

Near UV Excited Line and Broad Band Photoluminescence of an Anion-Ordered Oxyfluoride

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Received November 12, 2009; E-mail: tvogt@mailbox.sc.edu

Photoluminescence (PL) has a broad range of applications such as industrial and residential lighting using fluorescent and light emitting diode (LED) based technologies, cathode ray tubes, and field-emission displays.¹ White light can be made by mixing blue light from an LED with light in the yellow part of the visible spectrum made by a phosphor down-converting part of the blue light. The first such white light LED combined the blue light of a InGaN device emitting near 460 nm which excited a cerium doped YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$) phosphor to emit yellow light.^{2,3} Another approach in creating white light is to use a near UV LED producing light near 400 nm and down-converting it using a white emitting phosphor blend with blue, green and red emitting components. A family of anion ordered oxyfluorides with the general composition $\text{Sr}_{3-x}\text{A}_x\text{MO}_4\text{F}^{4,5}$ (with $\text{A} = \text{Ca}, \text{Ba}$ and $0 \leq x \leq 1$ and $\text{M} = \text{Ga}_{1-z}\text{Al}_z$ and $0 \leq z \leq 1$) show line emission when doped with rare-earth activators.⁶ Doping Eu^{3+} into $\text{Sr}_3\text{AlO}_4\text{F}$ results in red PL when excited near 300 nm due to the dominant $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} at 619 nm. A related compound $\text{Sr}_{2.8}\text{Eu}_{0.1}\text{Na}_{0.1}\text{AlO}_4\text{F}$ also shows red PL at 618 nm assigned to the same transition.⁷ Chen et al.⁸ explored the tunable UV- and cathodoluminescence properties of another member of this family, $\text{Sr}_{3-2x}\text{Ce}_x\text{Na}_x\text{GaO}_4\text{F}$. We have recently shown that members of the $\text{Sr}_{3-x}\text{A}_x\text{MO}_4\text{F}$ ($\text{A} = \text{Ca}, \text{Ba}$ and $0 \leq x \leq 1$ and $\text{M} = \text{Ga}_{1-z}\text{Al}_z$ and $0 \leq z \leq 1$ and $\text{Al}_w\text{In}_{1-w}$ and $0 \leq w \leq 0.1$) family can be transformed into self-activating UV-excitable PL phosphors with broad-band PL by controlling their defect structure using appropriate postsynthesis reduction conditions.⁹ The partial substitution of Al in the lattice by In shifts the excitation spectrum to near 400 nm making these materials potentially useful phosphors for solid state lighting for $\text{In}_x\text{Ga}_{1-x}\text{N}$ -based LEDs (see Figure 2a).

Samples of $\text{Sr}_{2.85}\text{Eu}_{0.1}\text{Al}_{1-z}\text{In}_z\text{O}_4\text{F}$ ($z = 0, 0.01, 0.1$) were prepared by heating the appropriate amounts of SrCO_3 (Alfa 99%), SrF_2 (Alfa 99%), Al_2O_3 (Alfa 99.95%), Eu_2O_3 (Alfa 99.9%), and In_2O_3 (Alfa 99.9%) at 1050 °C in air. The as-made samples were annealed at 900 °C for 1 h under a reducing atmosphere using 5% $\text{H}_2/95\%$ Ar. The pressure of 5% $\text{H}_2/95\%$ Ar gas was fixed at 10 psi and a needle valve was used to control the flow rates. A 500 mL flask connected to the tube furnace was used to collect the reducing gas which finally passed through a bubbler, which had a ~1 in. diameter filled with ethylene glycol (3.5 in. height). The reducing gas flow rates were controlled by counting the bubbles per seconds as indicated in Figure 2a and 2c. Phase purity was established using a MiniFlex (Rigaku) diffractometer (Cu $\text{K}\alpha$ radiation). The excitation and emission spectra of the phosphor materials were measured using a spectrofluorometer (Fluorat-02-Panorama).

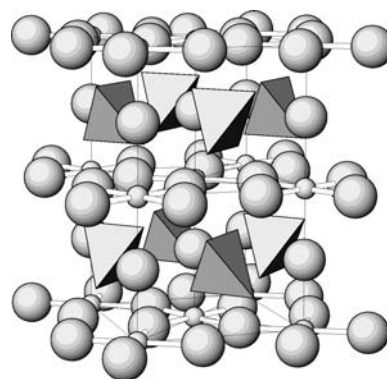


Figure 1. Structure of $\text{A}_3\text{MO}_4\text{F}$ with $\text{A} = \text{Sr}_{1-x}, \text{Ca}_x, \text{Ba}_x$ ($0 \leq x \leq 1$) and $\text{M} = \text{Ga}_{1-z}\text{Al}_z$ ($0 \leq z \leq 1$) and $\text{Al}_{1-w}\text{In}_w$ ($0 \leq w \leq 0.1$) revealing the stacked $(\text{A})_2\text{F}_3^{3+}$ and $\text{A}(\text{1})\text{MO}_4^{3-}$ layers.

