 900 and 950 cm\(^{-1}\), respectively [9,10].

With this phonon frequency, more than four phonons needed to bridge the energy gap between the \(^3P_0\) and \(^1D_2\) levels is much less likely to be significant [11,12]. This supposition is supported by the weakness of \(^1D_2\) luminescence.

The intensity of the \(^1D_2\) emission was more sensitive to the doping concentration than that caused by \(^3P_0\) transitions. The effects of the concentration of \(^1D_2\)\(\rightarrow\)^3H\(_4\) transition behavior of \(\text{La}_{1-x}\text{Pr}_x\text{AlGe}_2\text{O}_7\) as a function of \(x\) under excitation at 448 nm are illustrated in Fig. 3. As can be seen, samples with various Pr\(^{3+}\) content had different relative emission intensity between the \(^1D_2\)\(\rightarrow\)^3H\(_4\) and \(^3P_0\)\(\rightarrow\)^3H\(_{5,6}\), \(^3F_2\) transitions. It is obvious that the emission intensity of \(^1D_2\)\(\rightarrow\)^3H\(_4\) transition drops sharply as the Pr\(^{3+}\) concentration increases. This phenomenon has been attributed to cross-relaxation between neighboring Pr\(^{3+}\) ions [13]. Cross-relaxation is the process whereby excitation energy from an ion decaying from a highly excited state promotes a nearby ion from the ground state to the metastable level. In trivalent praseodymium, the energy gap between the \(^1D_2\) and \(^1G_4\) levels approaches that between the \(^3H_4\) and \(^3F_4\) levels, and the energy gap between the \(^1D_2\) and \(^3F_4\) levels is close to that between the \(^3H_4\) and \(^1G_4\) levels. As a result, at sufficiently high Pr\(^{3+}\) concentrations, the population of the metastable state may be increased by the decay of an ion from the \(^1D_2\) level and the consequent promotion of a nearby ion from the ground state. Using this mechanism, the following cross-relaxation may occur [14,15]

\[
\begin{align*}
\text{Eq. 1:} & \quad ^1D_2 (\text{Pr}^{3+} \text{I}) + ^3H_4 (\text{Pr}^{3+} \text{II}) \rightarrow ^1G_4 (\text{Pr}^{3+} \text{I}) + ^3F_4 (\text{Pr}^{3+} \text{II}), \\
\text{Eq. 2:} & \quad ^1D_2 (\text{Pr}^{3+} \text{I}) + ^3H_4 (\text{Pr}^{3+} \text{II}) \rightarrow ^3F_4 (\text{Pr}^{3+} \text{I}) + ^1G_4 (\text{Pr}^{3+} \text{II}).
\end{align*}
\]

The emission from the \(^1D_2\) level is strongly dependent on the interaction between two nearby Pr\(^{3+}\) ions so that the distance between Pr\(^{3+}\) ions decreases as the Pr\(^{3+}\) concentration increases; subsequently, cross-relaxation become more frequent.

All excitation spectra of \(\text{LaAlGe}_2\text{O}_7: \) Pr\(^{3+}\) monitored from \(^3P_0\)\(\rightarrow\)^3H\(_{4,5,6}\), \(^3F_4\) and \(^1D_2\)\(\rightarrow\)^3H\(_4\) transitions are similar. No wavelength shift or peak for a new site has been observed for various concentrations. This suggests a good possibility of only one local Pr\(^{3+}\) environment existing, because different centers will have different excitation and emission spectra. The result is consistent with preliminary investigations of the LnAlGe\(_2\text{O}_7\)-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 [4–6]. Fig. 4 depicts the...
excitation spectra of Pr\(^{3+}\) in LaAlGe\(_2\)O\(_7\) at room temperature, which were obtained by monitoring emission at 487 nm (\(\text{Pr}^{3+} \rightarrow \text{Pr}^{4+}\)). The sharp excitation peaks between 440 and 500 nm are assigned to the typical 4\(f^2\) \(\rightarrow\) 4\(f^2\) forbidden transitions of Pr\(^{3+}\). The peaks at 448, 473 and 487 correspond to \(\text{Pr}^{4+} \rightarrow \text{Pr}^{5+}\), \(\text{Pr}^{4+} \rightarrow \text{Pr}^{6+}\), and \(\text{Pr}^{4+} \rightarrow \text{Pr}^{7+}\) transitions, respectively. A different phenomenon is noticed by comparing with the conventional Pr\(^{3+}\)-doped oxide phosphors, particularly noteworthy is that no obvious 4\(f\) \(\rightarrow\) 5\(d\) transition band of Pr\(^{3+}\) ions or host absorption band could be detected in the excitation spectra. This phenomenon is uncommon, because the typical Pr\(^{3+}\)-activated oxide phosphors always show strong 4\(f\) \(\rightarrow\) 5\(d\) transition band absorption around 200–330 nm [16–18].

