

# Ultra High Precision Phosphor Thermometry Near 1100 K

Michael R. Cates, Alvin J. Sanders<sup>†</sup>, Jason Newby<sup>†</sup>

*Oak Ridge National Laboratory*

*<sup>†</sup>The University of Tennessee*

**Abstract:** Studying the fluorescent emission of the dominant 611-nm line from  $Y_2O_3:Eu$  (6.8%) in the temperature region around 1100 K shows that the decay time changes correspond to changes in temperature with precisions of less than 10 mK. The apparatus used includes fluorescent activation by a 337-nm nitrogen gas laser and gradual cooling of an alumina thermal mass heated in a controlled-temperature furnace. Newton's cooling law and autocorrelation methods are used in the data analysis. Since the measurement technique involves the temperature response of molecular lattices it can be expected, with improvements of signal analysis and other laboratory refinements, to provide metrological precision and accuracy in the important temperature region above the aluminum freeze point.

## INTRODUCTION

Phosphors comprised of rare-earth metal oxides and similar strongly bound chemical structures have been used for more than a decade for temperature measurement of very hot surfaces.<sup>1-4</sup> Thin coatings, less than 50 micrometers thick, on components such as turbine rotors and vanes, automobile engine valves and pistons, sheets of galvanized steel, and the like, have been activated by pulsed and steady-state light sources to produce fluorescence signals that are analyzed to yield temperature. The temperature dependence of the fluorescence results from the competition for allowed de-excitation processes that take place within excited dopant (activator) ions. At increasing temperature, larger numbers of non-radiative (non-photon-emitting) transitions are allowed, thereby shortening the lifetime of photon emitting de-excitations through depopulation of the ionic excited states. Therefore, as temperature increases the characteristic fluorescence of these materials decreases in lifetime, as well as intensity. Because the temperature dependent fluorescence results from fundamental molecular processes within the phosphor itself, and because in many cases the temperature sensitivity of the fluorescence was high, it was recognized early that there was a potential for metrologically precise thermometry using phosphors.<sup>5</sup> We have become particularly interested in the temperature region above the freeze point of aluminum, both because precise temperature determination is more

challenging in this region and because of the important applications in higher temperature systems.<sup>6</sup> As a consequence, we explored the fluorescence response of europium activated yttrium oxide ( $Y_2O_3:Eu$ ), a well-known rare earth phosphor, at temperatures around 1100 K to evaluate the precision with which differential temperature can be determined. In the future we intend to investigate absolute temperature determination by the fluorescence method, and will include the use of standard freeze point cells for appropriate normalization.

## FLUORESCENCE CHARACTERISTICS OF $Y_2O_3:EU$

Figure 1 shows the emission spectrum of  $Y_2O_3:Eu$ . The Eu in the samples we used was 6.8% by weight, a standard formulation<sup>7</sup> to produce a cathode ray tube phosphor for the television industry. The emission line selected, a  $5D_0$  transition to the ground state in  $Eu^{+++}$ , is at about 611 nm, accounting for about half the energy emitted in the visible spectrum. The fluorescence was stimulated by a 337-nm nitrogen gas laser with a modest 100  $\mu J$  output pulse persisting for a few ns. For future purposes, when absolute temperature determination will be of major interest, the details of the phosphor composition, including the accuracy with which atomic concentrations can be

determined, will be important; but for this study the important factors were availability of well-studied material and its fluorescence intensity. We know from previous work<sup>4</sup> that the region around 1100 K lies in a region of strong temperature dependence, in fact, in a region where the temperature response is very close to linearly correlated to the natural log of the fluorescence lifetime.

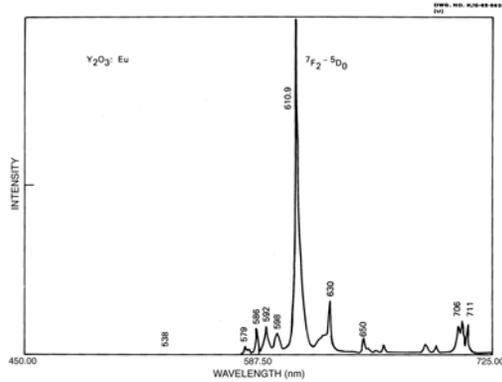


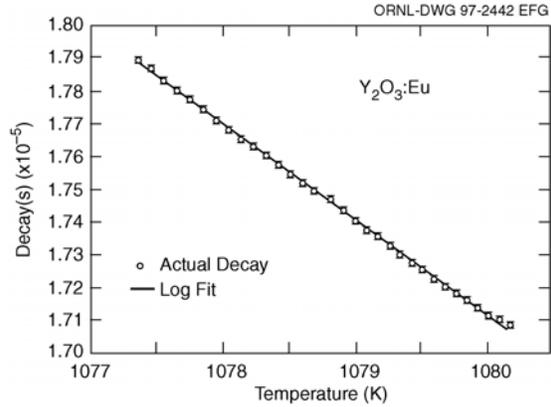
Fig. 1. Fluorescence spectrum of strongest lines.

