Green Light-Excitable Ce-Doped Nitridomagnesoaluminate Sr[Mg₂Al₂N₄] Phosphor for White Light-Emitting Diodes

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Efficiency in the conversion of electrical energy to light has been a paramount consideration in the search and development of energy-saving alternatives to conventional incandescent bulbs. Phosphor-converted white light-emitting diodes (pc-WLEDs) have emerged as a promising technology to revolutionize modern day lighting. This technology ensures energy-efficiency and improves color rendition and luminous efficacies.

A novel class of nitride of groups III and IV has been reported to have remarkable luminescence properties with Eu²⁺ as activator. These remarkable intense emissions ascribed to the 4F⁰(7F)⁵d transitions are manifested in the entire range of the visible spectrum. These new and structurally related phosphor materials offer a robust platform toward red-emitting phosphors and thus provide an opportunity to improve color rendition of pc-LEDs. These newly reported narrow-band red phosphors result in high color rendition and significantly increased luminous efficacies.

GPS is a simple approach toward the development and upscale phosphor synthesis. The Sr₁₋ₓ[MgₓAl₃N₄]:Ce³⁺ series was prepared from all-nitride (Sr₃N₂, Mg₃N₃, AlN, and CeN) precursors were loaded in Mo crucibles prior to sintering at 1450 °C for 4 h under 0.9 MPa N₂ atmosphere. Varying the amount of Ce³⁺ from x = 0.005−0.08 yielded a light pink colored product that emitted yellow light under UV (Figure S1). The synthesized phosphor correlated very well with CSD-425321 (Figure S2). Rietveld refinement revealed that almost all the peaks except for those of AlN (wt. ~12.3%) were in a tetragonal crystal system with I₄/m (No. 87) space group (Figure 1a). The crystallographic data of

Sr₃N₂, Mg₃N₃, AlN, and CeN were connected together by common edges and corners, thereby generating a highly condensed disordered framework, where the cation site is in the middle of vierer² ring channels along [001] and forms a cubic coordination environment. The cubic site in this class of nitride phosphors offers an opportunity for narrow-band emission that has huge advantages for practical applications. New phosphors are developed through several strategies, including chemical unit cosubstitution which has been successfully employed in finding new solid-state materials. Herein, we report a yellow-emitting Ce-doped Sr[Mg₂Al₂N₄] phosphor synthesized using all-nitride starting materials via gas pressure sintering (GPS). Its application as a component of a pc-LED package fabricated through a unique configuration is a promising approach to generate white light.

Supporting Information

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Sr$_{0.985}$Mg$_2$Al$_2$N$_4$:Ce$_{0.015}$ reveal $a = 8.17648(8)$ and $c = 3.35754(4)$ Å parameters (Table S1), which are comparable to the SrMg$_2$Al$_2$N$_4$ prepared using a radiofrequency synthetic approach (Table S2). Occupancies of Mg$^{2+}$ and Al$^{3+}$ ions were refined with the assumption that the sum of their occupancies is equal to 1. The concentration of Ce$^{3+}$ in the Sr$^{2+}$ site was not refined but was fixed according to the chemical formula due to its relatively small value. Refinement gave low $R$-factors (Table S1), and the coordinates of atoms and main bond lengths are shown in Tables S3 and S4. The elemental ratio of the elements from the EDS data (Figure S3) is in good agreement with the sum of their occupancies.

