Temperature-dependent fluorescence decay lifetimes of the phosphor $Y_3(Al_{0.5}Ga_{0.5})_5O_{12}$:Ce 1%

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The decay time of the phosphor YAG:Ce is temperature dependent. Selective incorporation of gallium into the YAG:Ce matrix permits tuning the temperature at which quenching begins. Also, the size of the phosphor particle and processing method affect this characteristic. We describe one such situation in which quenching of the combustion synthesized nanophosphor $Y_3(Al_{0.5}Ga_{0.5})_5O_{12}$:Ce 1% was observed from ambient to 125 C. By signal averaging of laser excited fluorescence, temperature uncertainties ranged from 0.05 to 0.15 C. The single shot temperature uncertainty at 115 C was ± 3 C, indicating the feasibility for transient thermometry with response rate exceeding 1 MHz.

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The phosphor YAG:Ce is employed routinely in many scientific, technological and industrial applications including, e.g., fluorescent lamps, flying spot scanners, scintillators, and white light LEDs.[1,2,3] Each different application will generally require its own formulation of the material, therefore its properties are often examined as a function of different techniques of synthesis.[4] As with many such phosphors, there is particular interest in characterizing how the luminescence changes with particle size. For instance, an advantage of nanoscale particles over larger ones for white light LED applications derives from reduced internal light scattering.[5] In parallel with such efforts are those aimed at investigating the temperature dependence of the laser-induced fluorescence of these materials. However, there is a notable gap in our knowledge in that regard, because only a few measurements of the thermal quenching curves for optical transitions in nanoscale particles of YAG:Ce have been reported to date.[6] In addition to providing a more well-rounded description of the physical properties of these materials, such data also establish the foundation for remote thermometry techniques that employ YAG:Ce as a fluorescent thermal sensor. A specific example of where better understanding and exploitation of such data is especially useful concerns thermal failure mechanisms that affect white light LEDs.[7] The incorporation of YAG:Ce into an LED during manufacture has been shown to be useful for *in situ* measurement of temperature during operation and characterization,[8] thus providing the potential for critical diagnostic functions.

Our laboratories have investigated the temperature dependence of the fluorescence decay times of a wide variety of laser-pumped thermographic phosphors; see our reviews.[9,10,11] In the present work we report the first results of such measurements as made on a unique new formulation of YAG:Ce that incorporated Ga as a partial substitute atom in the host matrix. The specific stoichiometry studied was $Y_3(Al_{0.5}Ga_{0.5})_5O_{12}$:Ce 1%. This material was generated by a novel means of combustion synthesis. By the intentional introduction of gallium atoms into the YAG, it might be possible to modify the structure of the host matrix in a manner that would permit controlled variation of the temperature-dependent fluorescence decay times. That, in turn, might extend the range and scope of applications for non-contact thermal sensors based on this material. The work builds on previous studies we have carried out on other unusual types of co-doped phosphors.[12]

The phosphors were made by a combustion reaction combining aqueous solutions of $Al(NO_3)_3•9H_2O$, $Ce(NO_3)_3•6H_2O$, and $Ga(NO_3)_3•H_2O$. Urea was used as a fuel, with a stoichiometric oxidant-to-reductant ratio. The water was evaporated by placing each sample in a muffle furnace at a temperature of 500 C. An auto-combustion process then began, leaving a porous yellow powder, and unreacted carbon was eliminated by calcining the powder at 1000 C for five hours. Excitation and emission spectra were obtained for two species of the modified host-matrix phosphor $(Y_{1-x}Ce_x)_3(Al_{1-y}Ga_y)_5O_{12}$, where x = 0.01 and y = 0 (black) or 0.50 (gray). The former is a standard version of YAG:Ce, while the latter is the gallium-modified version that was the material of interest here. We found that the Ga-modified version was ≈ 40% less intense in its emission over the range from 500 to 550 nm than the unmodified YAG:Ce, but the signal strengths were still more than sufficient for detection and processing.[13]

