Phosphor Thermometry at ORNL

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Abstract. Phosphor materials are, by design, capable of efficiently converting excitation energy into fluorescence. The temperature-dependent characteristics of this fluorescence provide the basis for noncontact thermometry. In the past decade this approach has been applied to turbine engine diagnostics, liquid temperature measurements for heat pump research, combustion engine intake valve and piston measurements, galvanneal steel processing, transient thermometry of particle beam targets, and microcantilevers used in MEMS devices. The temperatures involved range from ambient to in excess of 1200 C. Some of these applications have involved fiber optics for light delivery and/or fluorescence signal collection. In addition to fielding these applications, there has been considerable work in the laboratory aimed at exploring further improvements and adding to the database of temperature-characterized phosphors. The activities involve investigation of short-decay time phosphors for use on imaging surfaces moving at high speeds, measuring and modeling pressure as well as temperature dependence, developing to phosphor adhesion methods, developing phase-based data acquisition approaches. A significant advance is that light-emitting diodes can now be used to provide adequate stimulation of fluorescence in some applications. Recently nanophosphors have become available. The spectral properties and, by implication, thermal dependence of these properties change which particle size. This has ramifications that need to be explored. The ways in which such materials can be exploited for micro- and nano-technology are just now being addressed. These applications and developments mentioned above will be surveyed and discussed as well as envisioned future improvements and new uses for this thermometry technique.

INTRODUCTION

Thermometry using phosphors has been a topic presented at previous Temperature Symposia as far back as 1971[1]. Presented here is progress at Oak Ridge National Lab over the past decade in developing and applying this method. The presentation is divided into two parts. The laboratory developments section describes results of laboratory measurements, which could prove significant for eventual applications. The second section discusses successful application to various temperature measurement problems. Due to space limitations, none of these topics are covered in fine detail. References are given for further investigation. Representative test arrangements, signals, and results provided here will hopefully convey the sense and scope of the activities.

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LABORATORY DEVELOPMENTS

Excitation with Blue Light Emitting Diodes

Red light emitting diodes (LEDs) have been used in the past for exciting red and infrared luminescence from some phosphors[2]. However, the availability of reasonably bright blue and even ultraviolet LEDs increases the number of phosphors that can be thus excited. A number of tests with a double quantum-well LED centered at 450 nm indicated that a wide range of phoshors can be so stimulated, even when the absorption bands are well away from this peak[3]. The advantages of LED light sources are cost, size, and flexibility of use. A decay time measurement or a phase-shift approach may be pursued with them.

Table 1 is a list of a number of phosphors, according to dopant category, which may be excited with this LED. Most of these materials have been used or proposed for various temperature measurement applications. Since phosphor absorption is mainly dependent on the dopant, the table means that most any phosphor with these dopants will be exciteable in this manner. A possible exception is Ce-doped material as its absorption characteristics vary drastically depending on its host.