The value of the 4\(f\) \(\rightarrow\) 5\(d\) energy level for the free Pr\(^{3+}\) ion is located near 61 000 cm\(^{-1}\) (~164 nm). The position of the 4\(f\) \(\rightarrow\) 5\(d\) levels is greatly influenced by the crystal field interaction. This effect is known as the crystal field depression of the 5\(d\) level, and consequently the host crystal depresses 4\(f\) \(\rightarrow\) 5\(d\) energy levels for all lanthanides [18]. Additionally, when the lowest 4\(f\) \(\rightarrow\) 5\(d\) levels are above the \(1\text{S}_0\) state of Pr\(^{3+}\), the \(1\text{S}_0\) state is situated at 46 500 cm\(^{-1}\) (~215 nm) [19]. Nevertheless, transitions from the \(1\text{S}_0\) state were not detected. Hence, it is unlikely that the 4\(f\) \(\rightarrow\) 5\(d\) energy level of Pr\(^{3+}\) is located at the VUV region (~50 000 cm\(^{-1}\), <200 nm) in LaAlGe\(_2\)O\(_7\). The 4\(f\) \(\rightarrow\) 5\(d\) transitions have been observed easily if Ce\(^{3+}\), Pr\(^{3+}\) or Tb\(^{3+}\) are the activators. The Ce\(^{3+}\)-doped LaAlGe\(_2\)O\(_7\), however, is similar to LaAlGe\(_2\)O\(_7\): Pr\(^{3+}\), in which the 4\(f\) \(\rightarrow\) 5\(d\) transition was not detected in emission and excitation measurements even though a strongly reducing atmosphere was applied. Information on the 4\(f\) \(\rightarrow\) 5\(d\) transition of the Tb\(^{3+}\)-doped LaAlGe\(_2\)O\(_7\) has been reported before [7]. The excitation spectra showed only intense f–f transitions of Tb\(^{3+}\) ions around the near-UV region, while the remarkably weak 4\(f\) \(\rightarrow\) 5\(d\) transition band of the Tb\(^{3+}\) ion around 235 nm could be detected. The corresponding transition energy of 4\(f\) \(\rightarrow\) 5\(d\) levels of all lanthanide ions is always constant, independent of the type of host. The same phenomenon holds for Pr\(^{3+}\)-doped compounds, where the 4\(f\) \(\rightarrow\) 5\(d\) transition is usually located at a 1500 cm\(^{-1}\) lower energy than that when using Tb\(^{3+}\) as dopant [18]. This predicts the 4\(f\) \(\rightarrow\) 5\(d\) absorption band for Pr\(^{3+}\) in LaAlGe\(_2\)O\(_7\) at about 245 nm. Inspecting the data on the Pr\(^{3+}\)-doped LaAlGe\(_2\)O\(_7\), one observes that the 4\(f\) \(\rightarrow\) 5\(d\) transition band is not observed in emission and excitation measurements.

