Combinatorial Synthesis and Screening of Cerium Doped Garnet Phosphors for Application in White GaN-based LEDs

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ABSTRACT

A combinatorial approach has been used to generate solid state thin-film of different garnet structures \((A_{1-x}B_x)_{1-z}(C_{1-x}D_x)_{5/3}O_{12}:Ce^{3+}\) (called libraries), where \(A, B = Y, Gd, Lu, La; C, D = Al, Ga, Sc; x and y = 0 to 1.0; and z = 0.03\). X-ray diffraction was used to select library samples of the crystalline garnet phase. Combinatorial chemistry methods were used as a tool to rapidly synthesize and screen potential inorganic phosphors for use as blue to yellow conversion phosphors in white LEDs. Libraries of these various garnets were then characterized spectroscopically. Emission and excitation trends are reported for various libraries and were found to reproduce previous trends in literature. Lattice constants, chromaticity, and PL intensity are also examined as a function of the different compositions. Emission and excitation trends reveal that as larger cations are substituted for the \(Y\) (dodecahedral) site in YAG, emission and excitation are red-shifted and as larger cations are substituted for the \(Al\) (octahedral and tetrahedral) site, emission and excitation are blue-shifted. If smaller ions are substituted for those respective sites an opposite trend is observed.

Keywords: White LEDs, garnet, cerium, YAG, luminescence, combinatorial chemistry

1. INTRODUCTION

With the availability of blue InGaN light emitting diodes (LEDs), there has been increasing interest in the development of luminescence converting phosphors for application in white LEDs. In such devices, a blue InGaN LED acts as the primary light source, serving as an efficient pump to excite photoluminescence in a phosphor with subsequent emission occurring at lower energies1-5, cf., Figure 1. The combination of blue light from the LED chip and emission from the phosphor(s) produces white light. Solid state LED lamps offer a number of advantages over incandescent bulbs, halogen bulbs, and other lamps, including improved reliability and exceptionally long lifetime (~100,000 h).

![Figure 1. Structure of a GaN-based white light emitting diode using YAG:Ce³⁺ as a conversion phosphor.](http://proceedings.spiedigitallibrary.org/proceedings/resource/10712/0277-786X/01/$15.00)
The emission of Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ (YAG:Ce) is well-suited for conversion phosphor applications. When properly mixed the yellow emission under blue-light excitation yields white light$^{2,3}$. The energy level scheme for YAG:Ce is illustrated in Figure 2. Trivalent cerium has a 4f$^1$5d$^0$ configuration; the ground state consists of $^2$F$_{5/2}$ and $^2$F$_{7/2}$ terms separated by approximately 2200 cm$^{-1}$. For the free ion, the 5d electron of the excited 4f$^1$5d$^1$ configuration forms a $^2$D level split into $^2$D$_{3/2}$ and $^2$D$_{5/2}$ states by spin-orbit coupling. Electronic structure and optical properties of Ce$^{3+}$ ions doped in YAG crystals are determined by the 4f and 5d electronic levels split by the spin-orbit interaction and the crystal field of D$_{2h}$ symmetry. The two lowest-lying 5d states are associated with strong absorption bands at 340 nm and 460 nm in YAG:Ce$^{3+}$. After excitation, subsequent broad double band luminescence into the $^5$F$_{5/2}$ ground state and the split-off $^5$F$_{7/2}$ state occurs under the emission of green (520 nm) and yellow/orange (580 nm) photons, respectively. The excitation and emission properties of YAG:Ce$^{3+}$ have been well examined$^{6,7}$. It is known that substitution of Gd$^{3+}$ and Ga$^{3+}$ for Y$^{3+}$ and Al$^{3+}$, respectively, in the garnet host shifts the emission of YAG:Ce$^{3+}$ so that different shades of white light can be realized$^{2-5}$. The addition of the larger ion Gd$^{3+}$ for Y$^{3+}$ red-shifts YAG:Ce$^{3+}$ emission and substitution of Ga$^{3+}$ for Al$^{3+}$ tends to blue shift the characteristic yellow emission.