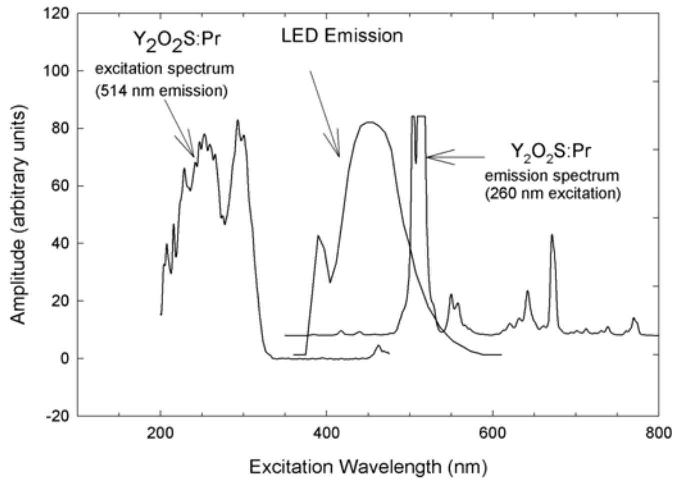

FIGURE 1. EMISSION AND EXCITATION SPECTRA OF Y_2O_2S:PR IN RELATION TO LED EMISSION SPECTRUM

Short Decay Phosphors

Many applications of phosphor thermometry require measurement of rapidly moving surfaces; usually the surface is part of a rotating system. If the phosphor used exhibits a sufficiently long decay time, it will move significantly during the measurement, perhaps even moving out of the field of view. This is especially true for imaging systems where pixel sizes are small. One way to overcome this is to use phosphors with a very short decay time. A survey elicited a number of interesting materials[4],[5]. Effort eventually concentrated on cerium-doped phosphors as it is the dopant with the shortest decay time among rare-earths. YAG:Ce is a commercial product with several formulations and uses. It was determined that the temperature dependence of the material could be somewhat controlled by adjusting the gallium content in the phosphor according to $Y_3(Ga_x Al_{1-x})_5O_{12}$:Ce. The higher the gallium content, the lower the quenching temperature. Figure 2 illustrates this for x = 0.25, 0.5 and 0.75. Several other cerium phosphors proved of interest for showing temperature dependence, for example Y_2SiO_5:Ce. When the yttrium in this material or any YAG material is replaced by Gd or La, a viable thermophosphor results. By choosing the proper host material, temperatures from below ambient to about 600 C may be measured. A wide temperature range is therefore addressed by these cerium doped phosphors.

TABLE 1. Various combinations of ceramic hosts and activators for 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_6	YAG	YAG	Y_2O_2S	YAG
Gd_2O_2S	Gd_2O_2S	YAG			YAlO		
Y_2O_3	YAG						

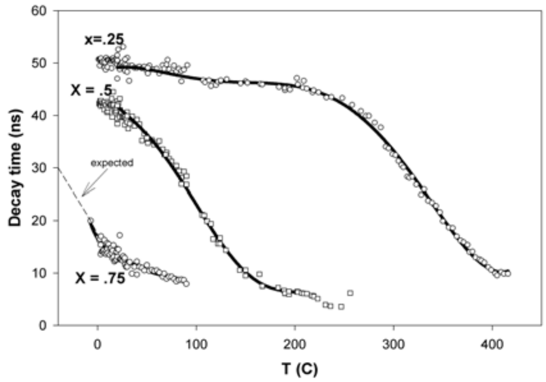

FIGURE 2. $Y_3(Ga_xAl_{1-x})_5O_{12}$**:Ce**

Pressure Measurement

It is well known that phosphor emission changes when subjected to high pressure. Studies of this dependence were conducted for the purpose of possibly exploiting the effects for measurement of high pressure transients and strain. Turley and collaborators[6,7] performed a significant number of characterizations of a number of phosphors. Also a survey of pressure effects and sensitivity was published in Reference 2. Two materials with the most pronounced dependence are La_2O_2S:Eu and Gd_2O_2S:Tb. The decay time of the latter decreases wth pressure. For the former, illustrated in figure 3 below, the decay time increases with pressure.

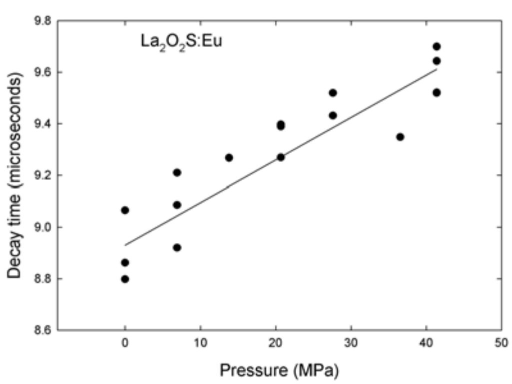

FIGURE 3. DECAY TIME VERSUS PRESSURE

High Temperature

Advances were made in characterizing additional high temperature materials and in taking existing ones to higher temperatures. Example materials that fluoresce above 1000 C are XPO_4:Re where X=Y, Sc, or Lu and Re = Eu or Dy and YAG:Re where Re also includes Tm and Tb. The highest temperature at which fluorescence has been observed is 1706 C. The phosphor is YAG:Dy and the signal is below. An Nd:YAG laser of about 3 mJ at 355 nm excited the phosphor. The signal, see Figure 4, is about .03 V riding on top of a 0.65 V blackbody background signal.

