Synthesis and Luminescence of Lu₃(Al,Si)₅(O,N)₁₂:Ce³⁺ Phosphors

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ABSTRACT

Si⁴⁺−N⁴⁻ was incorporated into Ce³⁺-doped lutetium aluminum garnet (Lu₃₋ₓCeₓAlₓ₂₋ₚSi₅₋ₚO₁₂₋ₚNₓ (Lu,Ce)AG:xSN). For 0.0 ≤ x ≤ 0.25, the synthesized powders consisted of the LuAG single phase, and the lattice constant decreased owing to the smaller Si⁴⁺ ions. However, for x > 0.25, a small amount of unknown impurity phases was observed, and the lattice constant increased. Under 450 nm excitation, the PL spectrum of LuAG:Ce³⁺ exhibited the green band, peaking at 505 nm. The incorporation of Si⁴⁺−N⁴⁻ into the Al³⁺−O²⁻ sites of LuAG:Ce³⁺ led to a red-shift of the emission peak wavelength from 505 to 570 nm with increasing x. Corresponding CIE chromaticity coordinates varied from the green to yellow regions. These behaviors were discussed based on the modification of the 5d¹ split levels and crystal field surroundings of Ce³⁺, which arose from the Ce−(O,N)8 bonds.

Key words : Lutetium aluminum garnet, Phosphors, Luminescence, Nitridation

1. Introduction

Solid-state lightings (SSLs) have attracted great attention because of their high luminous efficiency, long lifetime, energy-saving potential, etc. One of the prevailing SSL technologies is a phosphor-conversion white light-emitting diode (pc-WLED), which uses a phosphor blend to convert blue or near-ultraviolet light emitted from LED chips into white light. The most popular phosphor materials are nitrides, silicates, aluminates, and phosphates.¹⁻⁵

In addition, Ce³⁺-doped R₃Al₅O₁₂ garnet systems have been recognized as effective phosphors for use in pc-LEDs combined with blue chips. For example, yttrium aluminum garnet (Y₃Al₅O₁₂:Ce³⁺, YAG:Ce³⁺)⁶⁻¹⁰ and terbium (Tb₃Al₅O₁₂:Ce³⁺, TAG:Ce³⁺)ⁱ¹⁻¹⁵ are commercially used as yellow phosphors. Recently, Ce³⁺-doped lutetium aluminum garnet (Lu₃Al₅O₁₂:Ce³⁺, LuAG:Ce³⁺) was reported to have a value of thermal quenching lower than that of YAG:Ce³⁺; it is also commercially used as a green phosphor alternative to Eu²⁺-doped β-sialon for high-power pc-WLEDs.⁹⁻¹¹,¹⁵⁻²⁰

LuAG has 160 atoms in a cubic cell (space group: Ia₃d). The Lu and O atoms occupy 24 and 96 sites, respectively, and each Lu atom is coordinated by eight oxygen atoms in a distorted cube. Al atoms occupy two non-equivalent sites, 16 octahedral and 24 tetrahedral.¹¹ The photoluminescence excitation (PLE) spectra of the LuAG:Ce³⁺ powders consist of strong (~ 450 nm) and weak (~ 345 nm) peaks, which are assigned to the electrons excited from the ground state (4f doublet to the 5d¹ state of the Ce³⁺ ions).⁸,¹⁹,²² Corresponding photoluminescence (PL) spectra show single emission bands in the green region, which are the result of the two overlapping subbands assigned to the ⁵D → ⁵F₂, ⁵F₄ transitions of the Ce³⁺ ions.¹⁵⁻²⁰

For the YAG:Ce³⁺ powders, the effects of the incorporation of Si⁴⁺−N²⁻ on the luminescence have been reported in many earlier studies,⁵⁻¹³ whereas there are only a few works in the literature that consider LuAG:Ce³⁺.⁶⁻⁹ Even though the phase formation and the PL (PLE) spectra of LuAG:Ce³⁺ doped with Si⁴⁺−N²⁻ has been the subject of earlier studies, those studies are still lacking in certain aspects: there is very little information on the phase formation for large amounts of Si⁴⁺−N²⁻ or investigation into the PL (PLE) spectra assigned to Ce−(O,N)₈ bonds. In this work, we prepared LuAG:Ce³⁺ powders and investigated the effects of Si⁴⁺−N²⁻ incorporation on the phase formation and the luminescence.

