Excitation of thermographic phosphors using a blue LED: spectral characteristics and instrumentation applications

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ABSTRACT

A blue light emitting diode (LED) has been used as the excitation source in a series of sensor-related characterization studies carried out on thermographic phosphors. The motivation for the described effort is the potential utility of light emitting diodes for fluorescence based thermometry applications. The phosphors that were evaluated included La_2O_2S:Tb, Gd_2O_2S:Tb, Y_2O_2S:Pr, and various other rare-earth activated ceramics. Periodic and pulsed excitation of the phosphors was demonstrated, with LED gate-on times of 10 to 12 μs at operating levels of + 25 V. The spectral response of the phosphors under these conditions is described, and the implications of such devices for the design of electro-optic instrumentation systems (including remote thermometry applications) are discussed. A beneficial finding of this work is that a good match between the LED emission spectrum and the phosphor excitation spectrum is not required in order to produce useful, detectable fluorescence.

I. INTRODUCTION

Light emitting diodes (LED) with emission curves peaked in the blue are finding use as photo-optical sources for fluorescence lifetime measurements[1,2] and in photodetector characterization studies[3,4]. This has happened at a time when fluorescence thermometry based on thermographic phosphors has begun to find broad application in many fields[5,6], and could expand its utility even further if shorter wavelength and less physically cumbersome (i.e., non-laser) excitation sources were available for both laboratory and field applications. We have thus sought to evaluate the workability of using a blue LED to excite the temperature-dependent luminescence that can occur in such phosphors and in related solid state materials. Although this might seem an obvious route to follow given that thermographic phosphors (and the similar laser host materials) are very quantum efficient by design, there are several aspects of LED-excited luminescence that are unique to such investigational methods and are of potential interest to those involved with fluorescence-based sensing techniques.

In what follows, we describe the experimental arrangement and materials that were used in these studies, present the excitation spectra that were obtained, and evaluate the performance characteristics of both the source LED and of some specific LED/phosphor systems. We close with a discussion of some of the potential uses for this approach that might arise in optical, metrological and engineering applications.

II. EXPERIMENTAL ARRANGEMENT

A. Apparatus

For this effort, a single light emitting diode (as opposed to an array) was used. It was a Ledtronics model BP280CWB1k-3.6Vf-050T narrow beam LED. For continuous low current operation the emission peaks at 450 nm, extending from 380 to 600 nm with the full-width, half-maximum points of the emission peak ocurring at 425 and 480 nm. For pulsed operation, an additional peak appears at 380 nm, which is characteristic of double quantum well devices.

The LED was potted in an SMA fiberoptic bushing. The input end of the fiber was threaded into the bushing and butt-coupled to the LED. The light emerged from a 1-mm optical fiber and illuminated the phosphor sample which was located 25 cm away, at an angle of 30° to the normal. A photomultiplier in an aluminum housing that served as an electrical and optical shield viewed the phosphor's fluorescence through a bandpass filter. The detector was oriented normal to the sample. An ac signal generator powered the LED, which was put in series with a 50 Ω resistor. The photomultiplier signal was sampled across a 5 kΩ load resistor by a waveform processing oscilloscope, with the digitized waveform transfered to a laboratory computer for analysis and presentation via a LABVIEW™ program customized for this application.

B. Materials

The fluorescence from the phosphors shown in Table I was studied using the arrangement described above. These technologically important solid state laser and phosphor materials are typically comprised of a ceramic host matrix and a rare-earth activator. The activator (or dopant) is an added small-percentage impurity in the molecular configuration from which the fluorescence occurs. To date we have excited a variety of materials with the following activators: Eu^{3+}, Tb^{3+}, Dy^{3+}, Mn^{4+}, Ce^{3+}, Pr^{3+}, Sm^{3+}. Detailed descriptions of the physics of the

luminescence process in these materials are available elsewhere[7,8]. We have carried out detailed investigations of the spectral properties and emission intensities of several of them[9,10].