**FIGURE 1. FLUORESCENCE SPECTRUM OF STRONGEST LINES OF  $Y_2O_3:Eu$**

The measurement data consists of fluorescence intensity versus time. We used both the direct intensity and its natural log. The signal intensity  $I$  at any time can be written, to a very close approximation, as

$$I = I_0 e^{-t/\tau}, \quad (1)$$

where  $t$  is the time,  $I_0$  is the intensity at  $t = 0$ , and  $\tau$  is the “lifetime”. This lifetime  $\tau$  is the slope of the natural log of the time dependent emission, therefore, a critical parameter associated with temperature.



**FIGURE 3. PRECISION HIGH TEMPERATURE RESPONSE**

## EXPERIMENTAL ARRANGEMENT

Figure 2 is a block diagram of the experimental arrangement used. The nitrogen gas laser (337 nm emission) could be triggered by an internal or external pulser to produce a repetition rate up to about 20 Hz. The 337 nm emission was reflected from a tuned-frequency dichroic mirror and focused into a high-purity silica optical waveguide 1.5 mm in diameter housed in an alumina sleeve. The waveguide was inserted through the insulation into the hot zone of a Thermaline Model F46240CM controlled temperature furnace, terminating in a hole bored in a pressed alumina thermal mass with a volume of about 1000 cm<sup>3</sup>. Parallel to the optical waveguide was a similar alumina sleeve containing a calibrated thermocouple. The thermocouple junction was bent to come into near contact with the end of the waveguide, upon which a thin layer of phosphor had been deposited. With this assembly contained within the alumina block we could expect only gradual cooling or heating of the bored-out zone. In particular, we could allow the temperature to drift slowly downward without having to apply power to the furnace. Or, we could arrange conditions where a continuous application of power could produce a steady temperature increase. Since the furnace controller was a thermostatically activated, in cases where the temperature was set at some specific value, it could be expected to add occasional unpredictable power inputs to the furnace coils. The returning fluorescence, passing back down the same waveguide, transmits through the dichroic mirror and is focused through a narrowband filter or into a grating monochromator, then is sensed by a photomultiplier. The photomultiplier signal, an electric current pulse, is recorded as a function of time in an

oscilloscope linked to a personal computer. Software in the computer is used to analyze the collected waveforms to yield a value of  $\tau$ , which correlates to temperature.

## DATA ANALYSIS

We come here to the heart of this study. The information available from the measurement environment consisted of a waveform, digitized at a

100MHz rate, containing about 500 time increments for each of which an intensity, measured with 8-bit accuracy, was associated. Two or more consecutive waveforms could be averaged and the resultant waveform transmitted and stored directly in the memory and hard disk drive of the personal computer. The resultant waveform was analyzed by a LabView<sup>8</sup> virtual instrument (vi) software program written to encode the algorithms and procedures we developed. The elements

