Recent Developments Involving Thermographic Phosphors

S. W. Allison, M. R. Cates, D. L. Beshears

Oak Ridge National Laboratory, 2360 Cherahala Blvd., Knoxville, TN 37932

Abstract

In the past year we have made significant advances in identifying and testing short-decay time phosphors, testing high temperature binder materials, testing phosphors to very high temperatures, and measuring microcantilever temperatures. We tested a variety of cerium-doped phosphors, which, prior to quenching, exhibit decay times of 60 ns. The short decay means such phosphors are particularly good for imaging surfaces moving at high speeds. A new binder combination was mixed with any of several YAG phosphor compounds, and showed good adherence to at least 1000 C. Testing will shortly commence to 1500 C. Microcantilevers are key components of many MEMS (microelectromechanical systems) devices. We attached phosphor to one such cantilever. The piezoresistive cantilever heated with application of a current. The temperature rise was approximately 500 C for about 5 ma.

1. Introduction

Thermographic phosphors have been developed by ORNL and collaborators for nearly 20 years in a variety of applications, including monitoring temperatures in centrifuges, turbine engines, electric motors, automotive engines, and steel manufacturing lines (1). This thermometry technique makes use of the thermally sensitive properties of the fluorescence of certain ceramic compounds. Usually the fluorescing material is in the form of a fine powder (phosphor) but it may also be in the form of a small crystal or amorphous solid. Described here are developments over the past year.

II. Short Decay Time Phosphors

For transient measurements and for surfaces that are moving rapidly, short decay time phosphors are desirable. It is especially necessary for fluorescence imaging. Significant motion of a pixel will occur even if the decay time is a few microseconds. According to reference [2], cerium doped phosphors typically exhibit the shortest decay times. A number of these have been formulated and tested. Figure 1 shows a representative example yttrium aluminum garnet compound with temperature dependence exhibited at and below ambient temperature. Adjusting gallium content or substituting other rare earths for the yttrium adjusts the range over which the emission is temperature-dependent (3).

The oscilloscope used for these measurements was a Tektronix model 3052 with specification of 500 MHz. Excitation was with a 3 ns duration nitrogen laser, 337 nm. A Hamamatsu photomultiplier with a 3 ns rise time was used. The scatter in the data is larger than is usual for thermophosphors. This is due to the fact that the signals typically had some ringing due to slight impedance mismatch complicating the data analysis. Another example of experimental peculiarities for these short duration measurements was the fact that the phosphors are so bright, care had to be taken to prevent saturation of the photomultiplier tube. This occurs when too many photons arrive in a short period of time and the tube responds sublinearly to the signal. The laser had to be attenuated to the point that fluorescence was barely visible to the eye in order to keep from saturation. Linear response was established for signal levels of about a volt into 50 ohms.
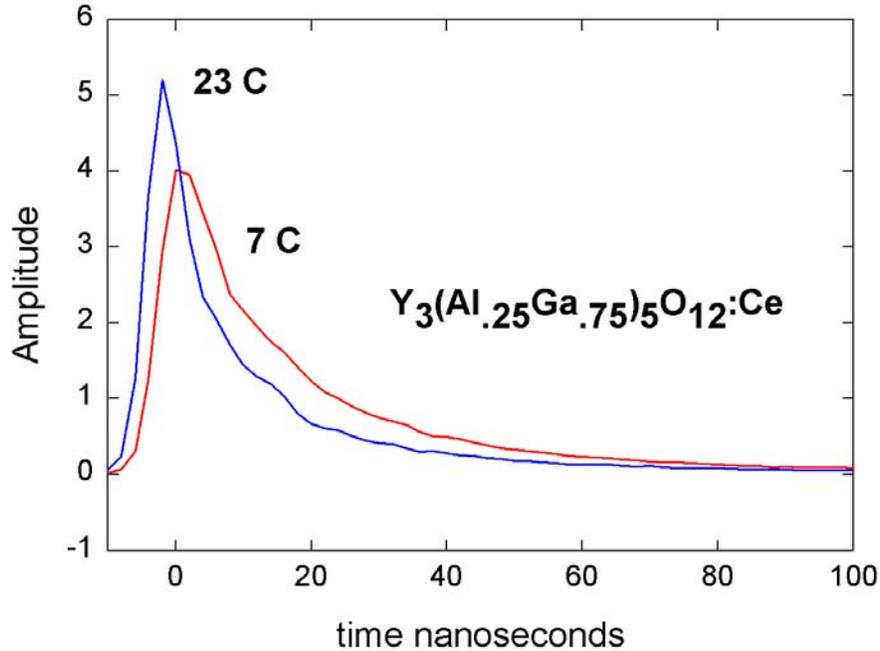
Figure 1. Emission from $Y_3(Al_{.25}Ga_{.75})_5O_{12}$:Ce.