In the crystal structure (Figure 1d), disordered (Mg/Al)N$_4$ forms strands of edge-sharing tetrahedral that creates a network of (Mg/Al)N$_4$ tetrahedra, and Sr$_2^+$ ions are found in every second nitrogen coordinated cuboid site. This cuboid coordination site is a feature of UC$_x$Cr$_3$O$_7$ structures that distinctly give rise to a 3D-network of (Mg/Al)N$_4$ tetrahedra, and Sr$^2+$ in Sr$_2$(Mg$_2$Al$_2$N$_4$)$_3$ shares this structural similarity with other nitridolithoaluminates. Figure 1b and 1c show the high-resolution transmission electron microscopy (HRTEM) image and corresponding select area electron diffraction (SAED) pattern of Sr$_{0.985}$Mg$_2$Al$_2$N$_4$:Ce$_{0.015}$, respectively. However, careful control of TEM conditions allows the structure to remain intact under the electron beam for up to 10 min. The distinct lattice fringes of 0.57 nm in Figure 1b corresponds to the (110) planes of the tetragonal structure. The AlN minor phase was also detected, but its structure is different (Figure S3).

Sr$_{0.985}$Mg$_2$Al$_2$N$_4$:Ce$_{0.015}$ reveals new electronic transitions. The photoluminescence excitation (PLE) and photoluminescence (PL) measured at room temperature are shown in Figure 2a,b, consist of a broad band with two emission maxima of similar intensities, due to the transitions from the lowest 5d level to $^2$F$_{7/2}$ and $^2$F$_{5/2}$ states of the ground electronic configuration (4f). The Ce$^{3+}$ replaces the Sr$^{2+}$ and is 8-fold coordinated by nitrogen forming a cuboid-like polyhedron. This is similar to Ce$^{3+}$ replacing Y$^{3+}$ in Y$_3$Al$_5$O$_{12}$ (YAG), where the crystal field causes the splitting of the 5d electronic manifold into the lower doubly degenerate $^4$E state and higher triply degenerate $^2$T$_2$ state. The electron–lattice interaction diminishes additionally the energy of the $^2$E electronic manifold that results in the appearance of homogeneously broadened luminescence band related to 5d$^1$($^2$F$_{7/2}$, $^2$F$_{5/2}$) transitions; black squares, maxima of PLE band (4f$^1$→5d$^1$) position under different pressures. (e) Decay curves of Sr$_{0.985}$Mg$_2$Al$_2$N$_4$.

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variable crystal field strength causes variable energy of the emitting $^2E$ state and the further broadening of the emission band. This effect is corroborated in contrast by the narrow emission bands of the ordered UC$_3$C$_4$-type, such as Sr[LiAl$_3$N$_4$], Ca[LiAl$_3$N$_4$], or Sr[Mg$_3$SiN$_4$].$^{1,2,4}$ It should be noted that the inhomogeneous broadening is responsible for narrowing of the luminescence bands seen after 460 nm excitation (Figure S4c). Only a part of the Ce$^{3+}$ ions is excited that causes the narrowing of the luminescence band. The internal quantum efficiency, IQE (Figure S5) of $\sim$35% for $x = 0.015$ ($\lambda_{exc} = 510$ nm) is the best in the series. The phosphor retains $\sim$65% of its original intensity at 150 °C (Figure S6).

The effect of pressure on the luminescence behavior of phosphors is a strategy to evaluate its luminescence dynamics and behavior. Increasing pressure causes the red shift of the PLE and PL spectra, whereas spectral profiles are not significantly altered. The PL spectra were decomposed into two Gaussian bands (which have the same widths), which are related to the transition from the $^2d^1$ ($^2E$) excited state to the $^2F_{7/2}$ and $^2F_{5/2}$ states of the ground electronic configuration $4f^3$ of Ce$^{3+}$ (Figure 2c). The positions of the peaks versus pressure are shown in Figure 2d. The energetic distance between $^2F_{5/2}$ and $^2F_{7/2}$ slightly decreases under pressure. However, after releasing the pressure, the emission spectrum reverts to its original position. The decay curves of Sr$_{0.985}$[Mg$_2$Al$_2$N$_4$]:Ce$^{3+}$ ($x = 0.015$) under different pressure condition are shown in Figure 2e reveals that under pressure become multiexponential with the appearance of faster components. In contrast to the luminescence line shape after releasing the pressure, the decay profile differs from that observed before the application of pressure, and the decay time is shorter which is accounted for by pressure-induced appearance of new channels of nonradiative deactivation. Further, the Ce L$_3$-edge XANES standard spectra indicate that Ce$^{3+}$ and Ce$^{4+}$ coexist in Sr[Mg$_3$Al$_2$N$_4$] although higher Ce$^{3+}$/Ce$^{4+}$ is noted at lower x values. XANES at the Ce L$_3$-edge involves the electronic transition from Ce 2p to outermost shell 4f5d6s level and has been widely used to study the electronic configurations of Ce.$^{11}$ Hence, more Ce$^{3+}$ exists when concentration is $x = 0.02$ than when $x$ is more. This behavior accounts for the observed higher intensity emission and the optimum Ce$^{3+}$ loading.