ORNL 99-1008C EFG

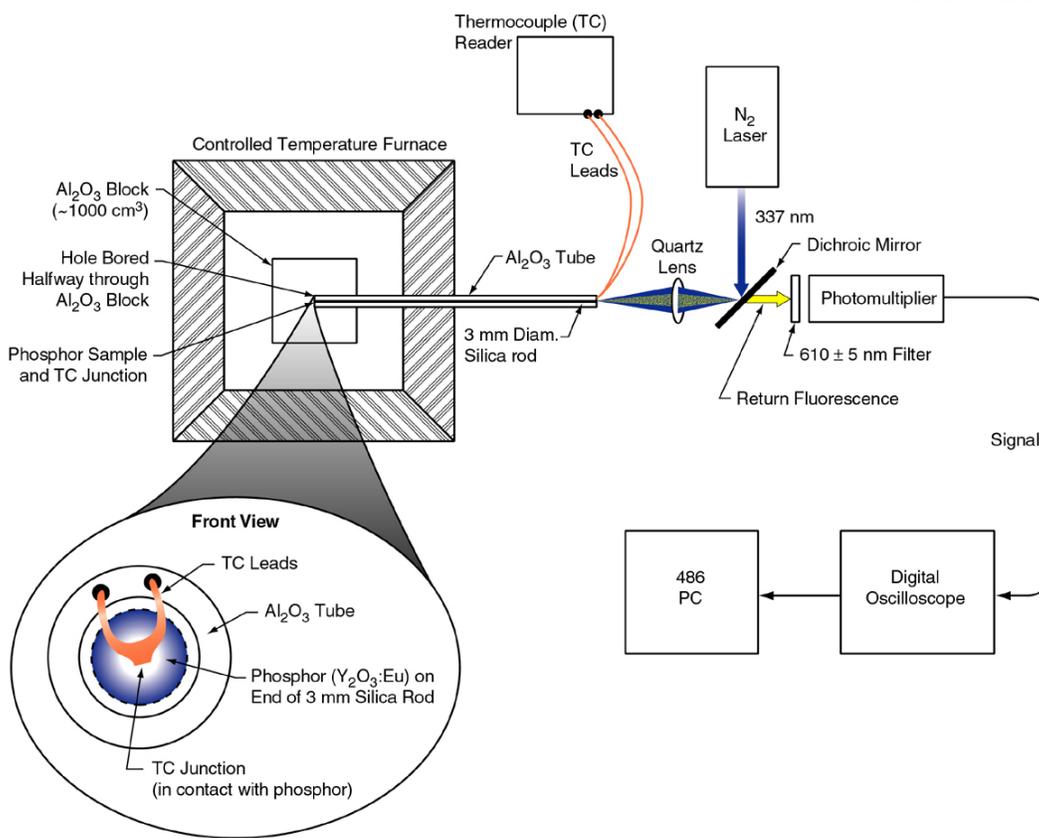


FIGURE 2. EXPERIMENTAL ARRANGEMENT

of the analysis used are as follows: (1) calculating the zero level (or dark level) of the signal by averaging the data just in advance of the laser pulse, (2) subtracting that zero level from the raw data to eliminate any ambient steady-state background, (3) taking the natural logarithm of the absolute value of the zero-referenced waveform intensities (after eliminating all zero data values), (4) selecting two times after the scope trigger

(cursor settings) between which to analyze the data, (5) doing a linear fit between the cursors with chi-square goodness of fit optimized, (6) determining the slope of the fit to obtain a value for  $\tau$ , and (7) calculating the temperature by insertion of  $\tau$  in a calibration function associating the two. This last step, calculating the temperature, relates to the precision metrology only in expressing  $\tau$ , the measured quantity, in terms of a

physical quantity. Any absolute determination of temperature would require comparison with established standards such as metallic freeze points, as well as further quantification of degree of correlation between the  $\tau$  of the phosphor's single exponential decay characteristic and all the physical quantities, including temperature, which can affect it.

### *Logarithms of Waveforms*

The first three steps in the analysis are the most critical. To characterize the accuracy of a waveform comprised of the fluorescent intensity versus time it is necessary to quantify the effects of (a) the linearity of the photomultiplier response to light, (b) background photomultiplier signal resulting from the flash of the laser (but not from any resultant fluorescence), (c) the non-laser-induced background signal (signal resulting from sources other than the laser flash), (d) the digital range of signal amplitude stored in the oscilloscope and computer, (e) the digital range of the time base stored in the scope and computer, and (f) digital range of the computer memory.

### *Cursor Settings*

Consistency of measurement requires that the cursor settings, determining the region in which to process the data, be set in such a way as to be relatively unaffected by noise fluctuations in the signal. Our method was to do a linear fit to the logarithm of the data, with starting and ending points for the fit established as a percentage of the maximum signal amplitude. The first microsecond after the laser flash was excluded from the analysis because of the likelihood that some laser-induced (but independent of the fluorescence of interest) excursion of the signal would occur. This first fit produces an analytically smooth function used to select the amplitude levels between which to extract the decay to be used in the analysis. By this process, random shifts in the cursor positions will not occur, eliminating any statistical effects in the extraction of  $\tau$  that result strictly from random movement of cursor positions.

We further refined this process by examining the goodness of fit of the final linear fit between the cursors. We moved the cursors a small percentage both to the left and right of the selected position, refit the data and examined the resulting goodness of fit numbers. If the fit improved in new locations we shifted the cursors appropriately. Our eventual plans in this regard are to actually find the minimum (best

fit) value within an allowed region of data. It turned out, however, that the slight improvement resulting from examining goodness of fit was not significant in the current analysis. Such an approach, however, is expected to be important as we further eliminate other background and noise effects.

