ADVANCES IN HIGH TEMPERATURE PHOSPHOR THERMOMETRY FOR AEROSPACE APPLICATIONS

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ABSTRACT

Phosphor thermometry has been used for many years for non-contact temperature measurements in hostile environments. Aerospace systems are particularly prone to adverse high temperature environments, including large blackbody background, vibration, rotation, fire/flame, pressure, or noise. These environments often restrict the use of more common thermocouples or infrared thermometric techniques. Temperature measurements inside jet turbines, rocket engines, or similar devices are especially amenable to fluorescence techniques. Often the phosphor powders are suspended in binders and applied like paint or applied as high temperature sprays. Thin coatings will quickly assume the same temperature as the surface to which they are applied. The temperature dependence of phosphors 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. Recently, a YAG:Cr phosphor paint emitted fluorescence during short duration tests in a high Mach number hydrogen flame at 2,200 °C. One of the biggest challenges is to locate a binder material that can withstand tremendous variations in temperature in an adverse aerospace environment. This presentation will give research results applicable to the use of phosphors for aerospace thermometry. Emphasis will be placed on the selection of phosphor and binder combinations that can withstand high temperatures.

INTRODUCTION

Phosphors are fine powders that are doped with trace elements that emit visible light when suitably excited. Most of these materials are ceramics that can withstand high temperatures. Many of the fluorescence characteristics of these phosphors can be temperature dependent. Thus, 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 Oak Ridge National Laboratory (ORNL) have demonstrated several useful applications[1-7]. Phosphor thermometry typically 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 desired temperature range, 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, like for a continuous steel galvanneal process, a simple puff of powder onto the surface provides an adequate fluorescent signal.

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

$$I = I_0 \exp\left\{-\frac{t}{\tau}\right\}, \qquad (1)$$

where:

I = Fluorescence light intensity (-),
I_0 = Initial fluorescence intensity (-),
t = Time since cessation of excitation (s), and
τ = Prompt fluorescence decay time (s).

The units for the florescence light intensity are arbitrary. 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. The decay time decreases by almost four orders of magnitude when the temperature is raised from 600 °C to 1,000 °C.

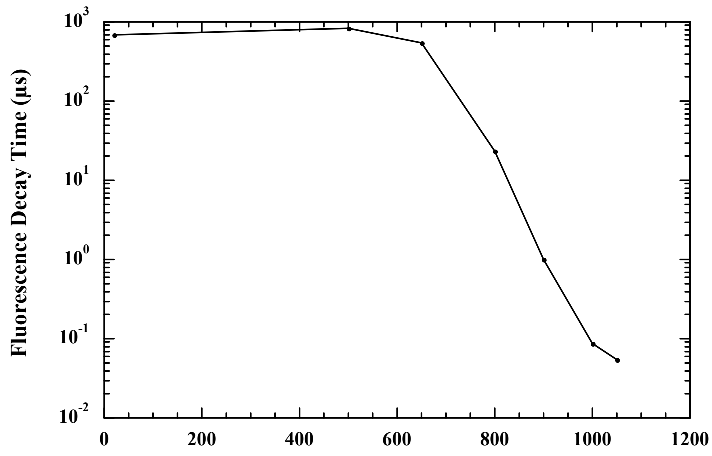

Figure 1. Prompt fluorescence decay time for Y_2O_3:Eu as a function of temperature

This paper will give an overview into recent research focused on finding binder and phosphor combinations that can emit light and remain mechanically viable at high temperatures. Emphasis will be placed on developing techniques for the application and the pre-treatment of candidate binder and phosphor combinations. These efforts were completed at the Oak Ridge National Laboratory (ORNL) National Transportation Research Center (NTRC) in Tennessee.

BINDER

Binders are materials that allow researchers to produce their own high-temperature coating by just adding the powder of choice. High temperature binders are typically made of refractory materials such as Y_2O_3, SiO_2, and P_2O_5. Once the binder has been mixed with appropriate additive such as phosphor, the mixture is applied as a paint using an airbrush.

Previous tests have evaluated a variety of binder materials designed for use in high temperature applications[8]. The LRC binder from Zyp Coatings of Oak Ridge, Tennessee was used in this analysis[9]. The LRC Binder is a very versatile water-based binder liquid. Coatings produced with this binder liquid typically have low hardness on drying and can be easily washed off if re-wetted. The binder has a high ability to suspend solids (can suspend relatively high-density powders) and generally produces high to medium viscosity coatings with most materials. With a pH of 2-3, careful consideration should be used concerning whether the powder to be used is stable in an acidic medium. Other properties, such as a solid density of about 1.0 g/cm^3, ability to remove 97% of volatiles by heating to 600 °C, non-toxic water and nitrogen oxides as the outgassing species, and long shelf life (>12 months). Theoretically the LRC binder can be used in all atmospheres to 1,900 °C.