III. RESULTS AND DISCUSSION

The fluorescence from fourteen different phosphors, both commercial and custom-prepared, has been produced and detected using a blue LED and the system described above. Several of the materials that were tested are listed in Table I. The principal finding was that a good match between the phosphor absorption spectrum and the blue LED luminescence spectrum is not required to obtain useful fluorescence signals. The data taken with the phosphor Y_2O_2S:Pr provide a case in point. Figure 1 shows the excitation spectra for this material at the phosphor's emission wavelength of 514 nm. It was obtained using a conventional Perkin-Elmer spectrometer. The plot shows the expected ultraviolet absorption band due to host absorption at wavelengths below + 325 nm, with an essentially flat region with no apparent signal strength above that. In fact, in the longer wavelength region of the excitation spectrum, magnification of the spectrum's structure is required to reveal the atomic bands in the near ultraviolet and blue zones. Also depicted are the LED and Y_2O_2S:Pr emission spectra. There is some overlap of the red side of the LED emission with an atomic emission/absorption band of Pr at 514 nm. Fig. 2 shows the phosphor's emission signal as a function of time during excitation by the blue LED. The gate-on time for the LED was + 12 μs at a drive level of 25 V. The fluorescence is clearly strong and with excellent signal to noise ratio and exhibiting the expected rise and fall time. The remarkable point is that this occurs even though the LED's emission is peaked at *ca.* 450 nm, where the phosphor's excitation spectrum is either very weak or flat. Similar results were found

when a blue LED was used to drive fluorescence in the other phosphors. The broadband excitation spectra for two of the other phosphors, La_2O_2S:Tb and Gd_2O_2S:Tb, are shown in Fig. 3. There is clearly very little overlap evident with LED emission. Fluorescence from these phosphors was weak but detectable, even for the latter material which had a very low activator concentration of 0.005 atomic per cent.

The high quantum efficiency of this class of materials is evidently responsible for the relatively large fluorescence signal that results from blue LED excitation. From an applications and instrumentation perspective, this means that a low-power, solid-state lamp like the blue LED can indeed be used to create new possibilities for fluorescence based sensors. Moreover, the blue LED is similar to a laser source in physical extent of the light emitting area, although its spectral content is much broader (and similar to a gas lamp in that regard). Therefore, it can be used to excite a wider variety of materials than a given narrow-band laser source. For those applications in which the fluorescent material has a low quantum efficiency, laser sources tuned to specific absorption bands in the material may remain the optimum means of excitation. However, for situations with efficient luminescent materials and particularly those where space limitations in the sensor design require a small physical volume and ruggedness, or where cost issues dominate, the blue LED can now provide a workable alternative.

FIGURE CAPTIONS

Figure 1. Excitation spectrum of Y_2O_2S:Pr.

Figure 2. Fluorescence signal vs. time for Y_2O_2S:Pr, also showing the temporal profile of the excitation pulse from the blue LED.

Figure 3. Excitation spectra of La_2O_2S:Tb and Gd_2O_2S:Tb.

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TABLE I. Various combinations of ceramic hosts and activators from which the blue LED-driven fluorescence was measured.

Eu^{3+}	Tb^{3+}	Dy^{3+}	Mn^{4+}	Cr^{4+}	Ce^{3+}	Pr^{3+}	Sm^{3+}
La_2O_2S	La_2O_2S	YVO_4	Mg_4FGeO	YAG	YAG	Y_2O_2S	YAG
Gd_2O_2S	Gd_2O_2S	YAG			YalO		