### *Linear Fits*

As mentioned, the fits were done to the natural logarithms of the data. An improved approach is to fit the original data with an exponential function. The two are identical processes when the data are free of noise, but as the signal decreases the noise on the logarithm is more and more significant, compared with the noise on the original signal. Again, we found little significant difference in the two approaches (for this present analysis), so we used the logarithm fits, since the straight-line evaluation was easier to monitor during the measurements. Through this careful cursor positioning, within a temperature range that did not correspond to large changes in lifetime, the comparisons between fits of logarithms were adequately precise that effects in the fourth and fifth significant figures were determined to be non-statistical.

### *Slopes of Linear Fits*

Evaluating  $\tau$  is straightforward after the linear fit is completed. In our results we maintained five significant figures because we were able to confirm meaningful changes in the fourth and fifth figures. This was originally noticed when we left the furnace at a fixed temperature setting. The furnace current and voltage could be monitored, so we could determine when the furnace controller activated the heating coils. As the temperature (according to the thermocouples used to control the furnace) drifted down between each one-degree centigrade precision of the setting, we confirmed changes in  $\tau$  that were consistent with the downward drift, and similarly consistent changes in  $\tau$  when the controller circuitry (after a full one-degree change had occurred in the thermocouple readings) activated the coils. It was these fluctuations, as mentioned previously, that led us to the conclusion to let the furnace temperature fall, with no coil current, during the analysis.

### *Temperature Determination*

The correlation of  $\tau$  with temperature, in our previous work, has been achieved by fitting calibration

data measured with standard thermocouples over the temperature range of interest for some particular phosphor and emission line. For the present work the main emphasis is on the correlation of  $\tau$  values measured as temperature is gradually changing, not the specific temperatures themselves. However, since temperature differentials approximately correspond to differentials in  $\log(\tau)$  over the measurement range chosen (near 1100 K), we can, if desired, also express the differentials in terms of temperature. Using temperature in this way has the advantage of allowing us to do correlations with a unit that has more immediate metrological meaning, and directly comparable with temperature precisions obtained using other measurement techniques.

The data study here focused on the decay time  $\tau$ , because the correspondence with temperature can be precisely related by an analytical function fit through calibration data previously obtained. An important note in this regard is that for  $Y_2O_3:Eu$  near the low temperature end of the temperature-sensitive range (between about 400 C to 600 C), the fit departs the approximate straight-line fit for the higher temperature end of the range. In this work, however, we remained in this higher temperature region; consequently, it is mathematically similar to analyze either as  $\log(\tau)$  or temperature. Figure 4 illustrates this logarithmic relationship, with  $\log(\tau)$  plotted versus temperature over a range of more than 100 degrees in the region of 1100 K. The temperatures used were taken from a smooth fit across the reference thermocouple readings correlated with the drift time, assuming a monotonic temperature decrease from Newton's law of cooling of the thermal mass.

#### *Discussion of the analysis*

As noted, it was observed that the decay time measurement, at a given temperature, varied only in the fourth or fifth decimal place. For this phosphor at these temperatures, the change in lifetime is about 1.5% over 1 K. This sensitivity is comparable to the material used by Zhang et al<sup>9</sup> in a related study near room temperature.

To determine the limits of precision of the temperature measurement, the analysis assumes that the change in the temperature of the phosphor as well as the change in decay time is gradual and smooth. An autocorrelation analysis (using the Allan variance<sup>10</sup>) indicates the smoothness of the data by comparing each decay time measurement with a number  $n$  of measurements before and after it. The difference between a measurement and that predicted by the

previous and following measurements therefore supplies a totally parameter-free comparison of the data to an unknown smooth curve. The variance  $\sigma^2$  of experimental data from this unknown curve can be shown to be

$$\sigma^2 = (2/3)[(\sigma_{AC})^2 - \langle \kappa_i^2 \rangle], \quad (2)$$

where  $\kappa_i$  is the curvature (second derivative) of the true function at the  $i$ th point, and  $(\sigma_{AC})^2$  is a measure of the root mean squared error determined by autocorrelation analysis and given by

$$(\sigma_{AC})^2 = 1/(n-1) \sum [y_i - (y_{i+1} + y_{i-1})/2]^2. \quad (3)$$

The particular data point is  $y_i$ . It should be noted that this expression overestimates the error slightly by implicitly assuming zero curvature in the experimental data. Because the relationship between decay time and temperature is approximately logarithmic, the data indeed have an element of curvature. If curvature error were removed, the calculated variance would be further reduced. In spite of unresolved noise due to instrumentation, data were collected with a variance as low as 0.00225  $\mu s$ , where the temperature determined by a thermocouple changed  $\sim 3.75$  K/ $\mu s$ . This suggests an uncertainty in relative temperature prediction of about 8.5 mK.

