LOW-VOLTAGE CATHODOLUMINESCENT PROPERTIES OF BLUE-EMITTING YTTRIUM SILICATES DOPED WITH CERIUM

E. J. BOSZE , G. A. HIRATA, J. McKITTRICK, and L. E. SHEA *
Department of Applied Mechanics and Engineering Sciences and Materials Science Program,
University of California at San Diego, La Jolla, CA , 92093-0418, ebosze@ucsd.edu
*Sandia National Laboratory, Albuquerque, NM 87185

ABSTRACT

Yttrium silicate activated with Ce^{3+}, $(Y_{1-x}Ce_x)_2SiO_5$, has been found to be an efficient phosphor that can potentially be used as the blue-emitting component in field emission flat panel displays. This highly refractory powder can be synthesized by combustion synthesis, a low cost technique used to fabricate multicomponent oxide powders in a single step process. The effect of activator concentration and post-synthesis annealing was examined on the fluorescent properties. The powders were found to be monoclinic space group $P2_1/c$ in the as-synthesized state, and transformed to monoclinic space group $C2/c$ after annealing. The maximum luminous emission intensity was reached after a one hour anneal at 1350 C for x=0.0075, with the peak Ce^{3+} emission wavelength between 420 and 450 nm. When co-doped with Gd^{3+}, no increase in the emission intensity was observed.

INTRODUCTION

Phosphors are inorganic materials that emit photons when bombarded by an external energy source such as high energy photons (photoluminescence, PL) or electrons (cathodoluminescence, CL). Typical phosphors are composed of an inert host lattice and an activator ion, usually a 3d or 4f electron metal. High efficiency CL phosphors are used in cathode ray tube (CRT) displays. Each pixel of a CRT screen is composed of three different phosphor dots that emit photons in the red, green or blue regions of the visual spectrum. The chromaticity of the phosphors (color coordinates x_c and y_c) needs to be optimized to ensure that full colors are achieved.

CRT screens are large and require high voltages, between 20-30 kV, to achieve high brightness and good contrast. An alternative to CRT's are flat panel displays, such as low voltage field emission displays (FED's). FED's require lower voltages, < 10 kV, but at low voltage excitations, the phosphor losses its efficiency, and thus its luminosity [1,2]. CL efficiency is the ratio of energy out (lumens) to the energy in (Watts). To achieve the brightness of a CRT screen, more efficient, low-voltage CL phosphors are necessary.

$(Y_{1-x}Ce_x)_2SiO_5$ is a blue-emitting phosphor with a peak CL emission intensity reported between 400 and 450 nm [3-7]. It was found to be an efficient phosphor at high voltages and can be used in full color CRT displays [3]. The Ce^{3+} (ionic radius 0.107 nm) substitute for the Y^{3+} (ionic radius 0.093 nm) in the host lattice. Only a small amount of Ce^{3+} (x < 0.10) is needed to produce luminescence. These small amounts do not alter the crystal structure nor cause concentration quenching [5]. Concentration quenching is a phenomena where the luminescent efficiency decreases as the activator concentration increases. This arises due to a non-radiative transfer of energy between adjacent activator ions [8].

Various techniques have been used to produce yttrium silicate phosphors. Single crystals have been grown by the Czochralski technique [3], thin films have been made with rf magnetron sputtering [4,5], and powders by a sol-gel technique [6]. For single crystals, the optimum cerium

concentration was found to be x=0.0025 and had a peak emission intensity around 400 nm. Efficiencies measured at 30 kV were high enough for CRT displays [3]. For polycrystalline powders it was found that with increasing x=0.001 to 0.1, the peak emission intensity red shifted in wavelength from 400 nm to around 470 nm [7]. The optimum concentration was found to be x=0.01 at an excitation voltage of 20 kV. Co-doping with gadolinium (Gd^{3+}) to form ($Y_{1-x-y}Ce_xGd_y)_2SiO_5$ in single crystals showed an increase in efficiency, with an optimum concentration of y=0.025 and x=0.025 [3]. This was reportedly due to a non-radiative transfer of energy from Gd^{3+} to the Ce^{3+} [3]. The peak emission intensity of ($Y_{1-x-y}Ce_xGd_y)_2SiO_5$ also red shifted with addition of Gd^{3+} from a peak emission intensity around 400 nm to 425 nm [3]. The Gd^{3+}emission intensity is much lower than that for the Ce^{3+}, suggesting an efficient energy transfer from the Gd^{3+} to the Ce^{3+} [3]. For polycrystalline ($Y_{1-x-y}Ce_xGd_y)_2SiO_5$, with y=0.49 and x=0.01, the peak emission intensity was found to be around 425 nm [7].