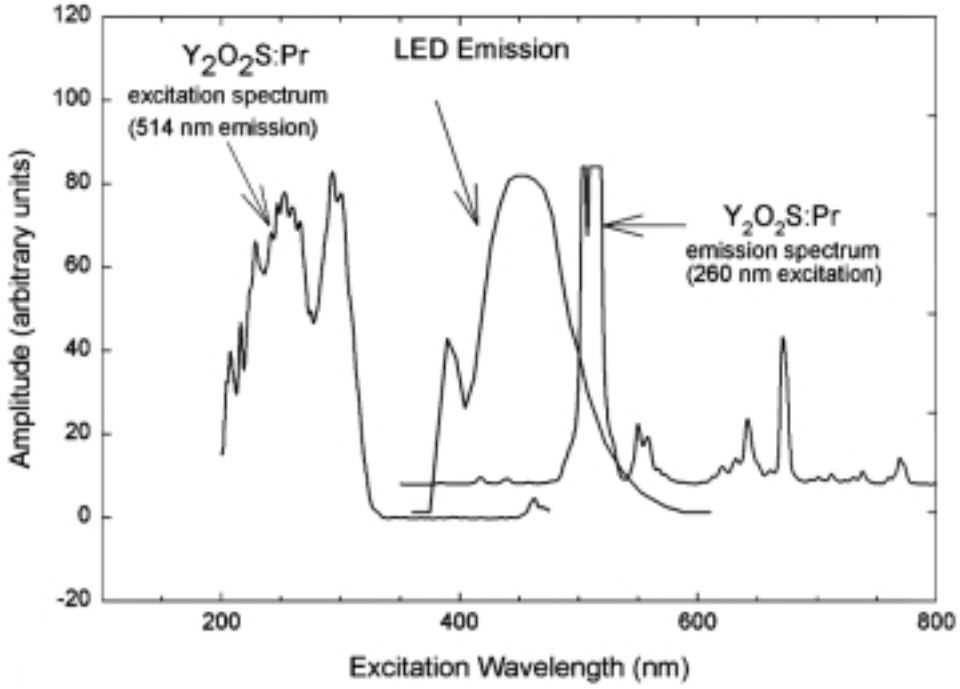
Y_2O_2S:Pr
excitation spectrum
(514 nm emission)
LED Emission
Y_2O_2S:Pr
emission spectrum
(260 nm excitation)
Amplitude (arbitrary units)
Excitation Wavelength (nm)
120
100
80
60
40
20
0
-20
200
400
600
800

Figure 1.

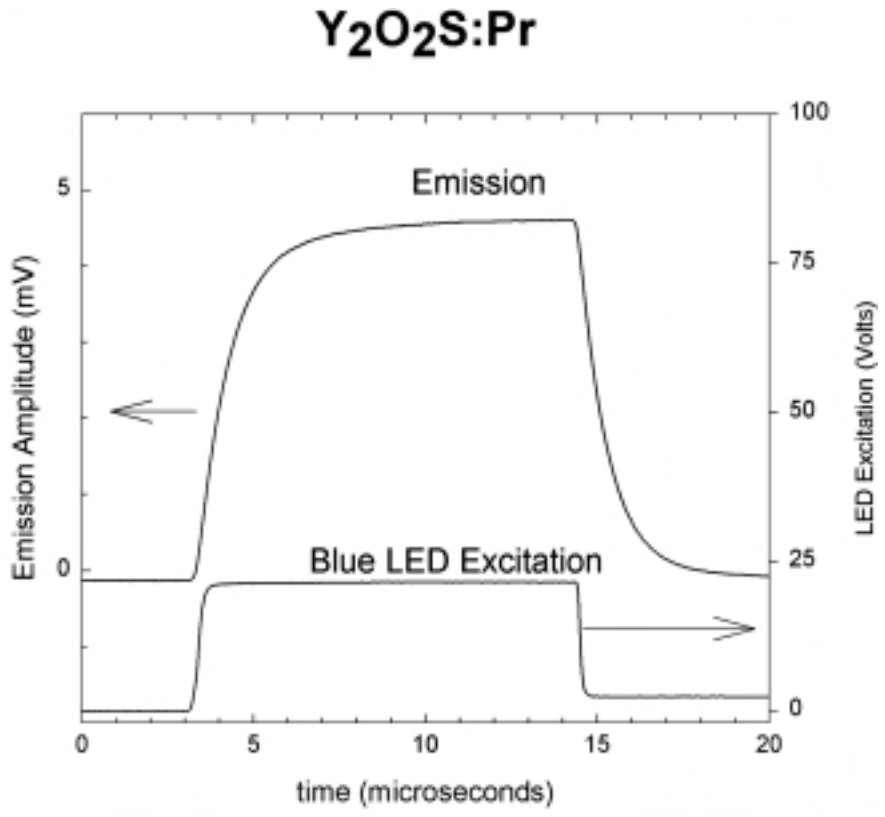
Y2O2S:Pr
Emission
Blue LED Excitation
Emission Amplitude (mV)
LED Excitation (Volts)
time (microseconds)
5
0
100
75
50
25
0
0
5
10
15
20

