DEVELOPMENT OF FLUORESCENT COATINGS FOR HIGH TEMPERATURE AEROSPACE APPLICATIONS

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ABSTRACT

For many years, phosphor thermometry has been used for non-contact measurements in hostile high temperature environments, including large blackbody radiation backgrounds, vibration, rotation, fire/flame, pressure, or noise. Often these environments restrict the use of more common thermocouples or infrared thermometric techniques. In particular, temperature measurements inside jet turbines, rocket engines, or similar devices are especially amenable to fluorescence techniques. Often the fluorescent materials are used as powders, either suspended in binders and applied like paint or applied as high temperature sprays. These coatings will quickly assume the same temperature as the surface to which they are applied. The temperature dependence of fluorescent materials is a function of the base matrix atoms and a small quantity of added activator or "dopant" ions. Often for high temperature applications, the selected materials are refractory and include rare earth ions. Phosphors like $Y_3Al_5O_{12}$ (YAG) doped with Eu, Dy, or Tm, Y_2O_3 doped with Eu, or similar rare earth compounds, will survive high temperatures and can be configured to emit light that changes rapidly in lifetime and intensity. For example, fluorescence from YAG:Dy and YAG:Tm was recently observed at temperatures above 1400 ºC at the Oak Ridge National Laboratory (ORNL) National Transportation Research Center (NTRC) in Tennessee. This paper will give research results applicable to the use of phosphors for thermometry purposes. Emphasis will be placed on using selected high temperature phosphor paints as a heat flux gauge.

INTRODUCTION

Phosphors are fine powders that are doped with trace elements that give off visible light when suitably excited. Many of them are ceramics and can withstand extremely high temperatures. The fluorescence characteristics change with temperature. A phosphor coating can indicate the temperature of the surface. There are a wide variety of ceramic phosphors that survive hazardous physical and chemical environments, are insoluble in water, durable, and easy to apply. Some phosphors have no trouble surviving and functioning in high temperatures such as those present during combustion.

The basic principle of thermal phosphors is well established, and researchers at ORNL have demonstrated several useful applications [ref. 1-7]. The method relies on measuring the rate of decay of the fluorescent response of an inorganic phosphor as a function of temperature. Having calibrated the phosphor over the temperature range of interest, a small surface deposit of phosphor is excited with a pulsed laser and the fluorescent decay is measured (typically in less than 1 ms) to calculate the temperature of the substrate. In many instances, (e.g., in a continuous steel galvanneal process) a simple puff of powder onto the surface provides an adequate fluorescent signal. Suitable phosphors are available to cover temperature ranges from –265 to 1600 °C [ref. 1-7]. Recently, a YAG:Cr phosphor paint emitted fluorescence in the presence of a high Mach number hydrogen flame at 2200 °C [ref. 8].

Often temperature measurements are made using thermocouples or optical pyrometry. However, in situations where rapid motion or reciprocating equipment is present at high temperatures, it is best to use other techniques. For certain phosphor paints, the prompt fluorescence decay time (τ) varies as a function of temperature and is defined by

$$\mathbf{I = I_0 \exp\left\{-\frac{t}{\tau}\right\}}, \tag{1}$$

where:

I	=	Fluorescence light intensity (arbitrary units),
I_0	=	Initial fluorescence light intensity (arbitrary units),
t	=	Time since cessation of excitation source (s), and
τ	=	Prompt fluorescence decay time (s) [ref. 9].

The time needed to reduce the light intensity to e^{-1} (36.8%) of its original value is defined as the prompt fluorescence decay time. An example of this quantity for Y_2O_3:Eu as a function of temperature is shown in Figure 1.

HEAT FLUX

Measurement of the prompt fluorescence decay time can be correlated with temperature to determine the amount of heat flux present in the sample environment. In the traditional sense, heat flux (q) can be measured through a slab of homogeneous material using

$$\mathbf{q = -k A \frac{\Delta T}{L}}, \tag{2}$$

where:

q	=	Heat flux (W),
k	=	Thermal conductivity (W/m•°C),
A	=	Surface area (m^2),
ΔT	=	Temperature difference across slab (°C), and
L	=	Thickness of the homogeneous slab (m).