PHOSPHOR POWDERS

Yttrium oxide (Y_2O_3) doped with europium (Eu) and yttrium vandadate (YVO_4) doped with europium (Eu) were used in for this research. The dopant concentrations are typically a few percent by mass and have grain sizes of about 10 µm or less in extent[8]. These phosphors emit copious fluorescence at high temperatures and can be excited by typical laser wavelengths. Sample emission spectra for Y_2O_3:Eu and YVO_4:Eu are shown in Figure 2.

Y_2O_3:Eu glows bright orange with emission peaks at 590, 612, and 630 nm when irradiated with a ultraviolet (UV) light at 254 nm. YVO_4:Eu also emits orange fluorescence at 600, 625, and 655 nm when illuminated with a 355 nm UV source.

The spectra shown in Figure 2 were collected at ORNL using a LS50-B Perkin Elmer Luminescence Spectrometer in phosphorescent mode with a 1 ms delay. A Schott type GG 395 ultraviolet cutoff filter was placed in front of the emission slit to block the higher harmonics of the excitation light for both measurements.

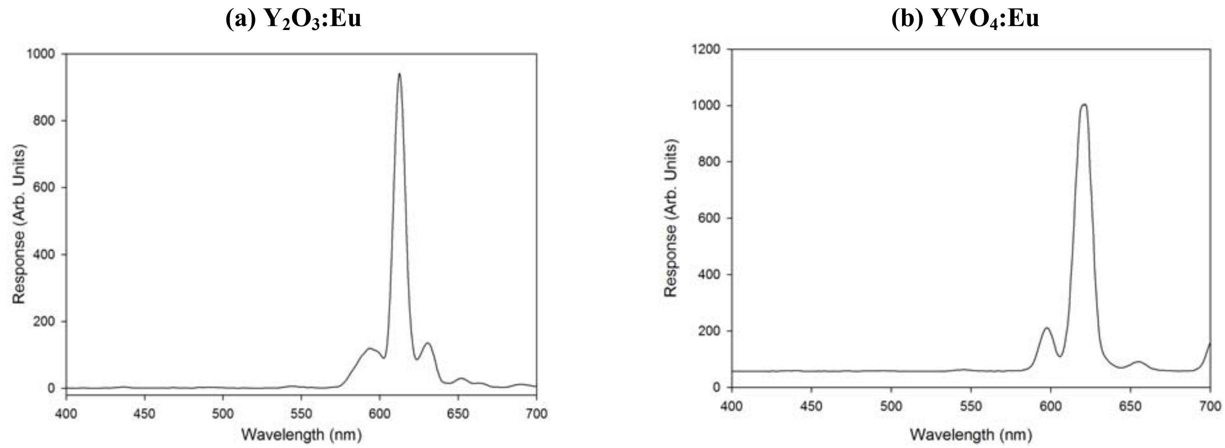

Figure 2. Sample Y_2O_2:Eu and YVO_4:Eu emission spectra

PAINT MIXTURES

Table 1 summarizes the phosphor and binder paint mixtures used in this research. The LRC binder and phosphor powder are mixed together to create a strong and durable paint. A maximum of 2 ml of phosphor powder was added to each mixture. Powdered magnesium oxide (MgO_2), with a volume of 1.0 to 1.5 mL, was added to mixtures two and four to determine if the addition of a powder with an increased thermal conductivity affects the survivability of a high temperature coating. Keeping the phosphor powder content low (around 20 %) allows the MgO_2 to be added to the mixture, without causing the paint to flake off or fail.

Paint mixtures were sprayed on two clean 25 mm x 25 mm (1 inch x 1 inch) ceramic card and cured based on specific binder instructions. Paint uniformity was checked using black light inspection during application. All samples were inspected after the cure cycle before being exposed to the high temperature environment for 60 minutes. After curing and before thermal cycling, the LS50-B was used to determine the baseline fluorescence spectrum for each paint sample. After each thermal cycle the paint sample was re-analyzed using the LS50-B.

Table 1. Selected paint mixture compositions

Paint Mixture	Base Paint Composition				Added MgO_2 (mL)	Total Mixture (mL)	Phosphor Content (%)
	LRC (mL)	Water (mL)	Phosphor Powder				
			Volume (mL)	Compound			
One	3.5	3.5	2.0	Y_2O_3:Eu	0.0	9.0	22.2
Two	3.5	3.5	2.0	YVO_4:Eu	1.5	10.5	19.0
Three	4.6	2.3	2.0	Y_2O_3:Eu	0.0	8.9	22.4
Four	4.6	2.3	2.0	Y_2O_3:Eu	1.0	9.9	20.2

RESULTS

Survivability

Results from these measurements can be found in Table 2. Each paint combination was exposed to the temperatures listed in Table 2 for 60 minutes and then slowly cooled. The heating rate was kept small in order to minimize effects due to the difference in expansion coefficient between the paint and the ceramic substrate.