Our work employs combinatorial chemistry as a tool to rapidly generate libraries of garnet phosphors to examine the spectral trends in phosphors for application in blue to yellow conversion LEDs. Combinatorial methods for luminescent materials discovery have been used previously by several groups$^{8-11}$. Various garnets of the formula, A$_{3-x}$B$_x$C$_{5-y}$D$_y$O$_{12}$:Ce$^{3+}$, where A, B = Y, Gd, Lu, La; C, D = Al, Ga, Sc; x and y = 0 to 1.0; and a Ce concentration of 1.0 mol% were synthesized and characterized. Trends in PL intensity, excitation and emission spectra, lattice constants, as well as chromaticity were studied as a function of composition across the garnet libraries.

![Energy levels of Ce$^{3+}$ (4f$^1$) in Y$_3$Al$_5$O$_{12}$ (YAG). The two lowest 5d states are associated with absorption bands at 340 nm and 460 nm. Upon excitation, broadband luminescence into the $^5$F$_{5/2}$ ground state (520 nm emission) and the split-off $^5$F$_{7/2}$ state (580 nm emission) occurs.](http://proceedings.spiedigitallibrary.org/)

**2. EXPERIMENTAL**

The thin film garnet libraries were prepared from solution precursors of Y, Gd, Lu, La, Al, Ga, Sc, B and Ce and deposited on silicon wafers using methods developed at Symyx Technologies$^{12}$. These metal precursor solutions were synthesized and then dispensed in the desired ratios in 96-well microtiter plates. Volumes of 2.50 µL were then transferred in a predetermined library design onto silicon wafers, Figure 3. Multiple libraries were synthesized with stoichiometries of (A$_1$, B$_{x}$)$_y$(C$_{5-y}$D$_y$)$_5$O$_{12}$:Ce$^{3+}$ with $x = y = 0$ to 1.0 and a constant Ce$^{3+}$ dopant concentration of 1 mol%. The A/B site of the garnet contained Y, Gd, Lu, or La, while the C/D site was a combination of Al, Ga, Sc, or B. Along the x-axis of a library, element B is substituted in 10 % increments for element A such that the first column of the library is pure A, the second column is 90 % A and 10 % B, the third column is 80 % A and 20 % B, until finally the last column is pure B. This same substitution ratio is used down the y-axis where D is substituted for C; the ratio of C:D is constant along each row of the library. These libraries were processed in air at temperatures from 900°C to 1100°C for 8 hours.
The combinatorial libraries were characterized using a high throughput screen that illuminated the library with blue light to rapidly screen for potential hits. A Ushio 200 W Hg/Xe lamp was used for illumination together with bandpass filters of 430, 450, and 465-nm (FWHM=25-35 nm) for phosphor excitation. Emitted light from the libraries was collected through a 505-nm long wave pass filter to block the reflected blue source light and imaged onto a charge-coupled device (CCD) through a macro lens, Figure 4. After screening of the libraries, detailed emission and excitation spectra were collected by fluorimetry, Figure 5.
3. RESULTS AND DISCUSSION

In a previous study\textsuperscript{13}, we showed that YAG:Ce\textsuperscript{3+} could be synthesized using solution chemistry techniques in thin-film library format and that its properties matched that of a bulk-synthesized YAG phosphor powder. We further demonstrated that compounds of the formula (Y\textsubscript{1-x}Gd\textsubscript{x})\textsubscript{3-z}(Al\textsubscript{1-y}Ga\textsubscript{y})\textsubscript{5}O\textsubscript{12}:Ce\textsuperscript{3+}\textsubscript{z}, where x and y range from 0 to 1.0 and z is equal to 1 mol\%, could be synthesized in a solid state thin-film array and that their excitation and emission properties are in agreement with earlier reports in the literature for Gd\textsuperscript{3+} and Ga\textsuperscript{3+} substituted YAG \textsuperscript{[2,4,5]}. These findings indicated that combinatorial techniques were effective in qualitatively evaluating the luminescence properties of blue to yellow luminescence conversion phosphors for application in white LEDs. Here we have further extended this work and examine the spectral trends of several new libraries using the combinatorial synthesis and screening.