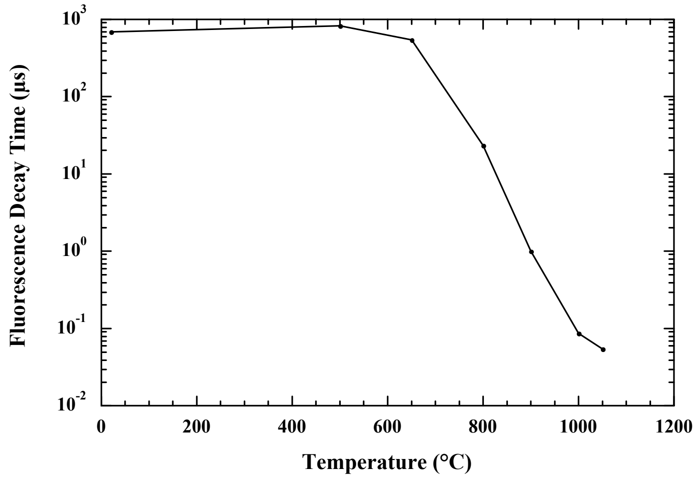

Figure 1. Fluorescence Decay Time for Y_2O_3:Eu as a Function of Temperature

Equation (2) shows the heat flux is proportional to the temperature difference on both sides of a homogeneous slab [ref. 10]. By measuring these temperatures, it is a simple matter to determine the heat flux across any gradient.

In order to measure the heat flux passing through a selected region, it will be necessary to simultaneously excite the phosphor on both surfaces of the material slab. The best excitation source for this task is the pulsed laser, because it emits a desired wavelength of coherent light with a large power density. Lasers used for this purpose should have sufficient power to excite the phosphor paint through the thickness of the gauge material.

This research was designed to determine if fluorescence from YAG:Eu and YAG:Ce could be detected through several thin yttrium stabilized zirconia (YSZ) samples. Results from this research could be used to develop an operational high temperature heat flux gauge.

SAMPLE PREPARATION AND DESCRIPTION

Yttrium Stabilized Zirconia (YSZ)

YSZ samples for this research are divided into crystal and polycrystalline forms as shown in Table 1. The YSZ compound is a combination of approximately 90 % zirconium oxide (ZrO_2) and 10% yttrium oxide (Y_2O_3).

Sample Type	Number of Samples	Diameter (mm)	Available Thicknesses (mm)
(1 0 0) Single Crystal	2	25.4	0.25 and 1.00
Polycrystalline Ceramic	6	25.4	0.11, 0.16, and 0.20

Table 1. YSZ Sample Information

The single crystal YSZ samples have a density of 5.8 g/cm^3 with a lattice constant of 0.541 nm [ref. 11]. The polycrystalline YSZ samples have a density of 6.6 g/cm^3 [ref. 11] with thicknesses of 0.11 mm (4.5 mil), 0.16 mm (6.4 mil), and 0.20 mm (7.4 mil). A thin layer of graphite was applied to one side of each polycrystalline YSZ sample to add strength. After application of the phosphor paint, each polycrystalline sample was heated to 800 °C for eight hours to remove the graphite. This heating cycle also cured the water-based phosphor paint.

Phosphor Paints

Yttrium aluminum garnet ($Y_3Al_5O_{12}$ - YAG) doped with europium (Eu) and cerium (Ce) was used as the active phosphors for this research. Both YAG formulations emit copious fluorescence to temperatures as large as 1000 °C and can easily be excited by a variety of laser wavelengths. Sample emission spectra for YAG:Eu and YAG:Ce on a YSZ substrate is shown in Figure 2. The YAG:Eu phosphor glows bright orange when irradiated with a standard ultraviolet light. Emission peaks at wavelengths of 592, 610, 631, 697, and 710 nm are clearly visible in the YAG:Ce spectrum. Conversely, YAG:Ce glows bright green when irradiated with ultraviolet radiation. The fluorescence emission is centered at 510 nm with a full width at half maximum of about 150 nm.

A mixture of 50% HPC and 50% LK (by volume) was used as a binder for each phosphor paint. Both HPC and LK are manufactured by Zyp Coatings, Incorporated of Oak Ridge, Tennessee [ref. 12]. When cured, HPC is not reactive and is composed of magnesium aluminum silicate. Engineers at Zyp indicate that HPC will withstand temperatures of about 1400 °C. HPC is water based with a shelf life of 12 months. The LK binder is not reactive and is composed 75% SiO_2, 20% K_2O, and 5% Li_2O. Engineers at Zyp indicate that LK will withstand temperatures of about 1100 °C if additional fillers are added to the mix. LK is also water based with a shelf life of 12 months.