The experimental arrangement that was employed follows our standard approach to this type of measurement.[14,15] The excitation light source was a SRS NL100 pulsed laser operating at a wavelength of 337 nm within a spectral bandwidth of 0.1 nm. Each 3.5 ns pulse delivered 170 μJ at an average power of 3 mW. The beam was sent through an optical fiber and then to a custom beam splitter having core fibers of 400 μm diameter. From the splitter, one leg went through an input/output cable to the sample under test, which was bonded by an epoxy bead onto the end of the output leg. The fluorescence was sent by the input/output cable back to the beam splitter, from which the other leg went through an output cable to a Hamamatsu H5783-01 photomultiplier tube (PMT) that had spectral response from 300 to 850 nm, a dark current rated at 0.4 nA, and a peak-to-peak ripple noise of < 1.2 mV. Data were taken with the detector's aperture fitted with either a 510 nm or 540 nm filter, both having a 5 nm bandwidth. The sample was immersed in fluid bath for thermal control. The bath was regulated by a Fluke/Hart Scientific 7102 Micro-Bath Controller. The fluorescence signals transduced by the PMT were registered by a Tektronix TDS 5034 digital oscilloscope. The analog bandwidth of this instrument was 350 MHz, the single-shot time resolution was 200 ps, and the single-channel real-time sampling rate was 5 GS/s. An external type K thermocouple was used to monitor the bath temperature. Those measurements were made with a National Instruments NI-USB-9162 thermocouple reader that was interfaced to the oscilloscope through a USB connection.

Figure 1 shows a signal resulting from a single laser pulse and the average of 2048 such waveforms. The inset presents the logarithm of those two signals that is straight over most of the decay with a slightly higher slope initially. No attempt beyond this was made to further increase the signal-to-noise ratio, as previous studies had shown that there are limits to the efficacy of the smoothing functions in waveform processing oscilloscopes.[16] The logarithmic slopes of the averaged waveforms yielded the exponential decay lifetimes in the usual way.[10,11] In this case data between the 70% and 7% of peak intensity was analyzed to determine temperature. The other regions were excluded because the initial part of the pulse where the amplitude is higher possesses a slight curvature, while below about 7%, the signal becomes noisy.

Figure 2 shows examples of averaged signals for three temperatures over an approximate 100 C range. The inset shows the quenching curve where decay times change from about 56 ns at ambient temperature to 44 ns at 125 C, the limit of the temperature bath. The linearized roll-off rate of the lifetime was ≈ 0.15 ns K^{-1} from 50 C through 125 C. The rate of change of lifetime with temperature observed here was the same as that reported over the temperature range from 25 C to 40 C for 30 nm particles of YAG:Ce phosphor that did not contain any gallium dopant. However, the roll-off in the quenching curve for the gallium-modified phosphor began at temperatures roughly twice that at which it occurred for the unmodified phosphor. Moreover, data obtained with micron-sized particles of the unmodified phosphor showed that the roll-off in quenching in that case occurred over the temperature span from roughly 150 C to 300 C, i.e., starting at a temperature roughly three times that of the gallium-modified phosphor. This demonstrates that by (1) selective adjustment of the gallium dopant concentration and (2) control of the size of the host phosphor particles, one can indeed tune the characteristics of the quenching process such that it is possible to have the roll-off in fluorescence lifetime begin at points intermediate between those associated with the nanoscale and micron-sized versions of the unmodified phosphor. This finding is further supported by comparison of our present results with those of Vitta et al., who used the phase-shift method for temperature measurement rather than the decay lifetime approach. Their samples did not incorporate gallium and the resulting quenching temperature was found to be higher than that of the gallium-modified phosphor studied in the present work, thus fitting with the findings discussed above.

One motivation for the work was to investigate temperature measurement uncertainty for both single pulse excited signals and averaged signals. Figure 3 shows a single shot waveform at 115 C, the waveform resulting from an average of 2048 such single shot waveforms, and a processed waveform. In order to gain insight into repeatability and uncertainty, at selected temperatures, four successive measurements were made where each was an acquisition of the average of 2048 waveforms. The first column of Table I shows the average and standard deviation of a thermocouple measurement. The thermocouple variations were roughly 0.02 C. The second column provides the decay time (τ) measurement and its standard deviation. The temperature uncertainty corresponding to that standard deviation is in the third column and it ranged from 0.05 to 0.15 C. This study was limited to 125 C, the maximum temperature achievable with the controller that was used. At higher temperatures, based on similar materials, the temperature sensitivity should approximately double due to the change in slope of the data. Under identical conditions then, the temperature uncertainty may approach 0.025 C over this range.

TABLE I. Thermocouple measurements, phosphor decay times and temperature uncertainty for the Ga-modified YAG:Ce phosphor.