Fig. 5 displays the absorption spectra of the LaAlGe\(_2\)O\(_7\) and LaAlGe\(_2\)O\(_7\): Pr\(^{3+}\) at room temperature. The absorption spectrum of the LaAlGe\(_2\)O\(_7\): Pr\(^{3+}\) is analogous to that of the excitation spectrum between 440 and 500 nm. In the spectrum, three relatively well-resolved peaks associated with transitions from the ground \(3\text{H}_4\) to the \(3\text{P}_{0,1,2}\) and \(1\text{I}_6\) excited states are present. The peak at 595 nm is associated with the ground \(3\text{H}_4\) level and the excited \(1\text{D}_2\) level. It shows that the samples do not contain Pr\(^{4+}\) or other optical impurities.

The UV-vis optical absorption spectrum of LaAlGe\(_2\)O\(_7\) demonstrated that the absorption bands correspond to the UV region at 215 and 300 nm, respectively. The broad absorption band located at about 300 nm is ascribed to the defects in the germanate host. The major absorption edge of pure LaAlGe\(_2\)O\(_7\) is situated at around 250 nm (~4.96 eV). After praseodymium was added to LaAlGe\(_2\)O\(_7\), the compounds still exhibited a strong broad host absorption band. Inspecting the absorption spectra on the Pr\(^{3+}\)-doped LaAlGe\(_2\)O\(_7\) in detail, however, one observes that there is a slight absorption variation at the host absorption edge. The position of the 4\(f\) \(\rightarrow\) 5\(d\) absorption band is assumed to be situated at 245 nm. This value is in good agreement with our experiment. However, there is no transition assigned to the host or 4\(f\) \(\rightarrow\) 5\(d\) absorption in the excitation spectrum. These two absorption bands are considerably different from the excitation spectrum of LaAlGe\(_2\)O\(_7\): Pr\(^{3+}\) (Fig. 4). This suggests that there are two kinds of absorption mechanisms: one (440–500 nm) resulted in luminescence, but the other (190–350 nm) did not.
Such a mismatch in the wavelength pattern is because the absorption spectrum is detected primarily by the numbers of occupied states in the ground level and the numbers of unoccupied states not only in the excited level but also on the transition probability. Nevertheless, excitation spectra represent a convolution of the absorption spectra with the quantum efficiency at that excitation wavelength. A comparison between doped and undoped LaAlGe$_2$O$_7$ samples indicates that the strong host absorption completely dominates at less than 250 nm. As previously mentioned, it has been shown that the corresponding 4f–5d transition of Pr$^{3+}$ is to be situated at 245 nm. It might be acceptable that the 4f–5d absorption band is obscured by the host lattice absorption band, so that the radiationless 4f–5d transition occurred. The absence of 4f–5d luminescence in LaAlGe$_2$O$_7$: Pr$^{3+}$ or Ce$^{3+}$ has been ascribed to quenching by photoionization [20,21], which implies that the lowest 5d level of Pr$^{3+}$ lies in the conduction band of the host crystal. The principle is illustrated in Fig. 6. In the excited state, an electron can be easily be ionized from the center to the conduction band and may recombine nonradiatively with a hole, so that the luminescence is quenched. In this case, the excitation/absorption spectra of LaAlGe$_2$O$_7$: Pr$^{3+}$ will not reveal its location. By analyzing absorption and excitation spectra, it is realized that only direct excitation of Pr$^{3+}$ ions could be observed and no efficient energy transfer occurs between Pr$^{3+}$ and the host lattice in LaAlGe$_2$O$_7$. All energy absorbed by the host which is not emitted as radiation is dissipated to the crystal lattice (nonradiative transitions). The nonradiative transitions can be interpreted on the basis of the configuration-coordinate model [22]. The nonradiative processes may compete with the emission process. There are, however, also nonradiative processes which favor a high-light output, which ensure a more effective feeding of the luminescent activator or population of the emitting level.