The high throughput screen for Gd\textsubscript{3-x}Lu\textsubscript{x}Al\textsubscript{5-y}B\textsubscript{y}O\textsubscript{12}:Ce at 430, 450, and 465 nm excitation is shown in Figure 6, and the associated emission and excitation data in Figure 7. Figures 8 to 18 show the high throughput screens and emission/excitation maxima for 1 mol% cerium doped Y\textsubscript{3-x}Lu\textsubscript{x}Al\textsubscript{5-y}B\textsubscript{y}O\textsubscript{12}, Y\textsubscript{3-x}Gd\textsubscript{x}Al\textsubscript{5-y}B\textsubscript{y}O\textsubscript{12}, Y\textsubscript{3-x}La\textsubscript{x}Al\textsubscript{5-y}Ga\textsubscript{y}O\textsubscript{12}, and Y\textsubscript{3-x}La\textsubscript{x}Al\textsubscript{5-y}Sc\textsubscript{y}O\textsubscript{12}, respectively. Figure 18 shows the excitation and emission trends for Y\textsubscript{3-x}Gd\textsubscript{x}Al\textsubscript{y}Ga\textsubscript{y}O\textsubscript{12}:Ce, were the high throughput screen was previously report\textsuperscript{13}. The high throughput screens of the A\textsubscript{3-x}B\textsubscript{x}C\textsubscript{5-y}D\textsubscript{y}O\textsubscript{12}:Ce garnet libraries reveal changes in luminescence intensity due to compositional variations. The most intense elements of a library are dependent on the excitation wavelength. This is observed in many of the libraries, but is readily apparent in Figure 12. Using a row/column notation (row, column), element (4,1) is the most intense at 430-nm excitation, but as the excitation wavelength is increased, note that the surrounding elements close in composition to element (1,1) have increased in intensity relative to that of (4,1). At 465-nm excitation, element (1,1) is now the brightest element of the library.

Taken together, the data from all the libraries reveal several key points. At 465-nm excitation, YAG:Ce still has the largest observed relative PL intensity. However, as the excitation shifts to lower wavelengths, Ga and Sc-substituted elements increase in relative intensity, especially noting elements (2,1) through (5,1) for Ga and Sc substituted libraries, cf., Figures 12, 14 and 16. This composition ranges from 10 to 40% substitution of Ga or Sc for Al in YAG. The most intense garnet compositions from those libraries were identified and were then synthesized in bulk to compare bulk and thin-film trends. A closer examination of their spectroscopic properties of those compositions will be reported in a future publication\textsuperscript{14}. 

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Figure 5. Schematic of the fluorescence spectrometer used to measure library excitation and emission profiles. Xe: xenon lamp. XM: excitation monochromator (SPEX 1680 double monochromator). S: sample. EM: emission monochromator (SPEX 1680 double monochromator). PMT: photomultiplier tube (photon counting Hamamatsu R928HA PMT with a Pacific Instruments AD-126 amplifier/discriminator and Model 126 photometer). Source compensation was performed by post-referencing against Rhodamine B in ethylene glycol.

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Figure 6. Digital images from the high throughput screen of Gd$_{3-x}$Lu$_x$Al$_{5-y}$B$_y$O$_{12}$:Ce library (above) along with histograms of the measured luminescent intensities at excitations of a) 430-nm, b) 450-nm and c) 465-nm.

Figure 7. a) Excitation and b) emission maxima from various compositions of Gd$_{3-x}$Lu$_x$Al$_{5-y}$B$_y$O$_{12}$:Ce library samples.
Figure 8. Digital image from the high throughput screen of $Y_{3-x}Lu_xAl_{5-y}B_yO_{12}:Ce$ library (above) along with a histogram of the corresponding relative luminescent intensities from 450-nm excitation. The 430 and 465-nm images (not shown) are similar.

Figure 9. a) Excitation and b) emission maxima from various compositions of $Y_{3-x}Lu_xAl_{5-y}B_yO_{12}:Ce$ library samples.

Figure 10. Digital image from the high throughput screen of $Y_{3-x}Gd_xAl_{5-y}B_yO_{12}:Ce$ library (above) along with a histogram of the corresponding relative luminescent intensities from 465-nm excitation. The 430 and 450-nm images (not shown) are similar.
Figure 11. a) Excitation and b) emission maxima from various compositions of Y$_{3-x}$Gd$_x$Al$_{5-y}$B$_y$O$_{12}$:Ce library samples.

Figure 12. Digital images from the high throughput screen of Y$_{3-x}$Lu$_x$Al$_{5-y}$Ga$_y$O$_{12}$:Ce library (above) along with histograms of the measured luminescent intensities at excitations of a) 430-nm, b) 450-nm and c) 465-nm.
Figure 13. a) Excitation and b) emission maxima from various compositions of $Y_{3-x}Lu_xAl_{5-y}Ga_yO_{12}:Ce$ library samples.