Combustion synthesis is a novel powder processing technique that has been successfully used to form a variety of oxide phosphor compositions [9]. This technique involves a highly exothermic reaction between metal nitrates and an organic fuel. The exothermic reaction yields reaction temperatures, typically 1500°C, long enough for the product to form. The escaping gases from the reaction (CO_2, N_2 and H_2O) break up large agglomerates and yield a highly porous mass of powder. It has been shown that this technique yields phosphors that are almost defect free, are high purity, single phase, and chemically homogenous [10]. Details on combustion synthesis can be found elsewhere [9-13].

The purpose of this study was to make an efficient blue-emitting phosphor with potential applications for FED's. The goal was to identify the optimal Ce^{3+} and Gd^{3+} concentrations in ($Y_{1-x-y}Ce_xGd_y)_2SiO_5$, produce phosphors that have a higher efficiency at low voltages, and evaluate its cathodoluminescent properties for use in FED's.

EXPERIMENTAL

Yttrium silicate ($Y_{1-x-y}Ce_xGd_y)_2SiO_5$ powders, with y=0.0 and x=0.002, 0.005, 0.0075, 0.01, 0.05, were made by combustion synthesis. Once the optimum concentration of Ce^{3+} was determined, gadolinium (Gd^{3+}) was added as a co-dopant, with y=0.025, 0.030, 0.040, 0.050. The starting materials were $Y(NO_3)_3$- H_2O (Alfa Asear REacton 99.99% [REO]), $Ce(NO_3)_3$-5 H_2O (Alfa Asear REacton 99.99% [REO]), $Gd(NO_3)_3$ (Aldrich 99.999%) and fumed SiO_2 (Aldrich 99.8%). These were mixed with the appropriate amount of either urea (CH_4N_2O, Fisher A.C.S) or carbohydrazide (CH_6N_4O, Aldrich 98%) fuels and put into a 300 ml pyrex dish with 50 ml of deionized water. The solution was mixed for 30 minutes and put into a preheated muffle furnace at 500C. Once the water boiled off, the reactants ignited and the powder formed. The product was then ground with a mortar and pestle and a fraction of each composition was annealed at 1350°C for one hour. The as-synthesized and annealed samples were examined by a X-ray diffractometer (XRD) scanning in 2θ mode at 1 /minute from 20 to 45°. The crystallite size was determined from the 100% peak of the XRD pattern by [14]:

$$\frac{}{B\cos(q)} \tag{1}$$

where t is the crystallite size (nm), B is the broading (measured in radians at the full width at half maximum of the 100% peak) and λ is 0.154 nm.

Low voltage cathodoluminescent efficiencies of the annealed powders and an industrial standard[*] were measured. Phosphors were tested at four voltages, 250 V, 500 V, 750 V, and 1000 V, at a constant power of 5 mW/cm^2. The spot size of the electron beam was 0.196 cm^2. The luminance (cd/m^2) and the chromaticity, x_c and y_c, were measured. The efficiency (h in lm/W [15]) was calculated by:

$$h = \frac{\text{luminance} \ * \ \text{spot size} \ * \ p}{\text{Volts} \ * \ \text{Amps}}$$

(2)