$T_{ave} \pm 1\ \sigma$ (C)	$\tau_{ave} \pm 1\ \sigma$ (ns)	Δ T (C)
89.95 ± 0.01	47.66 ± 0.01	0.05
95.03 ± 0.01	47.18 ± 0.03	0.15
100.03 ± 0.03	46.49 ± 0.02	0.10
110.14 ± 0.02	45.21 ± 0.02	0.11
115.24 ± 0.02	44.04 ± 0.01	0.06
120.27 ± 0.02	43.74 ± 0.01	0.06

With regard to single shot temperature uncertainty, the decay times of ten single shots at 115 C were analyzed. First, a simple running average of a typical single shot is formed. For this each point in this curve is the average of the preceeding and following 8 ns. This is depicted in Fig. 3 and is visually very similar to the curve resulting from 2048 averages. For the ten single shots, the mean was 44.3 ± 0.6 ns. This corresponds to an uncertainty of ± 3 C for a single data acquisition. This points to the feasibility of rapid response or transient temperature measurement. An adequate decay time can be determined from about 200 ns worth of data (or possibly less). In our arrangement, the signal decayed to background by 500 ns. This would indicate that a temperature response rate of at least 2 MHz may be achieved.

More comprehensive studies are presently underway, in which other concentrations of gallium will be tested. Also, these results imply that there are metrological implications for other classes of phosphors, such as the Ce-doped materials studied by Särner et al.[17] and nanosized particles of various rare-Earth doped ceramic oxides and oxysulfides, such as $Y_2O_3:Eu^{3+}$, with which we have extensive laboratory- and applications-based experience.[10,11]

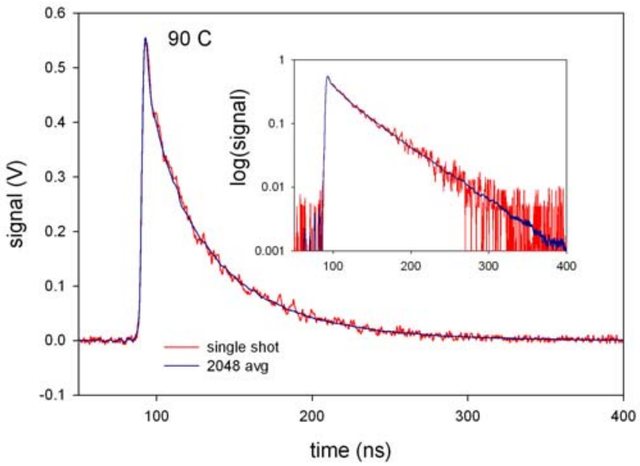

FIG. 1. A single-shot and a 2048-shot average of a typical laser-induced fluorescence signal from $Y_3(Al_{0.5}Ga_{0.5})_5O_{12}$:Ce 1% obtained in the span from 50 C to 125 C.

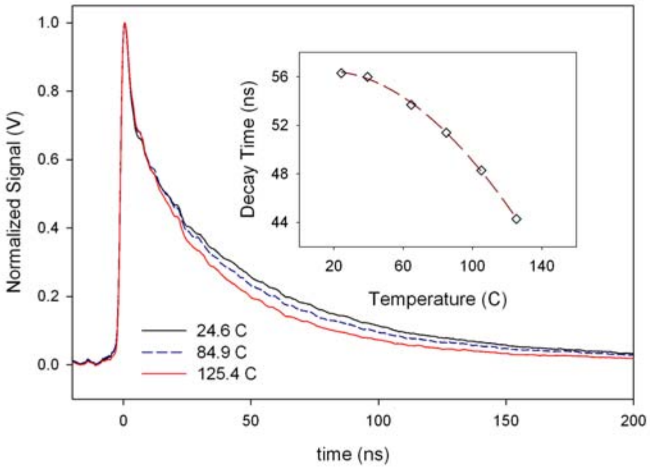

FIG. 2. Temperature-dependent lifetime of $Y_3(Al_{0.5}Ga_{0.5})_5O_{12}$:Ce 1% over the range from 25 to 125 C.

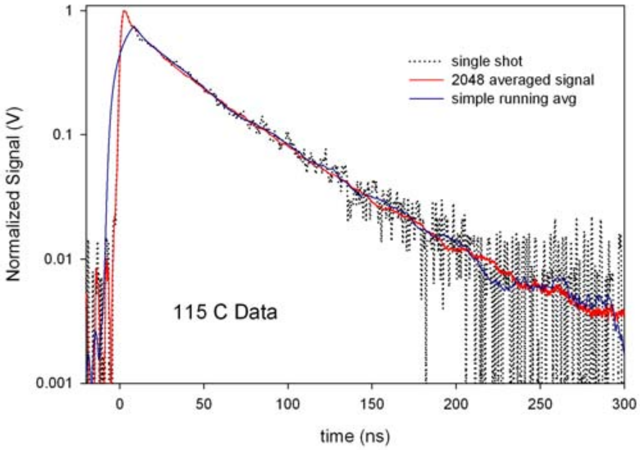

FIG. 3. Single shot, average of 2048 signals, and processed single shot waveform example at 115 C.

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