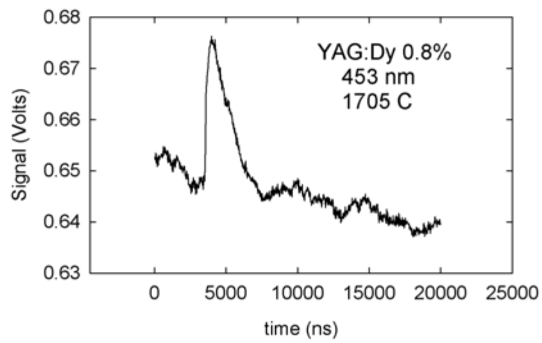

FIGURE 4. FLUORESCENCE DETECTABLE AT 1705 C

APPLICATIONS

Combustion Engine

Temperature measurement of internal components and surfaces inside internal combustion engines enhances understanding during engine operation. Two examples of this are results of measuring the temperature of an intake valve and a piston during the first few minutes after ignition[8,9]. For the intake valve measurement, phosphor is coated on the stem side of the valve. Light is delivered and emission is viewed with a 1-mm optical fiber accessed through the head of an X-car engine. To view the piston, a sapphire window is mounted so the optical axis is normal to the piston surface, Figure 5.

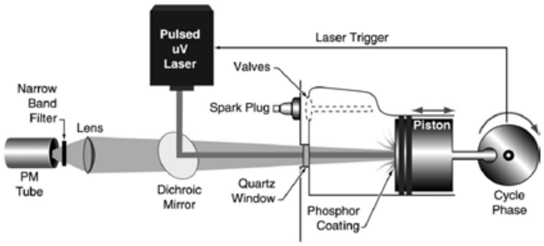

FIGURE 5. PISTON MEASUREMENT APPROACH

For both tests, a nitrogen laser excites fluorescence from a La_2O_2S:Eu phosphor. At low temperatures, to about 70 C, the 514 emission line is monitored. At higher temperatures, the 538 nm emission line is monitored. Results are depicted in Figure 6. The break in the data occurs due to the time required to change bandpass filters. In both cases there is a very rapid increase in temperature followed by a slower increase that approaches a constant value.

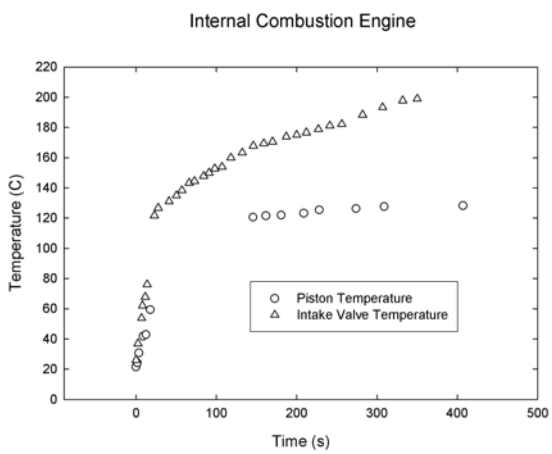

FIGURE 6. DATA FOR PISTON AND INTAKE VALVE

Lithium Bromide Vertical Falling Film

Absorption chillers are based on a thin falling film of lithium bromide (LiBr). Incorporating phosphor in the liquid facilitated thermal measurements which improved the understanding of heat and mass transfer along the chiller tube[10,11]. Temperature in the film ranged from 35 to 50 C with a resolution of 1.5 C. The results showed that a specific approximation used in such studies is valid and can be scaled with absorber tube length and diameter.