RESULTS

Figure 1 shows the XRD patterns for as-synthesized and annealed powders along with the industrial standard. The powder in the as-synthesized condition matches JCPDS Card #41-4 [16], which is monoclinic with space group P2$_1$/c (14). After annealing, the XRD pattern matches the JCPDS Card #37-1476 [16] and is a monoclinic structure with space group C2/c (15) [17]. As shown in Figure 1, the XRD pattern for the standard matches the annealed combustion synthesized powder. The peak at 29.2 for both the standard and the annealed powders was not found in either Y$_2$SiO$_5$ JCPDS cards. However, this peak matches the 50% peak (111) of the Y$_2$O$_3$ card #39-1063, suggesting there is some unreacted Y$_2$O$_3$. The 100% peak of card #39-1063 falls under the 100% peak (4 02) for Y$_2$SiO$_5$. The unreacted Y$_2$O$_3$ (111) peak disappears when the combustion synthesized powders are annealed at 1600 C for two hours. The only difference between the standard and the annealed powder is the presence of an unidentified peak around 28.8 in the standard. The crystallite sizes were determined from line broading measurements done on the 100% peaks, and were found to be 146 nm for the standard, 137 nm for the annealed powder and 21 nm for the as-synthesized powder.
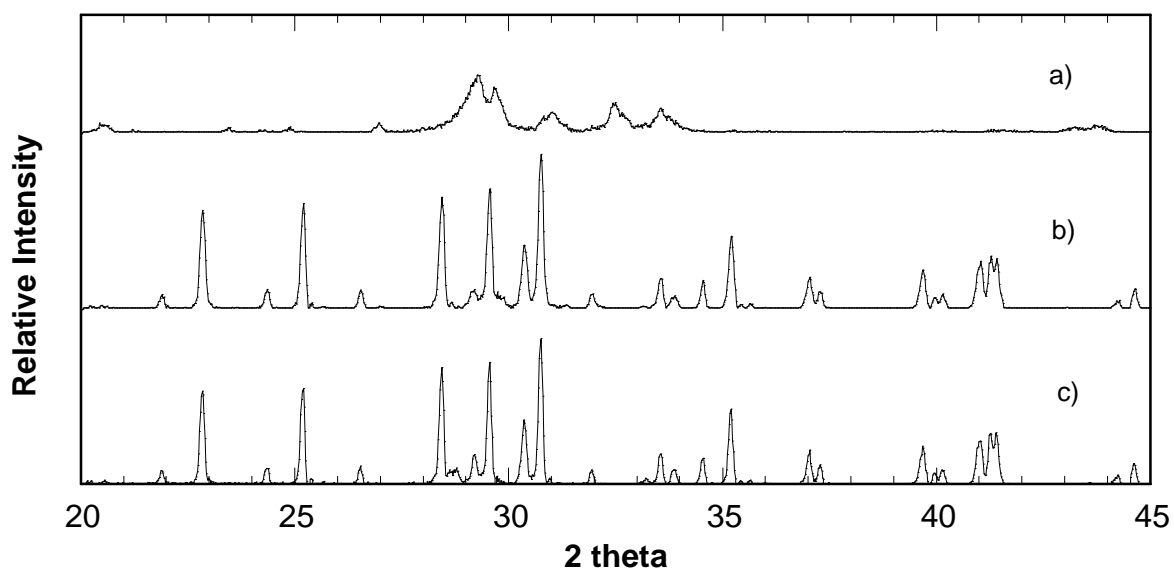

Figure 1. XRD patterns of (Y$_{1-x}$Ce$_x$)$_2$SiO$_5$. a) As-synthesized, b) annealed powder for one hour at 1350 C, c) the industrial standard.

The efficiency (η) as a function of voltage of the annealed powders and the standard are shown in Figure 2. At low voltages (< 500 volts) the efficiencies of the annealed powders are