Figure 2 shows a plot of decay time versus temperature for Ce-doped garnet phosphors with varying gallium content as shown. The general formula is $Y_3(Ga_xAl_{1-x})_5O_{12}$:Ce and x varied from 0 to 0.75   All but one of the phosphors were procured from Phosphor Technology of Essex, England.   The one exception is sample 1 for x = 0 which came from GTE Sylvania (now known as Osram Sylvania). From the plot it is seen that no one phosphor can cover the entire range from ambient to 300. The effect of the gallium is to shift the temperature dependence. High gallium content moves the calibration curve to lower temperatures. There are two exceptions to this trend. It is seen that there is little difference between the two Phosphor Technology samples X = 0.25 and X = 0 sample 2. There is a considerable difference between the X = 0 sample 1 (GTE Sylvania) and X = 0 sample 2 (Phosphor Technology). Our first conjecture is that cerium concentration may play a role.   This could be addressed in future investigations. The garnets seem to exhibit most of the characteristics that are required including the fact that they may be excited with blue light emitting diodes. An emission spectrum in relation to a pressure sensitive paint spectrum is depicted in reference 1. The emission peaks at around 500 nm but there is a tail that extends into the red. The degree to which this may interfere with PSP emission should be addressed. There appeared to be a slight change in decay time with emission wavelength.
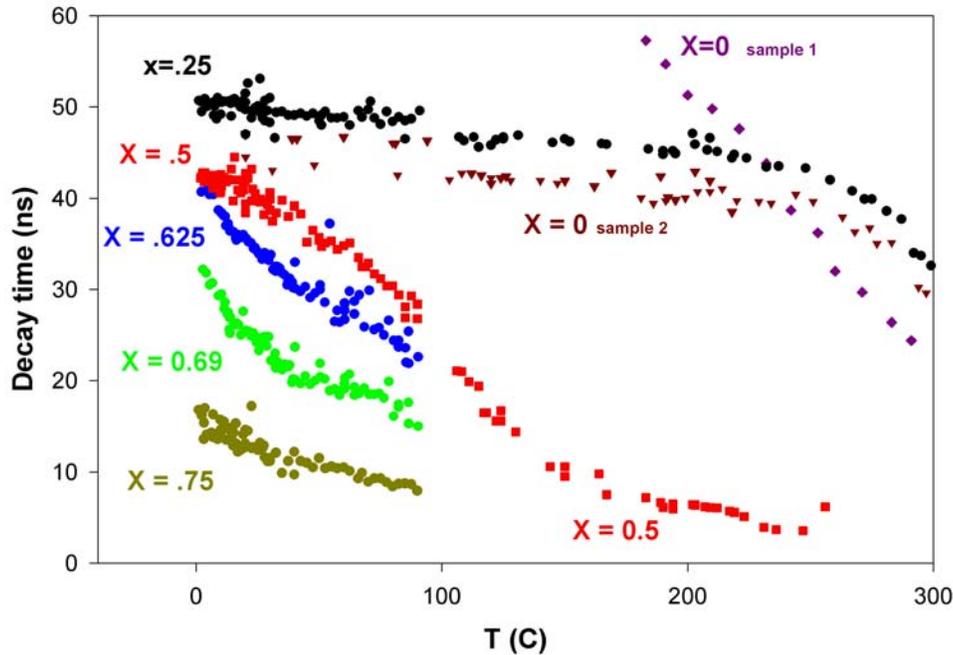
Figure 2. Final YAG:Ce

The garnet materials hold much promise for fast response applications with pressure sensitive paints. Of course testing and further development will be required to establish this. We have some other additional samples on hand for further testing wherein the yttrium is replaced with lanthanum or gadolinium. Cerium-doped silicates are also of interest, these tend to fluorescence in the blue and near UV. The silicates cannot be excited with a blue LED but should be excitable with an ultraviolet LED, nitrogen laser, or tripled YAG laser.

