

Nanoscale thermometry via the fluorescence of YAG:Ce phosphor particles: measurements from 7 to 77 °C

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Abstract

The laser-induced fluorescence lifetime of 30 nm particles of YAG:Ce was measured as a function of temperature from 7 to 77 °C. The fluorescence decay lifetimes for the nanoparticles of this phosphor varied from ≈ 18 to 27 ns, i.e. $\approx 33\%$ relative to the longest lifetime measured. This large variation in lifetime, coupled with the high signal strength that was observed, suggest that YAG:Ce nanoparticles will be useful thermographic phosphors. We describe the material and the apparatus used to characterize its fluorescence, present the results of measurements made over the range of temperatures tested and comment on some possible applications for this novel material.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The luminescence properties of rare-Earth-doped ceramic oxide and oxysulfide phosphors have characteristic temperature dependencies that make these materials useful in a variety of thermometry applications [1]. Although their fluorescence is easily excited by short duration uv laser pulses, stimulation is also now possible with blue light emitting diodes [2], thus expanding significantly the scope of potential applications for them. Most of the previous work, for example, on the temperature-dependent fluorescence decay lifetimes of these materials, has been done using micron-sized particles of them. However, we have recently begun exploring the fluorescence characteristics of much smaller powders, e.g., using 8–12 nm particles of $Y_2O_3:Eu^{3+}$ to probe the structure of brain phantom gels that are employed as *in vitro* models of novel neurosurgical therapies for diffuse neoplasms in the central nervous system [3]. Moreover, Meltzer *et al* [4] have examined the temperature dependence of linewidths in nanocrystals of

europium-doped yttrium oxide, and Peng *et al* [5] have carried out a detailed study of the temperature dependence of the emission intensity, linewidths and decay lifetimes of $Y_2O_3:Eu^{3+}$.

The fluorescence in these materials, which are referred to typically as ‘thermographic phosphors’, originates from the photo-optical excitation of the dopant atoms in them. The temperature dependence of the fluorescence decay lifetimes arises from the presence of charge-transfer states in the host ceramic matrix [6, 7] that offer nonradiative de-excitation pathways which become energetically favourable with increasing temperature, thus leading to thermal quenching of the excitation. Nanoscale particles of the phosphor open new windows for investigation into the physics of this thermal quenching phenomenon because they offer the possibility of exploring the limiting case of detecting lifetime changes arising from a single dopant atom inside a nanocrystalline structure, and this would simplify the modelling of the quenching process significantly. There are growing numbers of scientific and industrial applications [3, 8] for the novel

form of noncontact thermometry made possible by remote measurement of the fluorescence of phosphors bonded onto either static or moving surfaces. In turn, this calls for the development of a better understanding of the physical basis for the method in order to improve and broaden its performance characteristics.

Therefore, as a step in that direction, we have measured the laser-induced fluorescence lifetime of 30 nm particles of YAG:Ce as a function of temperature from 7 to 77 °C. The specific goal of the work was to see if the fluorescence lifetime of the particles varied strongly enough with temperature over this span to provide a useful means of nanoscale thermometry, at least for measurements that must be made within this range of temperatures. In what follows, we present the relevant details of the materials and methods used in the work, describe the results of the fluorescence lifetime measurements, and discuss the limitations and implications of the findings.

2. Experimental arrangement

2.1. Materials

Two samples of coarse 30 nm YAG:Ce particles were synthesized using a procedure similar to that of Inoue *et al* [9, 10]. A total of 0.3 g aluminum isopropoxide was refluxed in 20 ml 2-methoxyethanol under argon for 1 h. All solvent was pulled off under vacuum leaving the dried product. Then, 0.3 g yttrium acetate and 0.03 g cerium acetate were added to 10 ml 1, 4-butanediol and mixed with the dried aluminum methoxyethoxide. Following this, 0.25 ml distilled oleic acid and 15 ml phenyl ether were added to the 1, 4-butanediol. The mixture was stirred vigorously under argon to form an emulsion.

The emulsion was poured into an autoclave and heated to 305 °C for 12 h. One particular sample (no 18) was run at a pressure of 8.6 MPa, while another (no 28) was run at 3.1 MPa. X-ray and TEM analysis revealed single-phase YAG in roughly 30 nm irregularly shaped particles with relatively broad (>25%) size distribution. There was no significant difference in the morphology of the two samples.