2. Experimental Procedure

Lu₃₋ₓCeₓAlₓ₂₋ₚSi₅₋ₚO₁₂₋ₚNₓ (Lu,Ce)AG:xSN powders were prepared by a solid-state reaction process using Lu₂O₃ (99.99%, Solvay), Al₂O₃ (99.99%, High Purity Chemicals), α-Si₃N₄ (Ube Industry, Ltd., E10, 99.9%), and CeO₂ (99.99%, Grand Chemical & Materials) as starting materials. 2 wt% AlF₃ (95%, Junsei) flux was added to the starting mixtures, and the relative amounts of AlF₃ and Al₂O₃ were calculated to maintain a stoichiometric Al content. The starting mixtures were ball-milled for 24 h and synthesized at 1700°C for 7 h under a hydrogen (5% H₂ + 95% N₂) atmosphere.

The crystal structure was determined using an X-ray diffractometer (XRD, PANalytical, XPert Powder) with CuKα radiation (λ = 1.5406 Å). Rietveld refinement was performed...
indicating that Ce is partly substituted for the Al sites, of the YAG lattices, resulting in an expansion of the unit cell. An SEM micrograph of the powder prepared with powder was too small to be exactly measured. Nevertheless, we were able to confirm that nitrogen ions were incorporated into the LuAG lattices. It was most probable that the Si ions are located in the centers of tetrahedra and octahedra, respectively, but the site occupancy factor of the Si ions at the Al sites is unclear at this stage. On the other hand, further increase to $x = 0.5$ led to the formation of an impurity phase (marked with *) owing to the solubility limit for Si. Wang et al. also reported similar results for $Y_{1-x}Al_{x}Si_{12-N_x}N_xCe^{3+}$, in which an impurity phase was produced for $x > 0.39$. Liu et al. demonstrated that Si–N could be fully dissolved into the LuAG:Ce $^{3+}$ lattices up to $x = 0.27$; this finding is nearly consistent with our results. The nitrogen content in the (Lu, Ce)AG:SN powders was measured using an oxygen and nitrogen analyzer. We were able to obtain the nitrogen content $[N (%) = 0.884]$ for $x = 0.1$, but not for the other samples. It can be inferred from these findings that the nitrogen content in the powders was too small to be exactly measured. Nevertheless, we were able to confirm that nitrogen ions were incorporated into the LuAG lattices, because the effects of nitrogen atoms on the PL spectra were evident (this will be explained during the discussion of the PL and PLE spectra).

3. Results and Discussion

The XRD patterns of the (Lu,Ce)AG:SN ($x = 0, 0.1, 0.25, 0.5$, and $1.0$) powders are shown in Fig. 1(a). For $x = 0-0.25$, the patterns correspond to those of ICSD #98-002-3846, indicating that Ce$^{3+}$, Si$^{4+}$, and N$^-$ ions were fully incorporated into the LuAG lattices. It was most probable that the Si$^{4+}$ ($r = 0.26 \AA$ for CN = 4, $r = 0.4 \AA$ for CN = 6) and N$^-$ ions ($r = 1.46 \AA$) were substituted for the Al$^{3+}$, Al$^{3+}$ ($r = 0.39 \AA$ for CN = 4, $r = 0.535 \AA$ for CN = 6) and O$^2-$ ions ($r = 1.38 \AA$), respectively. As a result, positive $Si_{Al}^{3+}$ and negative $N_{O}^{3-}$ defects were created simultaneously and compensated for each other to maintain the charge neutrality. As described above, the Al$^{3+}$ ions are located in the centers of tetrahedra and octahedra, respectively, but the site occupancy factor of the Si$^{4+}$ ions at the Al$^{3+}$ sites is unclear at this stage. On the other hand, further increase to $x = 0.5-1.0$, the XRD peak shifts inversely towards lower diffraction angles, and the lattice constant slightly increases. It is possible that this behavior can be attributed to the incorporation of a part of the Si ions into the interstitial sites of LuAG. Zhang et al. also reported the same phenomenon for $Y_{1-x}Al_{x}Si_{12-N_x}N_xCe^{3+}$ powders; they speculated that for $x \geq 0.3$, the Si$^{4+}$ ions can occupy the interstitial sites, as well as the substitutional sites, of the YAG lattices, resulting in an expansion of the unit cell. An SEM micrograph of the powder prepared with $x = 0.25$ is shown in Fig. 1(c). The particle size is in the range of approximately 1 - 2.5 $\mu$m, while the particle morphology was nearly independent of the $x$ values.

The PLE and PL spectra of the LuAG:0.035Ce$^{3+}$ powders are shown in Fig. 3. The PLE spectrum is composed of two excitation bands, peaking at 345 nm and 450 nm, respectively; these spectra are assigned to the characteristic transition from the ground state ($d_F$) doublet ($^{2}F_{7/2}$ and $^{2}F_{5/2}$) to the excitation levels ($5d$) of the Ce$^{3+}$ ions. Under 450 nm

Fig. 1. (a) XRD patterns, (b) enlarged XRD patterns of the (Lu,Ce)AG:SN powders ($x = 0, 0.1, 0.25, 0.5$, and $1.0$), and (c) SEM micrograph for $x = 0.25$. Using X′Pert HighScore Plus (Ver. 4.1). The nitrogen and oxygen contents of the powders were measured using a nitrogen/oxygen analyzer (HORIBA EMGA-920). The PL spectra were measured using a PL system (PSI, Darsa-5000) with a 500 W xenon lamp as an excitation light source.