Figure 1 depicts the crystal structure of $\text{A}_3\text{MO}_4\text{F}$ with $\text{A} = \text{Sr}_{1-x}, \text{Ca}_x, \text{Ba}_x$ ($0 \leq x \leq 1$), $\text{M} = \text{Ga}_{1-z}\text{Al}_z$ ($0 \leq z \leq 1$) and $\text{Al}_{1-w}\text{In}_w$ ($0 \leq w \leq 0.1$) revealing the stacked $(\text{A})_2\text{F}_3^{3+}$ and $\text{A}(\text{1})\text{MO}_4^{3-}$ layers of these anion-ordered oxyfluorides. The A cations occupy two different sites, A(1) and A(2) as shown in Figure 1. The A(1) cation has a bicapped square antiprismatic 10-fold coordination, with eight oxygens forming the square antiprism and two fluorines providing the capping ($\text{A}(\text{1})\text{O}_8\text{F}_2$), while the A(2) cations are located in a smaller and distorted 8-fold coordination environment, with two fluorines and six oxygens near neighbors ($\text{A}(\text{2})\text{O}_6\text{F}_2$). Optical activators can be substituted into both coordination environments, and PL emissions from the two sites will be at different wavelengths. Prodjosantoso et al.⁵ showed that in $\text{Sr}_{3-x}\text{A}_x\text{AlO}_4\text{F}$ ($\text{A} = \text{Ca}, \text{Ba}$ and $0 \leq x \leq 1$) Ba^{2+} cations, which are larger than Sr^{2+} ions, will be substituted into the 10-fold A(1) site, while the smaller Ca^{2+} cations will go into the 8-fold coordinated A(2) site. Eu^{3+} ions in an 8-fold coordination environment are smaller than Sr^{2+} cations (1.07 Å vs. 1.26 Å), and we therefore propose that they are located in the A(2) site. Note that a formula such as $\text{Sr}_{2.85}\text{Eu}_{0.1}\text{Al}_{1-z}\text{In}_z\text{O}_4\text{F}$ takes into account the different charges on the cation sites.

When defects are created in this family of materials by exposing them to a 5% $\text{H}_2/95\%$ Ar reducing gas atmosphere, materials with $\text{A} = \text{Sr}, \text{Ca}, \text{Ba}$ and $\text{M} = \text{Al}, \text{Ga}$ will when excited in the far-UV near 250 nm show broad-band PL emissions centered at 500 nm while those with $\text{A} = \text{Sr}, \text{Ca}, \text{Ba}$ and $\text{M} = \text{Al}, \text{In}$ excited in the near-UV close to 400 nm will show broadband PL emissions located near 600 nm. In both cases the emissions have a spectral width of ~90 nm (fwhm).

Figure 2a reveals that $\text{Sr}_{3.0}\text{Al}_{0.9}\text{In}_{0.1}\text{O}_{4-\alpha}\text{F}_{1-\delta}$ made by exposing $\text{Sr}_{3.0}\text{Al}_{0.9}\text{In}_{0.1}\text{O}_4\text{F}$ to a reducing environment creates a material that is self-activating and has a broad-band PL centered near 605 nm.

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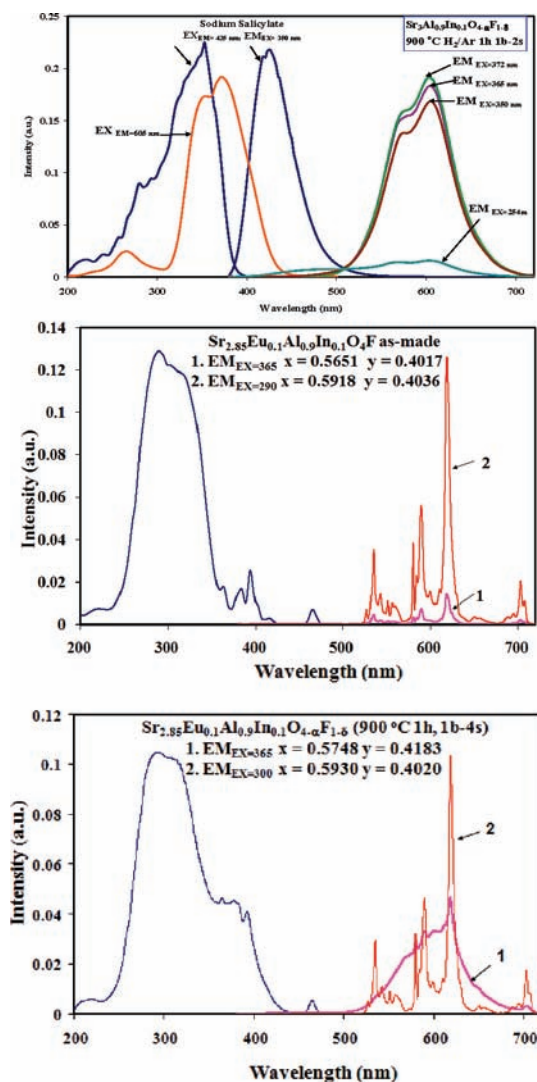