~20% better than the standard for x=0.0075. Above 500 volts, the efficiency of the standard is better than any of the combustion synthesized powders. The chromaticity values of the combustion synthesized powders were found to be independent of x or the acceleration voltage, with an average x_c=0.159 and y_c=0.106. Chromaticity values for the standard were also found to be constant, x_c=0.161 y_c=0.114. This is different from what was reported for single crystals, x_c=0.163 and y_c=0.052 [3].
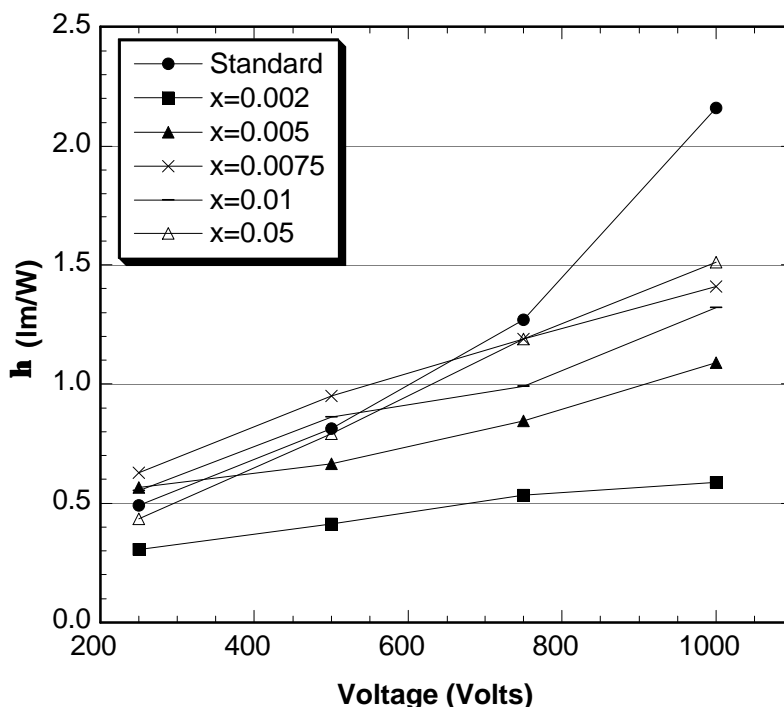

Figure 2. CL efficiency as a function of voltage for the various Ce^{3+} concentrations.

Figure 3(a) is a plot of the normalized CL efficiency as a function of Ce^{3+} concentration (x). Figure 3(b) plots the normalized integrated intensity for PL as a function of x. In both graphs, powders have been normalized with respect to the standard. These plots show that the optimum cerium concentration occurs at x=0.0075 for both PL and low voltage CL. For the CL voltages 250 V and 500V, the efficiencies of the annealed powder x=0.0075 were found to be 0.628 lm/W and 0.949 lm/W, respectively, compared with the standard at the same two voltages, 0.490 lm/W and 0.813 lm/W, respectively. These results are in contradiction to what was found in [3] and [7].