## CONCLUSION

Precision measurement using the temperature-dependent fluorescence properties of the rare-earth phosphor,  $Y_2O_3:Eu$ , has demonstrated, near 1100 K, the ability to measure differences of less than 10 mK. The technique demonstrated uses the change in fluorescence lifetime as a precise temperature metric. Since the method involves the temperature response of molecular lattices it yields absolute measurements and can be expected, with improvement of signal analysis and other laboratory refinements, to provide metrological precision and accuracy in the important temperature region above the aluminum freeze point.

## ACKNOWLEDGMENTS

The authors are deeply grateful to Stephen Allison of Oak Ridge National Laboratory for his efforts in many areas associated with this paper, especially his encouragement, and in helping maintain and manage the large amount of data accumulated in the experiments. Many thanks go to Todd Smith for writing the LabView analysis routines. Also, the support and discussions with Professor George Gillies of the University of Virginia have been especially useful in correlating the work with other metrological efforts.

## REFERENCES

1. M. R. Cates, S. W. Allison, M. A. Nelson, L. A. Franks, T. J. Davies, and B. W. Noel, "Remote Thermometry of Moving Surfaces by Laser-Induced Fluorescence of Bonded Phosphor," Proc. of the International Conf. on Applications of Lasers and Electro-optics, Los Angeles, (November 1983).
2. M. R. Cates, S. W. Allison, B. R. Marshall, T. J. Davies, L. A. Franks, M. A. Nelson, and B. W. Noel, "Laser-Based Data Acquisition in Gas Centrifuge Environments Using Optical Fibers," Proc. SPIE Conf. on Fiber Optics in Adverse Environments, San Diego, (August 1984).
3. A. R. Bugos, D. L. Beshears, M. R. Cates, and S. W. Allison, "Emission Properties of Phosphors for High Temperature Sensor Applications," published in the IEEE Proc. of Southeastcon '88.
4. K. W. Tobin, S. W. Allison, M. R. Cates, G. J. Capps, D. L. Beshears and M. Cyr, "Remote High-Temperature Thermometry of Rotating Test Blades Using YVO<sub>4</sub>:Eu and Y<sub>2</sub>O<sub>3</sub>:Eu Thermographic Phosphors," published in the Proc. of the AIAA/ASME/SAE/ASEE 24th Joint Propulsion Conference, Boston, Maine, July 11-13 (1988).
5. G. T. Gillies, "Ultra-Precision Phosphor Thermometry," University of Virginia report UVA/527594/MANE97/101, August 1996.
6. M. R. Cates, D. L. Beshears and S. W. Allison 1993. "Fluorescent Thermometry for Advanced High-Temperature Materials," Proc. 3rd Int. Conf. on Intelligent Materials/ 3rd European Conf. on Smart Structures and Materials, Lyon, France, June 3-5,1996.
7. GTE Sylvania Corporation, Type 2342 Luminescent Material.
8. LabView version 3.1 for Windows, copyright, National Instruments Corporation, Austin, Texas, USA.
9. Z. Y. Zhang, K. T. V. Grattan, A. W. Palmer, B. T. Meggitt, "Spectral characteristics and effects of heat treatment on intrinsic Nd-doped fiber thermometer probes," Rev. Sci. Instr., 69, 139-145 (1998).
10. D. W. Allan, IEEE Trans. Instrum. Meas. 36 646 (1987), Proc. IEEE 54 221 (1966).
11. K. A. Wickersheim et al, "Study of Rare Earth Activated Materials for Radiation-Sensing Applications," Third Annual Report, Lockheed Missiles & Space Company, 4-17-69-1 (June 1969).
12. C. W. Struck and W. H. Fonger, "Role of the Charge Transfer States in Feeding and Thermally Emptying the 5D State of Eu<sup>3+</sup> in Y<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>," Journal of Luminescence, 1, No. 2, 456-469 (1970).

## **LIST OF FIGURES**

Figure 1. Fluorescence spectrum of strongest lines

Figure 2. Precision high temperature response

Figure 3. Experimental arrangement