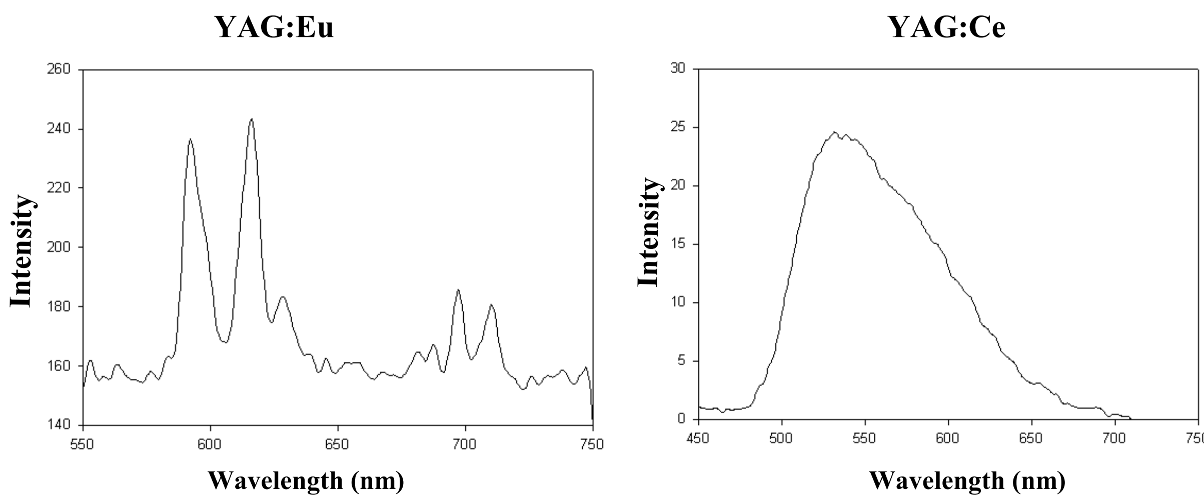

Figure 2. YAG:Ce and YAG:Eu Emission Spectra Painted on YSZ Substrates

The selected HPC and LK paint is a good combination for this research. By itself, HPC is thick and difficult to spray. Conversely, LK by itself cannot be used safely at 1000°C. The selected combination is easy to spray and provides consistent results to temperatures in excess of 1000 °C. A detailed listing of other related binder and phosphor combinations that emit fluorescence at high temperature can be found in Table 2. Several of the binder and phosphor combinations shown in Table 2 emit light to 1500 °C. ZAP is manufactured by Zyp Coatings and has a maximum use temperature of 1800 °C [ref. 12].

Binder (Composition)	Coating		Emission Lines (nm)	Phosphor Emission?			
	Fraction (Vol. %)	Phosphor		1200 °C	1300 °C	1400 °C	1500 °C
100% HPC	20%	Y_2O_3:Eu	611			Yes	Yes
100% HPC	10%	Y_2O_3:Eu	611			Yes	Yes
75% HPC 25% LK	20%	Y_2O_3:Eu	611				No
75% HPC 25% LK	10%	Y_2O_3:Eu	611				Yes
50% HPC 50% LK	20%	Y_2O_3:Eu	611			Yes	Yes
50% HPC 50% LK	20%	Y_2O_3:Eu	611			Yes	No
100% ZAP	50%	Y_2O_3:Eu	611	Yes	Yes	Yes	Yes
100% ZAP	30%	YAG:Dy	585	Yes	Yes	Yes	Yes
100% ZAP	30%	YAG:Tm	420 480				Yes
100% ZAP	30%	YAG:Eu	595 611				Yes

Table 2. Related Binder and Phosphor Paint Combinations

Sample Matrix

The sample matrix used in this research can be found in Table 3. Both the single crystal (set I) and polycrystalline (set II) samples were coated with a paint containing about 20% YAG:Eu by volume. The set III polycrystalline samples were coated with a paint containing approximately 20% YAG:Ce by volume. Fluor pigments and the HPC/LK binder was well mixed before application. Paint was applied to the each YSZ sample using a standard airbrush. Each sample was kept warm on a hotplate during the spraying process to help evaporate the water from the binder. Paint uniformity was checked using an ultraviolet lamp. The paint thickness for this research was estimated to be approximately 0.025 mm (1 mil). At the conclusion of the spraying process, samples were heated to 800 °C to set the binder.