SNS Particle Beam Target

The Spallation Neutron source (SNS) project at ORNL is under construction for the purpose of advancing materials science and developing new materials by application of neutron scattering. A study of the interaction of the high-energy proton beam and mercury-filled target containers is underway in order to understand the physics of the event and to enable container design to withstand thermal shock that occurs12,13. For some testing, phosphor-tipped optical fibers are inserted into the mercury to yield temperature. A schematic is in figure 7 where properly timed light from a pulsed (3ns) nitrogen laser is directed to a target with 40-m optical fiber as seen. The data presented here were obtained at the WNR facility of Los Alamos National Laboratory. The beam provided 800 MeV protons of 300 ns duration, about 1013 per shot.

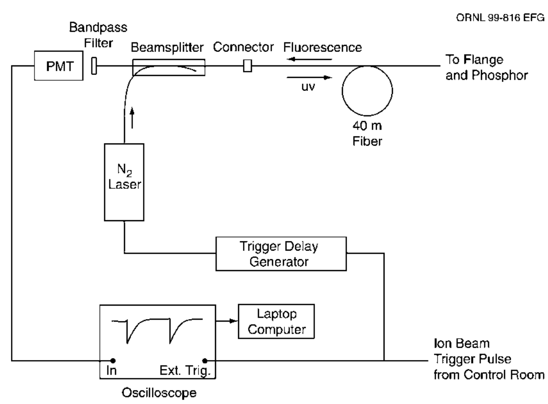

FIGURE 7. SNS HG TARGET SETUP

The phosphor approach allows the temperature to be sample at any time following the beam by adjusting the time delay between the beam and laser.

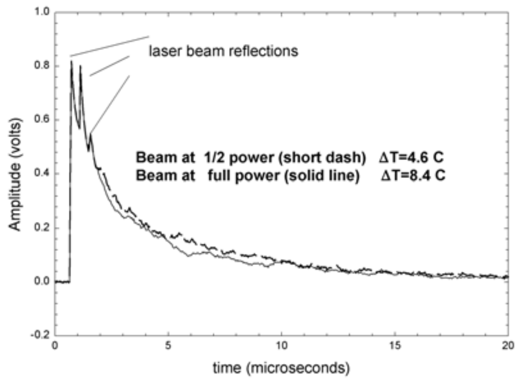

FIGURE 8. TEMPERATURE 1.1 MS AFTER PROTON BEAM

Figure 8 depicts two single shot fluorescence signals acquired 1.1 ms after the proton beam. Clearly the fluorescence decreases more rapidly for the proton beam at full power, indicating a hotter temperature. The beam induced temperature change was 4.6 and 8.4 C respectively. The results were similar to thermocouple data, indicating equilibration by 1.1 ms. Measurements within 50 μs of the beam arrival indicated less heating and that equilibration was not yet attained.

Galvanneal Manufacturing

Galvanneal steel is an important material widely used in production of automobiles. The accurate determination of temperature of galvanneal sheet during manufacture is a critical problem which fluorescence thermometry has recently addressed[14]. In the galvanneal process, steel strip is dipped into a zinc bath. After exiting the bath, the sheet with its molten-zinc coated surface passes through an annealing furnace, which promotes the diffusion of iron into the zinc coating. To control the final microstructure, which defines the end product quality, precise control over the time-temperature relationship is crucial. The constantly changing emissivity of the strip surface and the strip motion rules out most optical pyrometers and thermocouple approaches as practical measurement options. Figure 9 is a schematic of the approach to measurement. Representative data is shown in Figure 10. Other temperature ranges and processes can be addressed by using selecting an appropriate phosphor.