III. High Temperature Sprayable Binder

In efforts for NASA Glenn, we were tasked with identifying and testing phosphor binders that could be applied in-situ on large areas and which could adhere up to 1000 C. The effort, described in references 5 and 6, led to a binder mixture successfully applied to metal and composite surfaces. The two binder products, termed HPC and LK by the manufacturer, ZYP Coatings of Oak Ridge, TN, were combined in a 50/50 ratio by volume. HPC is composed of magnesium and aluminum silicate. Maximum recommended temperature use is 1500 C. To cure, the material should be raised to 700 C and brought back to room temperature slowly. LK is silica-based with other additives. Maximum recommended temperature use is 1100 C and it is cured in the same manner as HPC.

Figure 3 is a photo of the test specimens after 5 cycles to 1000 C for the HPC/LK combination. Adherence in this case is judged by scraping a finger across the surface. The adherence and uniformity were good. Illumination with a UV lamp produced the characteristic red fluorescence of the phosphor.
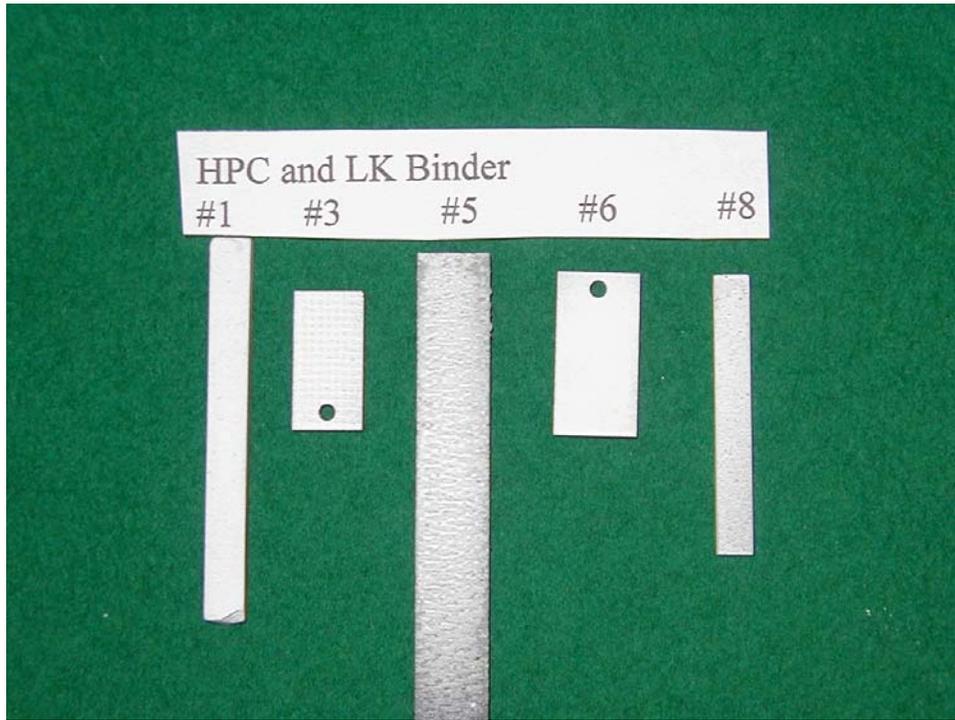
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**Figure 3. Phosphor/Binder coating on silicon nitride (sample #1),
SiC/SiC (samples #3,5,6), and silica (sample #8).**

IV. Thermometry of Microcantilever

Piezoresistive cantilevers have received much attention as potential sensors. When a prepared cantilever of this type bends in response to a change in its environment, its resistance changes. A simple Wheatstone bridge circuit measures this resistance, and, therefore, a bias current must be applied across the piezolever to measure its resistance. In the course of work aimed at characterizing such levers as magnetic field and electrical current sensors, we determined that the cantilever heated significantly. Bias currents as low as 10 mA cause the cantilever structure to glow like a light bulb filament. The phosphor method for measuring cantilever temperature was then pursued (7). Figure 4 shows a picture of a cantilever to which phosphor and Sperex binder were applied. The particle size of this particular sample of Mg_4FGeO_6:Mn phosphor was rather large and particles tended to clump together as seen. Nonetheless, temperature measurement was demonstrated.