Set	YSZ Sample	Sample Identifier	YSZ Thickness (mm)	Phosphor	Phosphor Ratio (Vol. %)
I	Single Crystal	1 2	1.00 0.25	YAG:Eu	20%
II	Polycrystalline	0 1 2	0.11 0.16 0.20	YAG:Eu	20%
III	Polycrystalline	0 1 2	0.11 0.16 0.20	YAG:Ce	20%

Table 3. YSZ and Phosphor Sample Matrix

Opposite halves of each YSZ crystal piece was coated with YAG:Eu paint mixture. This procedure was accomplished to allow the YAG:Eu to be excited through the thickness of the YSZ. The number of edges visible on the painted phosphor surface can identify the polycrystalline samples. A simple cardboard and tape mask was used during the spraying process to make a straight edge on the YSZ surface. When illuminated with an ultraviolet lamp, both sets of samples clearly show 2, 1, and 0 edges when looking left to right. These edges correspond to YSZ thicknesses of 0.20, 0.16, and 0.11 mm respectively. The surface of the painted YAG:Eu samples was bright white. However, the surface of the painted YAG:Ce samples was light green. The surface of the unpainted YSZ was light beige in color.

RESULTS

Single Crystal YSZ Samples

A Perkin Elmer Luminescence Spectrometer LS50-B was used to determine if fluorescence emission could be imaged through two different thicknesses of YSZ. Painted crystal samples were imaged using an excitation light source with wavelengths of 355, 405, and 532 nm. Emission lines from YAG:Eu have the highest intensity for the 405 nm excitation source. All the YAG:Eu emission peaks are clearly visible using the 405 nm excitation source. The same YAG:Eu emission peaks are also faintly observed using the 355 nm excitation source. No peaks were observed using the 532 nm excitation source.

The light transmission through the YSZ substrate is an important consideration to successfully design a heat flux gauge. An estimate of light transmission can be made by comparing the integrated light intensity for both the YSZ and YAG:Eu sides of the sample. The light transmission (T) is defined as shown by

$$\mathbf{T} = \frac{\mathbf{N_{YSZ}}}{\mathbf{N_{YAG}}}, \qquad \mathbf{(3)}$$

where:

T = Light transmission (dimensionless),
N_{YSZ} = Light intensity peak area (YSZ facing spectrometer), and
N_{YAG} = Light intensity peak area (YAG:Eu facing spectrometer).

The YAG:Eu emission peaks at 592, 631, 697, and 710 nm were used in the calculations as shown in Table 4. This data was obtained using a 405 nm excitation source. Note that the transmission was calculated twice for each YSZ sample. For the 405 nm excitation source, the average calculated transmissions are 0.53 and 0.29 for YSZ thicknesses of 0.25 and 1.00 mm respectively. Note that orange fluorescence light was also observed when each sample was irradiated with a 405 nm laser on its YSZ side.

YSZ Thickness (mm)	Emission Peak (nm)	Light Transmission
0.25	592	0.50 ± 0.09
	631	0.53 ± 0.09
	697	0.58 ± 0.12
	710	0.51 ± 0.08
	Average	**0.53 ± 0.02**
1.00	592	0.28 ± 0.02
	631	0.29 ± 0.01
	697	0.30 ± 0.02
	710	0.29 ± 0.01
	Average	**0.29 ± 0.01**

Table 4. YSZ Crystal Transmission Results (405 nm Excitation)

Polycrystalline YSZ Samples

The goal for this analysis was to measure the prompt fluorescence decay time for each polycrystalline YSZ thickness. A schematic diagram of the experimental apparatus used for this effort can be found in Figure 3. Lasers of three different wavelengths (355, 405, and 432 nm) were used to excite each phosphor through a given YSZ thickness. Each laser generated a pulsed output that was appropriate for measurement of the prompt fluorescence decay time.

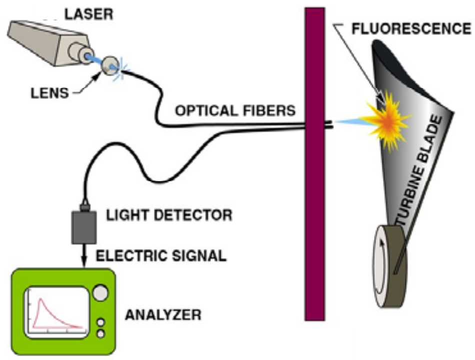

Figure 3. Prompt Fluorescence Decay Time Measurement Schematic Diagram

Specific information for the measurement of the prompt fluorescence decay time is shown in Table 5. A Big Sky Technologies YAG doped with neodymium (Nd) laser had a peak energy output of about 3 mJ, which was several orders of magnitude larger than the other light sources used in this research. The Big Sky Technologies laser emits light at 355, 532, and 1064 nm. A prism and iris assembly was used to select the 532 nm line for this research.