LaAlGe$_2$O$_7$: Pr$^{3+}$ shows remarkably intense f–f absorption, even if the 4f–5d transition for luminescence is limited. With excitation by 448 nm blue light, most of the emission is situated at 487 nm, showing prominent and bright blue-greenish white light. The luminescence intensity of phosphor materials is always dependent on the doping concentration. A series of La$_{1-x}$Pr$_x$AlGe$_2$O$_7$ samples were synthesized as the dopant concentration ranged from $x = 5 \times 10^{-4}$ to 0.3. Fig. 7 presents the luminescent intensity of the $^3P_0 \rightarrow ^3H_4$ transition in terms of Pr$^{3+}$ concentration in (La$_{1-x}$Pr$_x$)AlGe$_2$O$_7$ powders. The most efficient PL intensities occurred at a Pr$^{3+}$ content of $x = 0.01$ in the system (La$_{1-x}$Pr$_x$)AlGe$_2$O$_7$. The drop in intensity as the Pr$^{3+}$ content increased (concentration quenching effect) is caused by the rise in nonradiative decay channels, which is promoted by the interaction with quenching centers during the energy transfer processes among Pr$^{3+}$ ions. The probability of energy transfer is inversely proportional to $R^n$, where $R$ is the distance between the activator ions and $n$ is an integer [22,23]. It is thus possible to obtain the critical distance ($R_c$) from the concentration quenching data. $R_c$ is the critical separation between donor (activator) and acceptor (quenching site), for which the nonradiative transfer rate equals the internal decay rate. Blasse [24] assumed that for the critical concentration the average shortest distance between nearest activator ions is equal to the critical distance. The LaAlGe$_2$O$_7$ contains a unique crystallographic site available for the activator (substitute for La$^{3+}$), so that only one type of center is present. Therefore, we can obtain the critical distance from the concentration quenching data using the following equation:

$$R_c = 2 \left( \frac{3V}{4\pi x_c N} \right)^{1/3},$$

(3)

Fig. 6. Schematic energy band diagram of Pr$^{3+}$ energy levels in LaAlGe$_2$O$_7$ energy band. Photo-excitation to 4f–5d (arrow) may be followed by photoionization.

Fig. 7. The dependence of Pr$^{3+}$ emission intensity of $^3P_0 \rightarrow ^3H_4$ transition with Pr$^{3+}$ concentrations in (La$_{1-x}$Pr$_x$)AlGe$_2$O$_7$ under excitation at 448 nm. The signals were detected at 487 nm.
where $x_c$ is the critical concentration of the activator ion (Pr$^{3+}$ in the present system), $N$ is the number of La$^{3+}$ ions in the LaAlGe$_2$O$_7$ unit cell (activator ions are assumed to be introduced solely into La$^{3+}$ sites), and $V$ is the volume of the unit cell ($545.45 \times 10^{-30}\text{m}^3$ in this case). The critical concentration was estimated to be about 1 mol% for Pr$^{3+}$, where the emission intensity measured begins to decrease quickly. Using the above equation, the calculated $R_c \approx 29.6\text{Å}$.

4. Conclusions

Pr$^{3+}$-activated LaAlGe$_2$O$_7$ was synthesized and its luminescence properties were investigated. In response to excitation from 448 nm blue light, the emission spectra involved a major part of $^3\text{P}_0 \rightarrow ^3\text{H}_J$ transitions. The quenching of the $^1\text{D}_2$ level and its strong concentration dependence was observed for LaAlGe$_2$O$_7$: Pr$^{3+}$ and was attributed to cross-relaxations between Pr$^{3+}$ ions. Concentration quenching was also observed in relation to the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ emission, but is less pronounced than that related to the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ emission. In the photoluminescence excitation spectra, only the intense f-f transitions could be found, while no obvious 4f–5d transition band of Pr$^{3+}$ ions or host absorption band could be detected. The absence of 4f–5d luminescence in this host is ascribed to photoionization. In Pr$^{3+}$-doped LaAlGe$_2$O$_7$, the absorption spectra were different from the excitation spectra near room temperature, suggesting that there were two kinds of absorption mechanisms: one resulted in luminescence but the other did not.

Acknowledgements

The authors thank the National Science Council of the Republic of China for financially supporting this research through contract no. NSC-94-2216-E-006-009.

References