YAG:Ce is an important fluorescent material because of its chemically stable YAG matrix and because the Ce dopant emits strong fluorescence with sub-microsecond lifetimes. These short lifetimes allow the determination of fluorescence characteristics (which indicate temperature) very quickly, which are useful both for signal averaging and for following dynamic processes. When particle sizes are reduced to the nanometrical scale, as for this study, the material and fluorescence characteristics do not scale with the macroscopic behaviour of structures that are least 1 μm in size. We explored such differences within the context of laser-induced fluorescence of this material, as will be discussed in section 4. Figure 1 shows the emission spectrum from the YAG:Ce nanoparticles used here, the formulation for which was $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$. The broad, bright spectrum reaches its peak near 540 nm.

2.2. Fluorescence measurement and thermometry systems

A nitrogen laser (Laser Science Corporation, model VSL-337ND) [11] excited the fluorescence from the samples. The excitation wavelength was $\lambda = 337.1$ nm, with an excitation

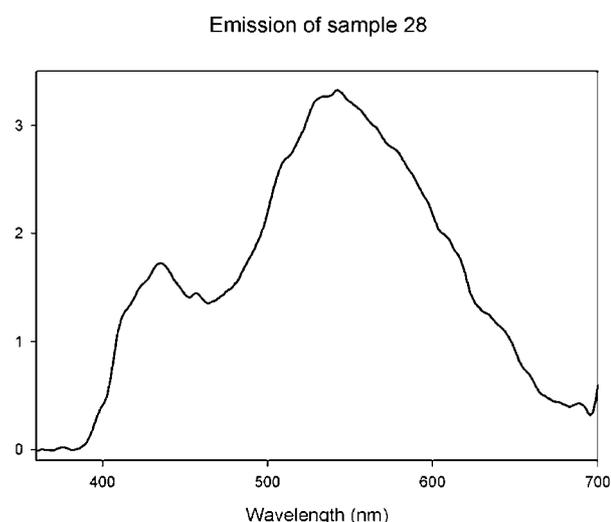


Figure 1. Emission spectrum of $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ sample 28 with excitation at 346 nm.

bandwidth of 0.1 nm. The pulse width was ≈ 4 ns at a characteristic energy of $300 \mu\text{J}$. The standard deviation of the variation in energy from pulse-to-pulse was rated by the manufacturer to be $\leq 4\%$ at an average power of 6 mW (20 Hz repetition rate). The excitation pulse was conveyed to the sample by a 1 mm optical fibre. An additional identical fibre collected and then transmitted the fluorescence to a photomultiplier tube that served as the detector. A waveform processing oscilloscope with a 500 MHz bandwidth and a sampling rate of $5 \times 10^9 \text{ s}^{-1}$ (Tektronix TDS3052) [12] displayed, digitized and stored the data for subsequent analysis. The oscilloscope had a 9 bit vertical resolution and was capable of measuring the signals with a $\pm 2\%$ accuracy. Owing to the brightness of the fluorescence, the typical signals driving the oscilloscope were large, having peak heights of ≈ 4 V at an input impedance of 50Ω . The nanophosphor sample was applied in a circular spot (1 cm in diameter) on a $5.5 \times 3.5 \times 0.5$ cm aluminum plate and was placed in a 100 mm diameter \times 15 mm deep Petri dish (BD Falcom 35-1029) containing approximately 75 cm^3 of tap water, for thermal equilibration. The phosphor adhered well to the aluminum under water. The Petri dish was placed on a laboratory hot plate (Thermolyne HP2305B, 325 W max) for adjustment and temperature control.