Figure 4. Piezoresisive Microcantilever with phosphor particles.

An example plot of cantilever temperature versus current is shown in figure 5. The cantilever's resistance was determined empirically to be a function of temperature. In the figure, it is seen that the temperature scales with ohmic heating (i^2R) up to about 2 ½ mamps. Above that, its possible that convective air currents and perhaps other effects prevent the phosphor form reaching equilibrium with the cantilever.
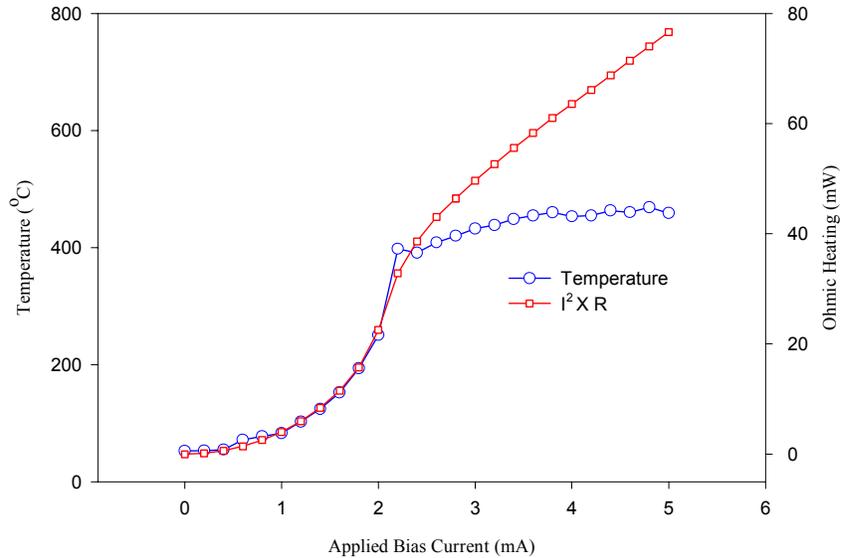

Figure 5. Comparison of measured temperature with expected temperature rise due to ohmic heating.

In other tests, when a pulse of current was applied to the cantilever, the time required for the phosphor method to equilibrate and provide a temperature measurement was about 5 ms. This is commensurate with the phosphor decay time, which is about 2 ms near 200 C, and about the temperature at which the transient measurement was performed. Future efforts could well improve upon the performance by using phosphor that is finer and applied intimately and uniformly, exhibits a short decay time, and which covers a higher temperature range.

IV. Signal Integration Method for Transient Thermometry

The phosphor method is well suited to measuring small temperature changes. We recently had an opportunity to perform transient temperature tests in an experiment related to the generation of spallation neutrons. To produce such neutrons, a high energy (800 MeV) beam of protons is incident on a container filled with liquid mercury. The rapid deposition of energy into the liquid by the proton beam leads to shock heating of the mercury and rapid strain of the container. In order to diagnose temperature inside the container, various probes were inserted into the liquid. A fiber with phosphor on the end was inserted so that it sampled the temperature on the beam axis 2 inches from the entrance of the container. Several thermocouples where inserted at other positions. The proton beam is a low duty cycle device. Shots may occur no sooner than about 10 minutes apart. Thus signal averaging is not a viable option.

For this situation, a new data analysis method was implemented. For the tests, within about a minute before the proton beam was fired, a phosphor signal was acquired by pulsing the laser thirty times and averaging the results. This acquired signal was designated as the "preshot" signal and, owing to the averaging, its signal-to-noise characteristic was fairly good. To determine temperature change, the preshot signal is compared with the after shot data by integrating the signals, I, from an initial time defined as zero to a later time, b, and forming the ratio.