The Sr$_{0.985}$[Mg$_2$Al$_2$N$_4$]:Ce$^{3+}$ was used to generate white LED (Figure 3b), as employed in a package using a prefabricated blue chip LED and $\beta$-SiAlON as green phosphor. By varying the relative amount (by wt) of $\beta$-SiAlON and Sr$_{0.985}$[Mg$_2$Al$_2$N$_4$]:Ce$^{3+}$, one can tune the white light (Table S4, Figure S8). The stepwise coating of the blue chip with the green phosphor ($\beta$-SiAlON) then the Sr[Mg$_3$Al$_2$N$_4$]:Ce$^{3+}$ (Figure 3a) took into consideration the latter’s more effective excitation by green light. This assembly circumvented the usual three-phosphor LEDs excited by the blue chip to generate white light (Figure 3b). In the configuration of the LED package (Figure 3b), the blue LED was allowed to excite the $\beta$-SiAlON:Eu$^{3+}$ in the package, which results in the production of green light emission. Consequently, this green light excited Sr$_{0.985}$[Mg$_3$Al$_2$N$_4$]:Ce$^{3+}$, exhibiting its yellow emission. This broad emission of the Sr$_{0.985}$[Mg$_3$Al$_2$N$_4$]:Ce$^{3+}$ spans up to the longer wavelength region (red), thereby covering a wider range in the visible spectrum thus, enabling the generation of white light (inset, Figure 3c). This configuration provides an opportunity for the application of the Ce$^{3+}$-doped Sr[LiAl$_3$N$_4$] phosphor toward the generation of white light (CIE $x = 0.3522$, $y = 0.3279$, correlated color temperature = 4595 K, $R_g = 61$, efficacy = 20 lm/W) in a two-component pc-LED package (Table S5).

In conclusion, we prepared a Ce$^{3+}$-doped nitridomagnesoluminate Sr[Mg$_2$Al$_2$N$_4$] phosphor from all-nitride precursors using GPS. The phosphor is effectively excitable by green light (510 nm). Homogeneous and inhomogeneous broadening is responsible for appearance of broad luminescence that cover the spectral region from 500 to 700 nm with maximum emissions at 580 and 620 nm. Pressure-dependent luminescence results show the significant red shift of the luminescence and excitation bands (equal to 14 cm$^{-1}$/kbar) and reveal the presence of additional pathway for nonradiative deactivation. The Sr$_{0.985}$[Mg$_3$Al$_2$N$_4$]:Ce$^{3+}$$^{5+}$ phosphor retained $\sim$65% of its intensity at 150 °C. With a blue LED excitable pc-LED package, where it is coated on top of the $\beta$-SiAlON:Eu$^{3+}$-coated blue LED chip and white light with CCT = 4595 K and $R_g = 61$ with 20 lm/W efficacy was generated. This Ce$^{3+}$-doped phosphor demonstrates how it can substitute for the emission of two phosphors. With its green-excitible property, the sequential coating rather than mixing the phosphors enables the generation of white light.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b03442.

Experimental details; crystallographic data; LED package performance; crystal structure; SXRD; photoluminescence; quantum efficiency; TEM, SAED and SEM images; electroluminescence, mechanism (PDF)

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Notes
The authors declare no competing financial interest.

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