Two thermometers were used to monitor the substrate temperature. The primary reference unit was a NIST-traceable platinum resistance thermometer (Wahl 392MX) with digital readout and an immersion tip (Wahl 202) that was submerged next to the substrate. It had a resolution of $0.1 \text{ }^\circ\text{C}$. The secondary device was a type K bare wire-thermocouple thermometer (Omega Engineering 871) also with digital readout and $0.1 \text{ }^\circ\text{C}$ resolution. The latter was periodically placed at different locations on the aluminum substrate as a check on equilibration at a given working temperature, and no such positional variations greater than the thermometer resolution were observed. Prior to use, both probes were inserted into one well of an ice-point reference bath (Wahl IPR-4-110) that remained at $(0.00 \pm 0.02) \text{ }^\circ\text{C}$ continuously, and they were found to read within about 250 mK of each other at that temperature. The temporal stability of the



Figure 2. Experimental arrangement showing green fluorescence of the phosphor nanoparticles.

platinum resistance thermometer was evaluated by calculating the standard deviation of 32 measurements each one of which was made at 30 s intervals with the probe inserted into a well of the ice-point reference. The drift measured in this way was found to be $<0.05\text{ }^{\circ}\text{C}$ over 16 min, i.e. $\lesssim 3\text{ mK min}^{-1}$. During subsequent measurements of the submerged YAG:Ce sample, both devices exhibited a stable level of readout offset between each other, consistent with that found during their ice-point reference calibration procedures.

The emission from YAG:Ce is broad and intense, peaking in the green as shown in figure 2. Our principal data were taken with an optical bandpass filter centred at 700 nm because the signal was intense enough at lower wavelengths that it would have saturated the photomultiplier tube. Additional experiments were also run using 550 and 620 nm bandpass filters to select those particular emission wavelengths for measurement. The temperature-dependent characteristics of the fluorescence signals as observed at each of these three wavelengths remained the same to within the overall estimated uncertainty of the measurement system ($\pm 1.4\%$ as discussed below) over the range of temperatures tested in these studies.

3. Results

Figure 3 shows some representative data. The signals are all normalized to their respective peaks. Each trace is the average of 32 acquired waveforms. The peak for the data at $77\text{ }^{\circ}\text{C}$ was approximately one-tenth of that for the data at $10\text{ }^{\circ}\text{C}$. Bubble formation in the water bath at the higher temperatures resulted in scattering that somewhat decreased the optical signal strengths, hence quantitative measurements of the variations in peak height with temperature were not made in that regime. A plot of the data on a log scale revealed that the decay waveforms could not be characterized by single

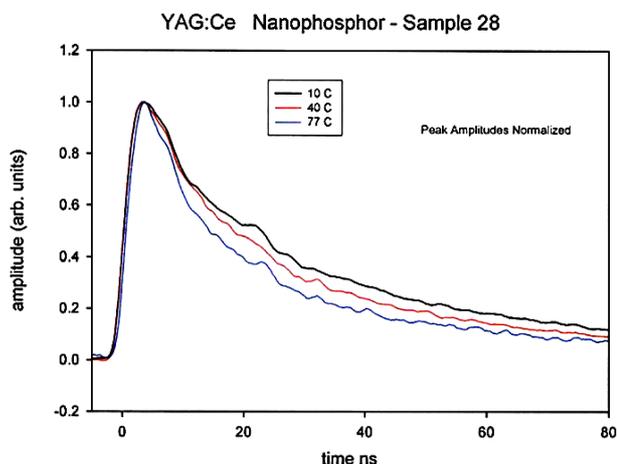


Figure 3. Representative signals versus temperature for $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ sample 28. The peaks at all three temperatures were normalized to the same height for comparison purposes. (top trace, $10\text{ }^{\circ}\text{C}$, middle trace $40\text{ }^{\circ}\text{C}$, bottom trace $77\text{ }^{\circ}\text{C}$.)

Table 1. Temperature versus decay time for the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ used here. The uncertainty in the temperature measurements was $\pm 0.1\text{ }^{\circ}\text{C}$ and that of the decay time measurements was $\pm 0.4\text{ ns}$.

Sample	Temperature ($^{\circ}\text{C}$)	Time to decay by $1/e$ (ns)
28	10	26.5
	16	26.0
	26	25.0
	32	23.5
	40	23.0
	77	18.5
18	25	23.5
	32	22.0
	42	21.0

exponential time dependence. Thus, for the present effort, an effective decay time was approximated by measuring the time for the emission to decay to $1/e$ of the peak. The values obtained in this manner are summarized in table 1.