Figure 2.

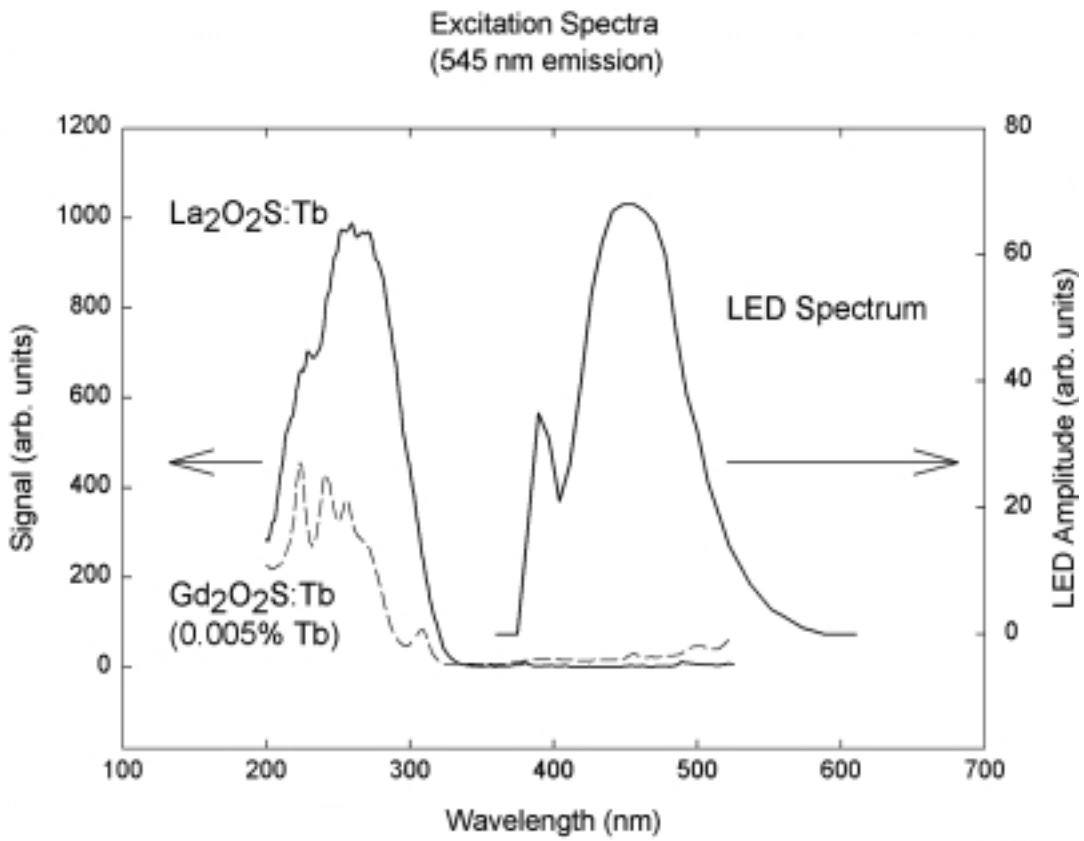
Excitation Spectra
(545 nm emission)
La2O2S:Tb
LED Spectrum
Gd2O2S:Tb
(0.005% Tb)
Signal (arb. units)
LED Amplitude (arb. units)
Wavelength (nm)
1200
1000
800
600
400
200
0
80
60
40
20
0
100
200
300
400
500
600
700

Figure 3.