Laser Wavelength (nm)	Laser Type and Manufacturer	PMT Filter Wavelength (nm)	PMT Position*	Measurement Notes
355	YAG:Nd (JDS Uniphase Model 2111 Nanolaser)	None	0°	1. A black cloth was used to reduce background light. 2. The PMT gain was set to maximum.
405	Diode (Power Technology, Incorporated Model LDCU12)	600	0°	1. Laser gated with a Racal-Dana pulse generator (5 V). 2. A blue filter was used at the output of the laser to pass the 405 nm line. 3. A 50 kΩ resistor was used in parallel with the usual oscilloscope input.
532	YAG:Nd (Big Sky Laser Technologies)	592	20°	1. A prism and iris was used to select the 532 nm (green) line (90° bend). 2. The PMT gains were set to minimum. 3. Maximum energy output of the 532 nm line is about 3 mJ. 4. Researchers should wear eye protection during each measurement.

*** Relative to the sample irradiation direction.**

Table 5. Prompt Fluorescence Decay Time Specific Equipment Information

A low voltage photomultiplier tube (PMT) detector was used to measure light emitted from the back of the phosphor and transported through the desired thickness of YSZ. For two of the three lasers, a filter was placed over the opening for the PMT to reduce background light. A

Tektronix TDS 3052 recording oscilloscope was used to display and save the raw data. The SigmaPlot 2001 software package was used to analyze the resulting data and calculate the prompt fluorescence decay time [ref. 13].

Results from this analysis are shown in Table 6. Visible fluorescence was observed through all three YSZ thicknesses at each of the tested laser wavelengths. It was not possible to measure the prompt fluorescence decay time for YAG:Eu because the reduction of light intensity did not follow a single exponential curve. This phenomenon is most likely caused by electrical noise, stray light, or the absorption and re-emission of fluorescence from the YSZ.

The average prompt fluorescence decay time for YAG:Ce was measured to be 62.7 ± 2.9 ns. The accepted value for YAG:Ce of 65 ns falls within the uncertainity of these measurements [ref. 9]. It should be noted that the prompt fluorescence decay time for YAG:Ce was measured through several thicknesses of YSZ.

Phosphor Paint	**Excitation Laser Wavelength (nm)**	**YSZ Thickness (mm)**	**Observed Fluorescence? (YSZ Side)**	**Measured Fluorescence Decay Time (τ)**
YAG:Eu	405	0.11	Very Faint	None
		0.16	Very Faint	None
		0.20	Very Faint	None
	532	0.20	Strong	Not Valid
YAG:Ce	355	0.11	Faint	57.5 ± 0.2 ns
		0.16	Faint	None
		0.20	Faint	None
	532	0.16	Strong	63.1 ± 0.2 ns
		0.20	Strong	67.5 ± 0.3 ns

Table 6. Polycrystalline YSZ Results

SUMMARY AND CONCLUSIONS

Selected rare earth phosphors can be used to measure temperatures as high as 1500°C. This research determined that fluorescence from two phosphors could be detected through several thin YSZ samples. Results could be used directly to develop an operational high temperature heat flux gauge. Analysis of the single crystal YSZ samples indicate that:

- Visible fluorescence was detected from YAG:Eu through both thicknesses of YSZ;
- An excitation wavelength of 405 nm generated the greatest amount of fluorescence light;
- Excitation wavelengths of 355 and 532 nm did not excite the YAG:Eu through both YSZ thicknesses; and
- The average calculated transmissions are 0.53 and 0.29 for YSZ thicknesses of 0.25 and 1.00 mm respectively.

Subsequent analysis of the polycrystalline YSZ samples indicate that:

- Visible fluorescence was observed through all three YSZ thicknesses at each of the tested laser wavelengths; and

- The average prompt fluorescence decay time for YAG:Ce was measured to be 62.7 ± 2.9 ns, which is close to the accepted value of 65 ns.

The prompt fluorescence decay time for YAG:Ce was measured at selected thicknesses of YSZ. These preliminary results demonstrate the feasibility of using a phosphor-coated YSZ sample to measure heat flux. Additional research is needed to quantify these results.

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[13] SigmaPlot 2001 is a registered trademark of SPSS Science (2001).

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