Figure 2. Excitation and emission spectra of (a) Sr₃Al_{0.9}In_{0.1}O_{4-α}F_{1-δ} (b) as-made Sr_{2.85}Eu_{0.1}Al_{0.9}In_{0.1}O₄F excited by 290 and 365 nm UV light and (c) of Sr_{2.85}Eu_{0.1}Al_{0.9}In_{0.1}O_{4-α}F_{1-δ} excited by 300 and 365 nm UV-light. The reducing conditions of (a) and (c) give the reducing temperature and 5% H₂/95% Ar gas flow conditions as described in the text. For (b) and (c) the Commission Internationale de l'Éclairage (CIE) color coordinates are given.

Sodium salicylate is shown as a comparison and used to approximate a quantum efficiency of ~70%. Figure 2b and 2c compare the PL excitation and emission spectra of as-made Sr_{2.85}Eu_{0.1}Al_{0.9}In_{0.1}O₄F with the one of Sr_{2.85}Eu_{0.1}Al_{0.9}In_{0.1}O_{4-α}F_{1-δ} made by reducing the former at 900 °C with a reducing gas flow rate of 1 bubble/4 s. One observes that the emission spectrum of Sr_{2.85}Eu_{0.1}Al_{1-x}In_xO₄F excited with 290 nm UV (curve 2 Figure 2b) light reveals a dominant ⁵D₀ → ⁷F₂ transition at 619 nm as well as weaker peaks between 500 and 600 nm assigned to ⁵D₁ → ⁷F₂, ⁵D₀ → ⁷F₀, ⁵D₁ → ⁷F₃, and ⁵D₀ → ⁷F₁. At 365 nm very little photoluminescence is observed (curve 1 Figure 2b).

After reducing Sr_{2.85}Eu_{0.1}Al_{1-x}In_xO₄F to Sr_{2.85}Eu_{0.1}Al_{0.9}In_{0.1}O_{4-α}F_{1-δ} the significant increase of the intensity in the excitation spectrum near 400 nm results in a broad-band photoluminescence emission at 600

nm while the strong line emission from the main Eu³⁺ energy terms at 619 nm is still visible (curve 1 Figure 2c). We therefore suggest that Eu³⁺ is present and continues to act as an activator. While the broad-band emission centered at 590 nm if excited with near-UV light at 365 nm is prominent, it disappears when 300 nm light is used. However, the same material displays the dominant transitions assigned to the Eu³⁺ activator when activated at 300 nm (curve 2 Figure 2c). Exciting Sr_{2.85}Eu_{0.1}Al_{0.9}In_{0.1}O_{4-α}F_{1-δ} with near-UV light at 365 nm reveals thus both a broad-band PL due to self-activation of the Sr₃Al_{1-x}In_xO₄F lattice and a line PL due to the Eu³⁺ activator. The changes in the excitation spectra can also be related to the defects created in the host lattice as Figure 2a shows.

The Commission Internationale de l'Éclairage (CIE) *x* and *y* coordinates of the emitted light indicate that the addition of the Eu³⁺ activator shifts the emission into the red part of the visible light. This is an often desired property for LED phosphors since it results in a “warmer” white light. Zukauskas et al.⁹ derived a solution to the minimal number of primary emitters and their peak wavelengths and bandwidths required for white light with optimal quality. One optimized approach was a trichromatic solution with two wide-band (fwhm 110 nm) emitting green and yellow phosphors centered at 496 and 608 nm respectively, supplemented with a narrow-band red (fwhm ≈ 10 nm) phosphor located at 659 nm. By doping a Eu³⁺ line emitter at 619 nm (⁵D₀ → ⁷F₂ transition) into a self-activating broad-band emitting yellow phosphor centered at 600 nm we can combine two of these requirements in one material, albeit with a line PL not at the optimal wavelength. Nevertheless, Sr_{2.85}Eu_{0.1}Al_{0.9}In_{0.1}O_{4-α}F_{1-δ} comes close to such a phosphor. However, its biggest drawback is its rather high reflectance, low absorption in the near-UV region, and low quantum efficiency approximated to be near 70%. Issues regarding the long-term stability of such phosphors with oxyfluoride-based host lattices also need to be explored. One attractive feature of the general approach outlined above is that only a single rare-earth activator, namely Eu³⁺, is required to make white light. The ubiquitous use of rare earths in established and emerging technologies for magnets, glass polishing, catalysis, ceramic pigments, phosphors, and magnetic refrigeration will create resource shortages.¹⁰ Research in cathodoluminescent properties of this class of oxyfluorides has shown that these materials might be candidates for field-emission displays.⁸

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JA909486J