Fig. 2. Lattice constant of the (Lu,Ce)AG:SN powders as a function of $x$. Such firing temperatures, flux, Ce$^{3+}$ concentration, etc.$^{9}$ The difference in ionic size between Si$^{4+}$ and Al$^{3+}$ ($6r = 0.13$ and $0.135 \AA$ for CN = 4 and 6, respectively) was larger than that between N$^-$ and O$^2-$ ($6r = 0.08 \AA$), leading to a shrinkage of the unit cell of LuAG. In addition, the Si$^{4+}$–N$^-$ bonds (1.685 - 1.76 \AA in SiN) are shorter than the Al$^{3+}$–O$^2-$ bonds (1.761 \AA in LuAG), which resulted in lattice shrinkage as well.\(^{5,10,11,12}\) Accordingly, upon increasing $x$ to 0.25, the main peak moves towards higher diffraction angles (Fig. 1(b)), and the lattice constant gradually decreases, as shown in Fig. 2. However, for $x = 0.5-1.0$, the XRD peak shifts inversely towards lower diffraction angles, and the lattice constant slightly increases. It is possible that this behavior can be attributed to the incorporation of a part of the Si$^{4+}$ ions into the interstitial sites of LuAG. Zhang et al.$^{10}$ also reported the same phenomenon for $Y_{1-x}Al_{x}Si_{12-N_x}N_xCe^{3+}$ powders; they speculated that for $x \geq 0.3$, the Si$^{4+}$ ions can occupy the interstitial sites, as well as the substitutional sites, of the YAG lattices, resulting in an expansion of the unit cell. An SEM micrograph of the powder prepared with $x = 0.25$ is shown in Fig. 1(c). The particle size is in the range of approximately 1 - 2.5 $\mu$m, while the particle morphology was nearly independent of the $x$ values.

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excitation, an asymmetrical emission spectrum was obtained in the green region (515 nm); this was the result of two overlapping subbands (dotted lines, centered at 507 and 546 nm, respectively), which can be assigned to the $^2D \rightarrow ^2F_{5/2}$ and $^2D \rightarrow ^2F_{7/2}$ transitions of the Ce$^{3+}$ ions, respectively.

Normalized PL emission spectra of the (Lu,Ce)AG:$x$SN powders are shown in Fig. 4(a). With increasing $x$, the full width at half maximum (FWHM) of the band gradually increases from 96 to 122 nm, and the dominant peak wavelength (DPW) shifts from 515 to 555 nm (red-shift), leading to an increase in the Stokes shift from 2805 to 4204 cm$^{-1}$. Increasing $x$ values led to a decrease in the emission intensity, as shown in Fig. 4(b). Corresponding CIE (Commission Internationale de l’Éclairage) chromaticity coordinates are shown in Fig. 5. These coordinates move from the green to yellow regions with increasing $x$; they are (0.3493, 0.5727), (0.3658, 0.5658), (0.3847, 0.5512), (0.3847, 0.5496), and (0.4093, 0.5319) for $x = 0$, 0.1, 0.25, 0.5, and 1.0, respectively. It is inferred from these findings that the (Lu,Ce)AG:$x$SN powders have a potential for use in warm pc-WLEDs with high color rendering index (CRI).

It is obvious that the aforementioned spectral evolution of the (Lu,Ce)AG:$x$SN powders can be attributed to the incorporation of Si$^{4+}$-$N^3-$ into the Al$^{3+}$-$O^2-$ sites of LuAG. These behaviors can be explained based on those of YAG:Ce$^{3+}$, because the crystal structures of LuAG and YAG are nearly the same. For the Y$_{3}$Al$_{5-x}$Si$_{x}$O$_{12}$:$N_{x}$:Ce$^{3+}$ powders, earlier works in the literature have described the effects of the incorporation of Si$^{4+}$-$N^3-$ into the YAG:Ce$^{3+}$ lattices differently. For example, some studies have reported that nitrogen was not detected in the synthesized powders, despite the addition of Si$_3$N$_4$. As a result, negative defects of were created to compensate for the three positive defects of , leading to a blue-shift of the DPWs, which is attributable to a change in the crystal field surroundings of the Ce$^{3+}$ ions. On the other hand, other studies have confirmed the presence of Si$^{4+}$-$N^3-$ bonds, which were found to cause a red-shift of the DPWs.