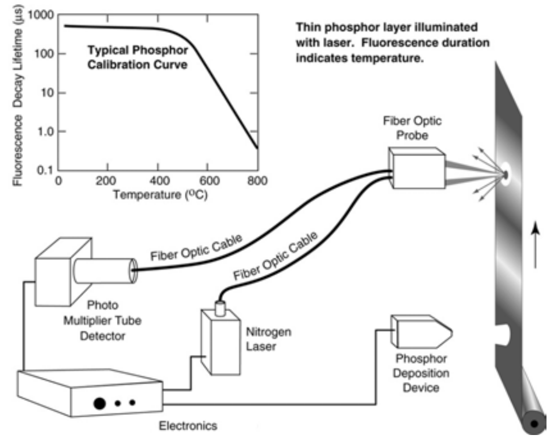

FIGURE 9. GALVANNEAL THERMOMETRY SETUP

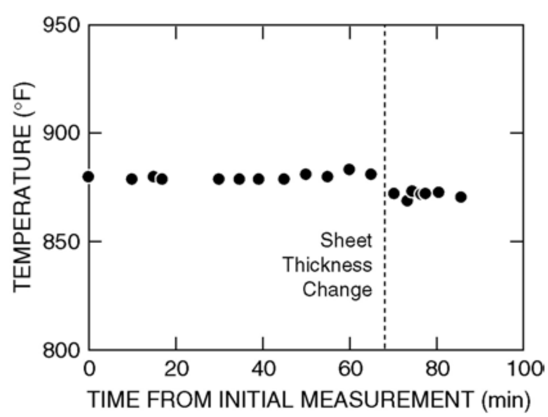

FIGURE 10. GALVANNEL DATA

MEMS

Microelectromechanical systems increased in importance in the last decade. In the course of some testing of piezoelectric microcantilevers, Goedeke noticed the lever glowing red hot[15]. Subsequent investigation using a phosphor determined the temperature versus current over a fairly wide range. A cantilever, similar to one depicted by sihouette in Figure 11 is illuminated with a 200 micron core fiber. The source was either a nitrogen laser or a blue LED (450 nm). Not discernible in the figure is an emission receiving fiber beside the delivery fiber. Measurements were made to about 500 C corresponding to a current of about 5 ma.

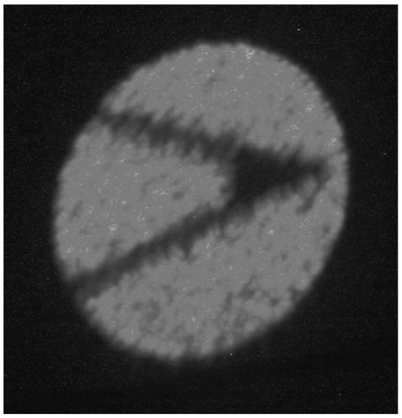

FIGURE 11. MICROCANTILEVER AND EXCITATION FIBER

Figure 12 shows averaged signal from a phosphor-coated cantilever with blue LED excitation. The signal was weak but detectable. The phosphor was magnesium fluorogermanate. For future tests, higher temperature and shorter decay time phosphors will be tested to make possible higher temperature measurement and faster time response. Plans are to use nanophosphors in future experiments, as well.

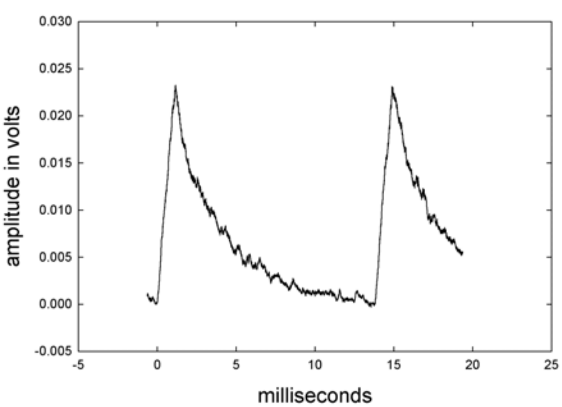

FIGURE 12. CANTILEVER DATA FOR BLUE LED EXCITATION.

CONCLUSIONS

The range and depth of phosphor thermometry applications is increasing. Examples presented here are typical of projects for which the method is best suited. It has turned out that most applications have tended to involve non-contact, difficult-to-access surfaces. It is also the case that many applications have concerned rapid temperature change or rapidly moving surfaces. The MEMS application, which is fairly recent, may indicate a trend toward diagnostics on the micrometer and nanometer level. We have begun experimentation with nanophosphors that may prove useful in this regard.

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