Figure 14. Digital images from the high throughput screen of $Y_{3-x}Gd_xAl_{5-y}Sc_yO_{12}:Ce$ library (above) along with histograms of the measured luminescent intensities at excitations of a) 430-nm, b) 450-nm and c) 465-nm.

Figure 15. a) Excitation and b) emission maxima from various compositions of $Y_{3-x}Gd_xAl_{5-y}Sc_yO_{12}:Ce$ library samples.
Figure 16. Digital images from the high throughput screen of $Y_{3-x}La_xAl_{5-y}Ga_yO_{12}:Ce$ library (above) along with histograms of the measured luminescent intensities at excitations of a) 430-nm, b) 450-nm and c) 465-nm.

Figure 17. a) Excitation and b) emission maxima from various compositions of $Y_{3-x}La_xAl_{5-y}Ga_yO_{12}:Ce$ library samples.
X-ray diffraction data confirm that as larger cations are substituted for A and C in the garnet lattice, the d-spacing increases—effectively showing that the lattice constants are increasing and that substitutions are occurring in this thin-film combinatorial approach. Figure 19a shows the lattice constant changes for the first six rows of a $\text{Y}_{3-x}\text{Gd}_x\text{Al}_{5-y}\text{Ga}_y\text{O}_{12}:\text{Ce}$ library. As expected, the lattice expands as increasing moles of Gd and Ga are substituted in YAG:Ce for Y and Al, respectively. In contrast, the lattice constant shrinks with the addition of Lu and B into the host; this is evidenced in a $\text{Y}_{3-x}\text{Lu}_x\text{Al}_{5-y}\text{B}_y\text{O}_{12}:\text{Ce}$ library, cf., Figure 19b. It should be noted that some Gd and Lu rich compounds when substituted in YAG, as well as > 50% substitution of Sc and B resulted in two-phase materials.

Data show that emission shifts are not purely a function of ionic radii; the emission maximum clearly depends on the crystalline site and degree of host lattice substitution. Along with shifting peak emission, $\lambda_{\text{ex,max}}$ decreases as larger cations are substituted in the Al site of YAG, while substitution in the Y site slightly increases $\lambda_{\text{ex,max}}$. The opposite is true when smaller cations are substituted in those respective garnet sites. Figure 20 shows a CIE plots of the various garnet libraries synthesized, illustrating the range of colors we can achieve through appropriate substitution in the garnet lattice. This covers colors ranging from dark green to red-orange.
Figure 20. CIE chromaticity coordinates corresponding to emission from $A_{3-x}B_xC_5D_yO_{12}:Ce$ garnet libraries.
4. CONCLUSIONS

The thin-film combinatorial approach to synthesizing and characterizing luminescence conversion phosphors allows for the rapid generation and screening of potential new luminescence conversion phosphors for application in white LEDs. The high throughput screen allows for characterization of an entire library at multiple excitation wavelengths. Relative PL intensity data show that amongst the garnet libraries of the format (A$_{1-x}$B$_x$)$_3$(C$_{1-y}$D$_y$)$_5$O$_{12}$:Ce$_{3+}$, where A, B = Y, Gd, Lu, La; C, D = Al, Ga, Sc; x and y = 0 to 1.0; and z = 0.03, B, Lu, and La appear to decrease overall light output of the samples. Samples ranging from Y$_3$Al$_4$D$_0.5$O$_{12}$:Ce to Y$_3$Al$_3$D$_2$O$_{12}$:Ce where D = Ga or Sc exhibit properties suitable for white lighting applications where wavelengths between 430 and 450 nm are desired. YAG:Ce appears to be well suited for applications using longer blue wavelengths (~470 nm). Emission and excitation trends reveal that as larger cations are substituted for the Y site in YAG, emission and excitation are red-shifted and as larger cations are substituted for the Al site, emission and excitation are blue-shifted. If smaller ions are substituted for those respective sites an opposite trend is observed. For the various garnet substitutions studied, peak excitation wavelengths from 415 to 465 nm and emission maxima from 480 to 590 nm are achievable. The ability to color tune and shift the excitation wavelength based on compositional variations among the garnet host allows for greater flexibility when fine tuning the color of white LEDs and matching excitation wavelengths with that possible with the InGaN diode.

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