The calibration curve used to determine the temperature change was obtained from decay time data by noting that:

$$I_1 = \int_0^b A \bullet \exp(-t/\tau)dt = A \cdot \tau \cdot (1 - e^{-\frac{b}{\tau}})$$

$$\approx A \cdot \tau \quad \text{for } b \gg \tau$$

Since A is essentially independent of temperature for changes in temperature of less than 50 C and the data follows a straight line, this is valid. For two signals, the ratio of the integrated signals will indicate temperature by:

$$I_1 = A \cdot \tau_1 \qquad I_2 = B \cdot \tau_2$$

$$\frac{I_1}{I_2} = \frac{A}{B} \cdot \frac{\tau_1}{\tau_2}$$

The data used to plot the calibration curve was fit to a first order linear regression with the result:

$$\Delta T = 95.76 - 47.94 \cdot \log(\frac{I_{preshot}}{I_{signal}})$$

Where the ratio is suitably normalized with A/B. For the subsequent data analysis, the first three microseconds of the signals are ignored since laser leakage contributes to the signal. {Further description in Reference 8}
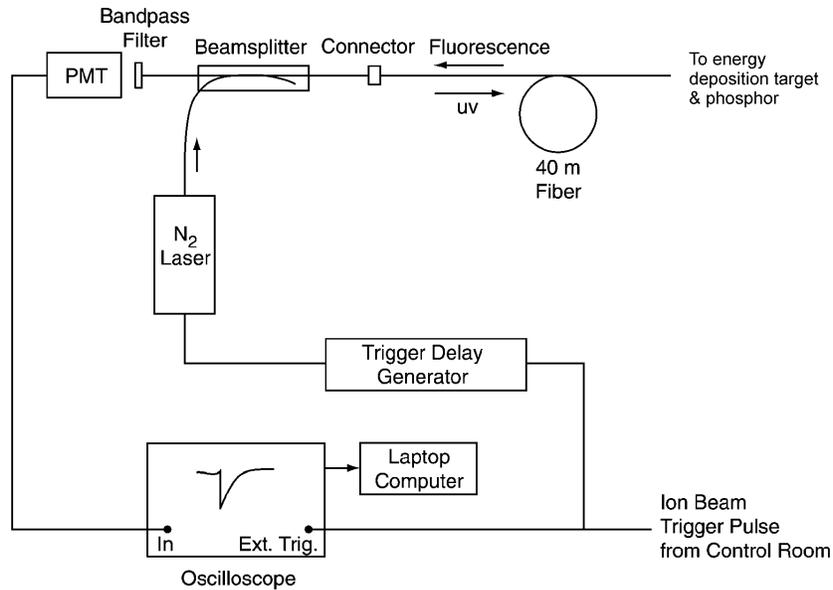
Figure 6. Block Diagram of Thermal Shock Tests.

The arrangement for acquiring phosphor data is in Figure 6. The timing of the laser could be varied with respect to the ion beam trigger, which occurred about 9 microseconds before the actual proton beam pulse.