The efficiency as a function of voltage for the annealed powders with Gd^{3+} (x=0.0075), is shown in Figure 4. These samples showed virtually no improvement in the efficiency of the yttrium silicate phosphors. It shows a surprising result that for Gd^{3+} concentrations, y=0.025, 0.03, the powders efficiency actually decreased, matching those efficiencies found for the anneal powders with just Ce^{3+}. The optimum Gd^{3+} concentration was found to be y=0.040. The chromaticity values for the Gd^{3+} samples were found to be on average x_c=0.158 and y_c=0.098. CL data shows that there is a blue shift in the peak emission intensity for the as-synthesized to the annealed powders. For the as-synthesized Gd^{3+} powders, the peak emission intensity was around 425 nm, while after being annealed at 1350 C for one hour, the peak emission intensity was around 400 nm. No red shift was seen in the combustion synthesized powders when Gd^{3+} was added, which is contradictory to results reported in reference [3]. In that work, upon the
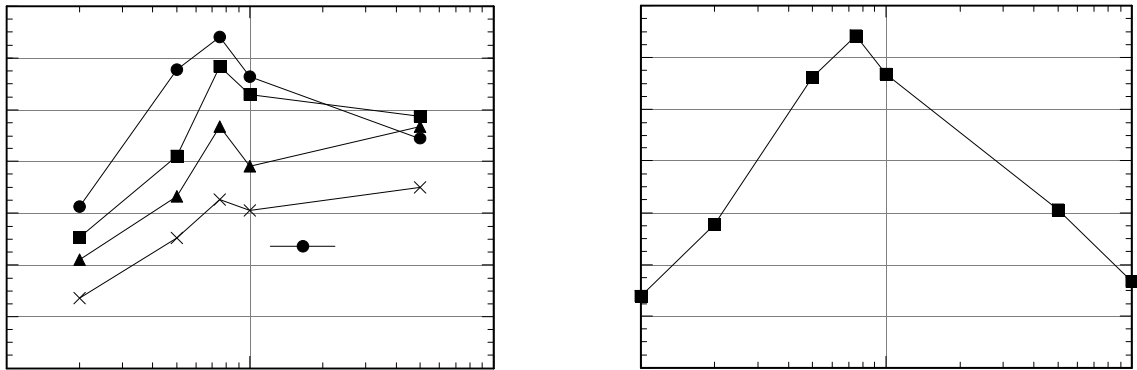
Figure 3. a) Normalized CL efficiency as a function of Ce^{3+} concentration, b) Normalized PL integrated intensity as a function of Ce^{3+} concentration.
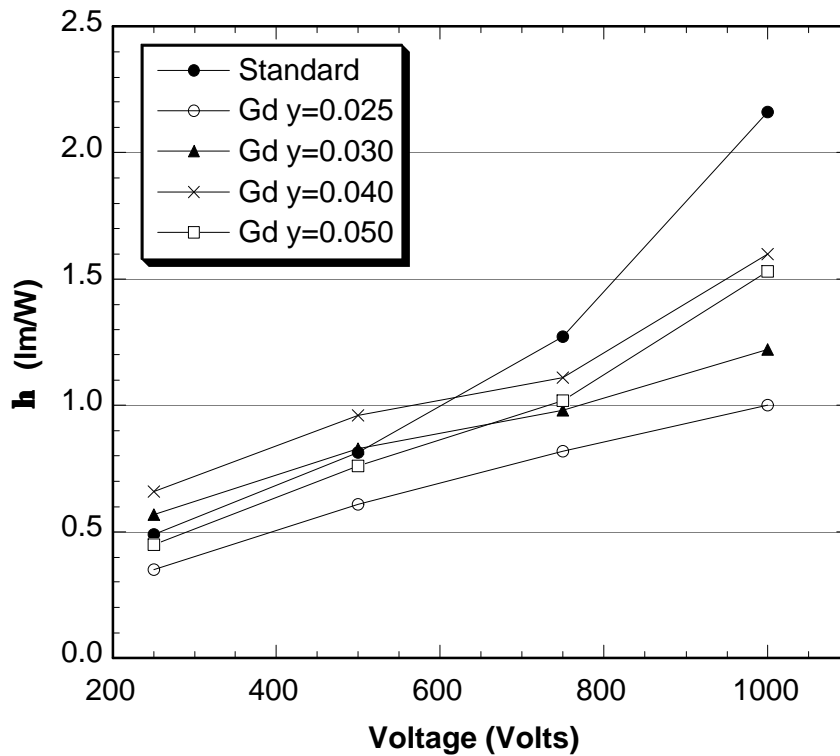

Figure 4. CL efficiency as a function of voltage curve for annealed powders $(Y_{0.9925-y}Ce_{0.0075}Gd_y)_2SiO_5$.

addition of Gd^{3+}, the peak emission intensity had red shifted from 400 nm to 425 nm with a Gd concentration of y=0.025 [3].

CONCLUSIONS

Combustion synthesis successfully produced blue-emitting yttrium silicate ($Y_{1-x-y}Ce_xGd_y)_2SiO_5$ powders. It was found that the optimum cerium concentration of x=0.0075 was the same for both PL or low voltage CL excitation, and yielded the most efficient CL (< 500 V) $(Y_{1.9925}Ce_{0.0075})_2SiO_5$ phosphors. Chromaticity values were found to be constant as a function of Ce^{3+} concentration. After a 1350 C anneal for 1 hour, the space group of the as-synthesized powder had changed, but no change was seen in the spectral energy distribution. When co-doped with gadolinium, no change in the efficiency was observed. Below the optimum (y=0.040) Gd^{3+} concentration, the efficiencies were found to be comparable to those powders with just Ce^{3+}. No red shift was seen upon the addition of Gd^{3+}. The chromaticity of the annealed powders were found to be independent of the voltage and dopant concentrations.

ACKNOWLEDGMENTS

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