To verify the origin of the asymmetrical broadening and the red-shift of the emission band of the (Lu,Ce)AG:$x$SN powders, the emission spectrum ($\lambda_{ex} = 450$ nm) of the powders prepared with $x = 1.0$ was fitted using the Gaussian peak function, as shown in Fig. 6(a). The spectrum was split into three bands of (I), (II), and (III) centered at approximately 501, 545, and 597 nm, respectively. Increasing $x$ values led to a decrease in the emission intensity, as shown in Fig. 4(b). Corresponding CIE (Commission Internationale de l’Éclairage) chromaticity coordinates are shown in Fig. 5. These coordinates move from the green to yellow regions with increasing $x$; they are (0.3493, 0.5727), (0.3658, 0.5658), (0.3847, 0.5512), (0.3847, 0.5496), and (0.4093, 0.5319) for $x = 0$, 0.1, 0.25, 0.5, and 1.0, respectively. It is inferred from these findings that the (Lu,Ce)AG:$x$SN powders have a potential for use in warm pc-WLEDs with high color rendering index (CRI).

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energy tails were observed in the range of 500–550 nm, and their intensities were found to increase with increasing x values, as shown in Fig. 6(b). The synthesized powders were activated by the wavelength of 520 nm belonging to the low energy tails; the PL spectra are shown in Fig. 6(c). The position and shape of the PL spectra for x = 0.25–1.0 evidently correspond to those of the band (II) in Fig. 6(a). For x = 0.1, the emission intensity at 597 nm rapidly drops; it is not observed for the LuAG:Ce³⁺ powders (x = 0). It was obvious from these findings that the band (III) and the low energy tail of the PLE spectrum were correlated with each other, and that they can be attributed to the incorporation of Si⁺⁺–N⁰ into the Al³⁺–O²⁻ sites. The fact that the intensity of the low energy tail increases with increasing x values is a crucial piece of evidence for this speculation. These behaviors coincided with those in the earlier studies for Y₃Al₅O₁₂:N₃:Ce³⁺,⁹,¹¹,¹³ and (Lu,Co)AG:Si₃N₄.¹⁶ The addition of Si₃N₄ led to the local substitution of nitrogen ions for oxygen ions, which created two kinds of crystal field surroundings of the Ce³⁺ ions, Ce–O₈ and Ce–(O,N)₈ bonds. The latter have higher covalency and polarizability than the former, and the electronegativity of N⁰ (~3.0) is lower than that of O²⁻ (~3.4). As a result, the Ce–(O,N)₈ bonds enhanced the crystal field strength and lowered the centroid energy of the 5d¹ split levels of the Ce³⁺ ions. The Ce–O₈ bond gave rise to the characteristic PLE and PL spectra of LuAG:Ce³⁺. On the other hand, the Ce–(O,N)₈ bonds caused extra 5d¹ split levels of the Ce³⁺ ions, whose lowest excited level is closer to the ground state than is the lowest excited level of the Ce–O₈ bond. This, in turn, resulted in low energy tails of the PLE spectra and the band (III) in the red region. In addition to the effects of local nitridation, it was probable that the substitution of the Si⁺⁺ ions for the Al³⁺ ions also contributed to the red-shift of the DPWs. The incorporation of smaller Si⁺⁺ ions distorted the cubic structure of LuAG and increased the degree of the crystal asymmetry, leading to an increase in the crystal field splitting.

Previous works have reported that the thermal stability of LuAG:Ce³⁺ was very high,¹⁶,¹⁹ being comparable to nitride phosphors.²,⁴,⁵ Liu et al. reported that the incorporation of Si⁺⁺–N⁰ rarely affected the thermal stability up to 150°C, irrespective of the x values.¹⁹

4. Conclusions

(Lu,Co)AG:Si₃N₄ powders were prepared with the addition of Si₃N₄ to LuAG:Ce³⁺. XRD data confirmed that Si⁺⁺–N⁰ was fully incorporated into the LuAG lattices for x = 0–0.25, resulting in a decrease in the lattice constant because the Si⁺⁺ ions were smaller than the Al³⁺ ions. However, for x > 0.25, the lattice constant slightly increased because of the incorporation of a part of the Si⁺⁺ ions into the interstitial sites of LuAG.

The incorporation of Si⁺⁺–N⁰ into the Al³⁺–O²⁻ sites of (Lu,Co)AG:Si₃N₄ resulted in a red-shift of the DPWs and low energy tails of the PLE spectra, leading to a migration of the CIE chromaticity coordinates from the green to yellow regions. These behaviors were attributed to the Ce–(O,N)₈ bonds, which modified the 5d¹ split levels and crystal field surroundings of the Ce³⁺ ions. These findings demonstrate that the (Lu,Co)AG:Si₃N₄ powders have potential for use in warm pc-WLEDs with high CRI.

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