Figure 7 shows the preshot averaged signal (black curve). Also shown are single shot signals for ¼ (green), ½ (red), and full power (blue), respectively. They were produced by triggering the laser 1.1 ms after the proton beam. They are of course much noisier than the averaged curve, probably due to shot-noise from the photomultiplier.   A fraction of the laser beam reflects from the connector of figure 6 and the end of the fiber where it connects to the fiber in the target. The laser reflections that are indicated in figure 7 are a result of reflection at a fiber coupler and the end of the fiber. Consequently, analysis of the fluorescence begins at a point in time after these reflections. Figure 8 shows the results of plotting the integrated signal as it changes in time. It appears that the values of the integrated signal do approach a limiting value from which a temperature may be obtained. These data also correlate well with thermocouple data placed in the vicinity.
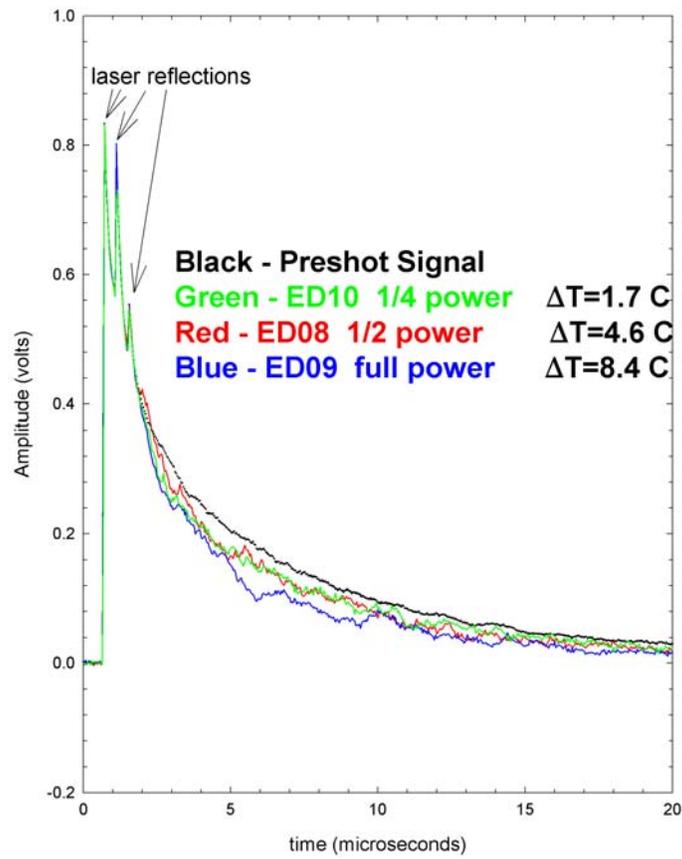
**Figure 7. Phosphor fluorescence 1.1 ms after proton beam
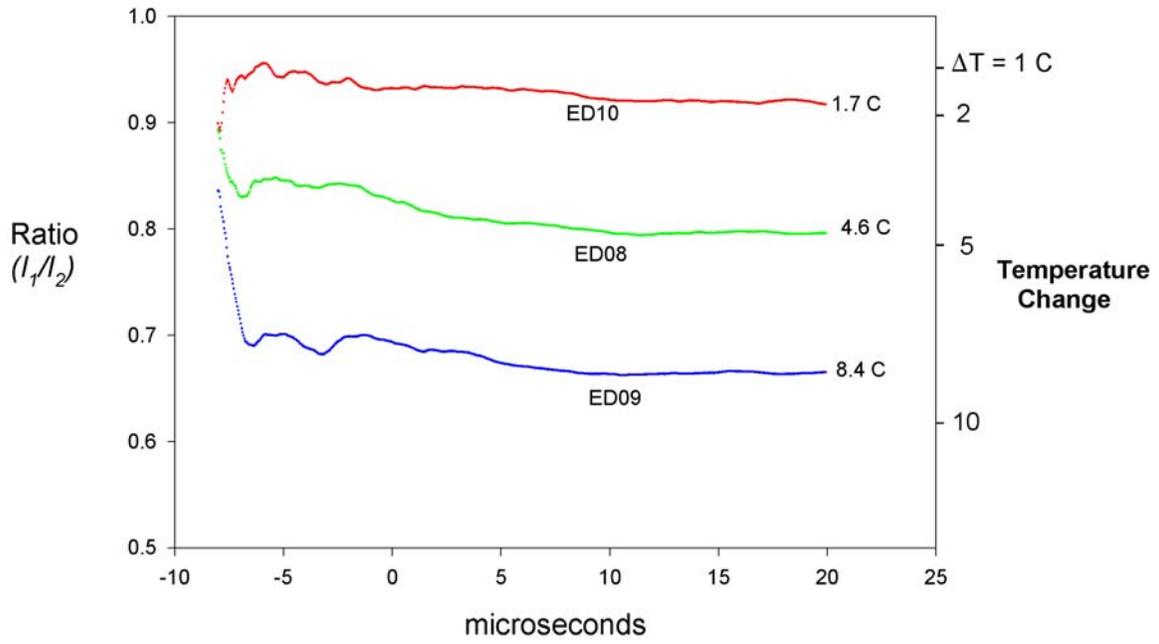for 1/4, 1/2, and full power.**

**Figure 8. Comparison of integrated signals for proton beam at
¼ (ED10), ½ (ED08), and full power (ED10).**

6. Conclusions

We have described phosphor thermometry activities aimed at specific applications to imaging, pressure sensitive paint calibration, high temperature thermometry, MEMS device thermometry, and diagnostics for the Spallation Neutron Source project. These efforts are examples of the wide variety of situations that may be addressed by utilizing phosphor fluorescence. The data obtained while useful to the projects at hand also add to a growing body of knowledge involving this approach.   It will therefore serve as an experience and information base for even more challenging thermal measurement problems in the future.

7. References

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