The experimental uncertainty was found by calculating the standard deviation (1σ) of 32 measured values of the fluorescence-decay lifetime. Each of those individual values was extracted from a signal-averaged set of 32 separate fluorescence waveforms, using one version of our waveform parameter estimation algorithms [13, 14]. The resulting standard deviation was 1.4% , corresponding to an uncertainty in the lifetime of $\pm 0.4\text{ ns}$ at room temperature. No attempt was made here to differentiate between the systematic and purely random components of the overall experimental uncertainty, although we have carried out analyses of that type on other phosphor thermography systems [15].

In figure 4 we compare the actual signals obtained with sample 28 at 10 and $77\text{ }^{\circ}\text{C}$ with the single exponential decay waveforms that were modelled for them. The captured signals fall at a rate that is faster than single exponential decay during the first 20 ns. However, at later times the signals fall less rapidly than the model. Late in the decay all the samples had the same time dependence. A plot of effective decay time versus temperature is shown in figure 5. Although there were a limited number of measurements made with sample 18, the data appear to indicate that its decay time at a given temperature

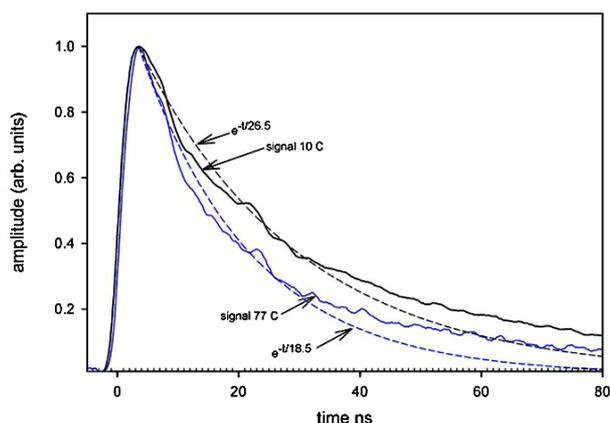


Figure 4. Comparison of measured signals (solid curves) with single exponential decay models (dashed curves).

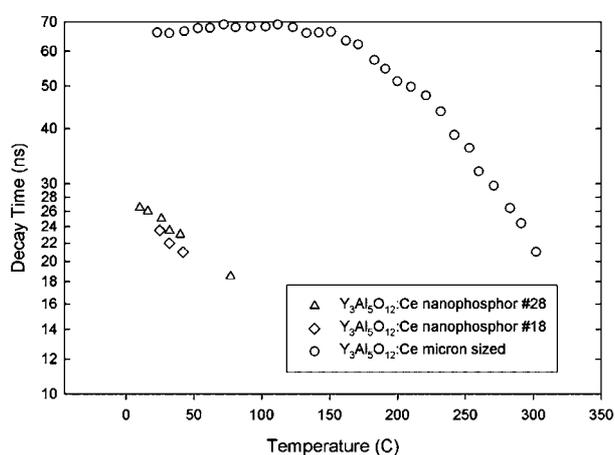


Figure 5. The YAG:Ce nanophosphor particles exhibit fluorescence quenching at much lower temperatures than do micron-sized particles of the same material. No error bars are shown on the data points because the estimated uncertainties in the lifetimes, ± 0.4 ns, are of the order of the size of the symbols.

is a few nanoseconds less than that for sample 28. For purposes of comparison, quenching data from a YAG:Ce phosphor of a few microns in diameter are also depicted in figure 5. Typically, commercial YAG:Ce powder having no gallium content will exhibit a decay time of approximately 60 ns and this will not change until a temperature of about 200 °C is reached and thermal quenching of the fluorescence via the charge-transfer states of the phosphor begins.

4. Discussion

It was rather surprising to find that the fluorescence decay lifetimes of the $Y_3Al_5O_{12}$:Ce nanophosphor changed measurably over the temperature range of room temperature. This was not expected since, as shown in figure 5, the lifetimes of micron-sized phosphors do not reveal the onset of thermal quenching until temperatures approaching 150 °C are reached. The change in lifetime with temperature that was observed with the nanoparticles is moderate yet useful, approximately $150 \text{ ps } ^\circ\text{C}^{-1}$ (a linearized average taken over the span from 25 to 40 °C). It was subsequently learned that a decrease in quenching temperature has also been observed for nanoparticles of Y_2O_3 :Eu³⁺ [5].

Simons *et al* [16] proposed a simple model aimed at describing how strongly the fluorescence lifetime of a material depends on its temperature. The model has only one free parameter, Q . The relevant expression is

$$\frac{\tau}{\tau_0} = \exp[Q(T - T_0)].$$

By definition, then, the reciprocal of Q is simply the temperature change needed for the decay time to decrease by $1/e$. For YAG:Ce (sample 28) the value of $1/Q \approx 180$ °C. For a phosphor with a particularly striking temperature dependence, such as La_2O_2S :Eu, this value is about 30 °C. On the other hand, for a phosphor such as Mg_4FGeO_6 :Mn that has seen significant commercial use for fluorescence-based thermometry, $1/Q \approx 1400$ °C from room temperature to roughly 400 °C. Therefore, within the context of this model, the degree of temperature dependence observed for the YAG:Ce nanophosphors tested here is sufficient to indicate potential for practical temperature measurements in the room temperature range, where thermal quenching of most other types of thermographic phosphors does not occur. As La_2O_2S :Eu exhibits a small value of $1/Q$, we are also currently looking into techniques for the preparation of nanoscale samples of it, and plan a similar study of temperature versus fluorescence decay lifetime once a satisfactory material is obtained. We note that phosphor-based temperature measurements with resolutions of 50 mK are possible [1]. This clears the way for the use of the technique in a wide range of high-precision applications, including its possible use as a temperature transfer standard [1], which would call for accuracy and precision of <0.1 °C.

From an instrumental perspective, Ce-doped nanophosphors provide the following advantage. The short decay times they exhibit makes the fluorescence signal easier to acquire and analyse in comparison with phosphors with millisecond decay times (when roughly the same number of photons are emitted and detected in both cases). The reason for this improvement is that the peak values of the signals are greater and the rise times are faster, thus reducing triggering errors in the detection electronics. Another attractive characteristic of Ce nanophosphors is that they can typically be excited by inexpensive light emitting diodes, thus not only reducing the cost of the phosphor thermography system but also alleviating any concerns about heating of the phosphor substrate by the laser (with the resulting introduction of a systematic uncertainty in the temperature measurements).

To realize the goal of nanoscale thermometry using these materials, the fluorescence of individual phosphor nanoparticles would have to be detected and measured. Bartko *et al* [17] have accomplished this at Oak Ridge National Laboratory using emission-pattern imaging on 3–12 nm particles of Y_2O_3 :Eu³⁺, a material we have also used in previous nanotechnological studies [3]. Of course, single molecule spectroscopy is now a well established field in general, and many examples of its application in physics, chemistry and the life sciences exist; see the review by Moerner [18] for a survey of the relevant literature.

Finally, we note that different forms of atomic force microscopy (AFM) now have a long history of use in nanoscale thermometry. A few examples include the work of

Moon *et al* [19] who applied AFM to micro-thermal analysis of macromolecules, Mittereder *et al* [20] who used scanning thermal microscopy to measure channel temperatures in GaAs devices, and Igeta *et al* [21] who used scanning joule expansion microscopy to measure the thermal expansion coefficients of polymer films. Shi and Majumdar [22] have reviewed the field of micro and nanoscale thermometry. The fully noncontact nature of the photooptical technique we have developed may provide a helpful alternative to the scanning probe methods in applications where completely noncontact sensing of the target surface or object must be accomplished.

5. Conclusions

The temperature dependence of the fluorescence decay lifetime of 30 nm particles of YAG:Ce has been measured. The results show that this material undergoes a 33% variation in lifetime from 7 to 77°C, with nominal lifetimes in the range of approximately 20 ns. In this range of temperatures, the decay lifetimes are roughly half of those found with similar measurements of micron-sized particles of the same material. The characteristics of the measurement system and the nature of the uncertainties in the measurement are discussed. YAG:Ce shows promise of providing a useful means of implementing noncontact phosphor thermography in the range of temperatures spanning room temperature, where thermal quenching of the fluorescence of many other such materials does not occur.

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