Results in Table 2 show that all of the paint mixtures emitted fluorescence when heated to 1,400 °C. Paint from mixtures one and two is mostly gone after heating to 1,400 °C. Most of the paint for mixtures three and four was still intact after heating to 1,400 °C.

Figure 3(a) shows the surface appearance for a ceramic sample painted with mixture one before and after heating to a temperature of 1,400 °C. Before heating, the coating appears to be uniform over the entire surface. After heating, the edges of the coated region have a yellowish brown color that still seem to fluoresce under 254 nm UV light, as displayed on the bottom of Figure 3(a).

Figure 3(b) shows the surface of a ceramic sample painted with mixture four before and after heating to a temperature of 1,500 °C. Notice that the paint is flaking off after heating to 1,500 °C. When a UV light is applied, fluorescence can faintly be observed on the surface.

Table 2. Binder and phosphor paint results

Paint Mixture	Paint			Emission Lines (nm)	Phosphor Emission?				Preparation Comments
	Fraction (Vol. %)	Phosphor	MgO_2		1,100 °C	1,200 °C	1,300 °C	1,400 °C	
One	22.2	Y_2O_3:Eu	No	590 612 630		Yes		Yes	Paint mostly gone after heating to 1,400 °C
Two	19.0	YVO_4:Eu	Yes	600 625 655		Yes		Yes	Paint mostly gone after heating to 1,400 °C
Three	22.4	Y_2O_3:Eu	No	600 625 655	Yes	Yes	Yes	Yes	Some paint gone after heating to 1,400 °C. However, some color or wavelength shift and intensity changes observed above 1,200 °C
Four	19.2	Y_2O_3:Eu	Yes	600 625 655	Yes	Yes	Yes	Yes	Some paint gone after heating to 1,400 °C. However, no color or wavelength shift and small loss of intensity observed.

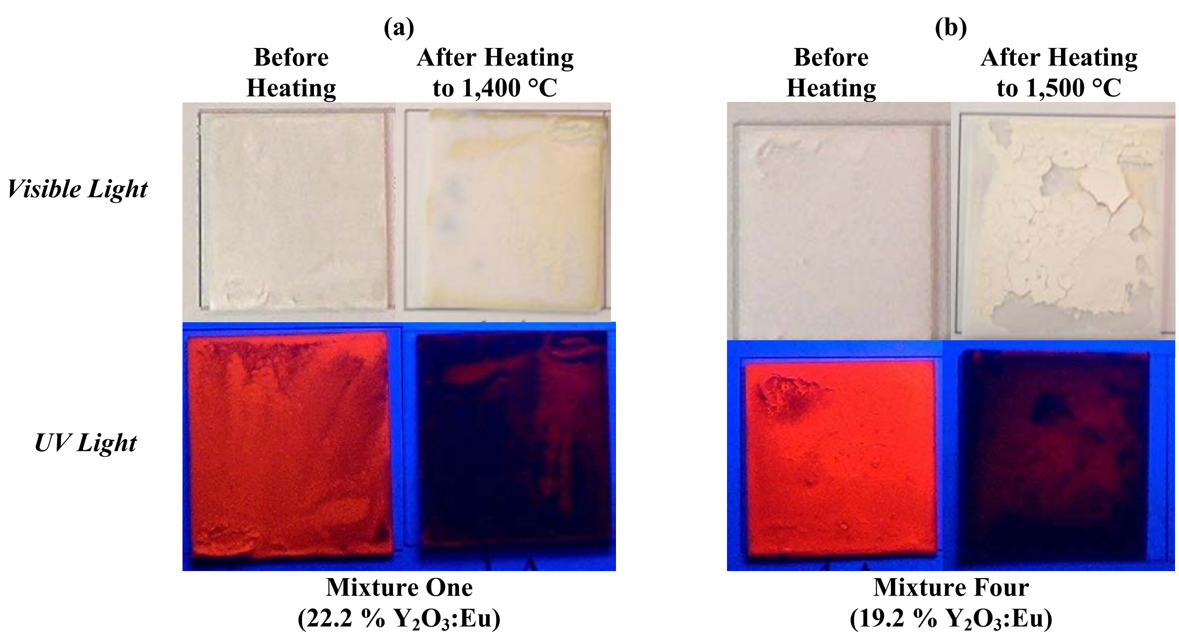

Figure 3. Two visual light and ultraviolet (UV) surface images of Y_2O_3:Eu paint samples

Curing Temperature

The LRC binder can be cured either at room temperature or the out gas temperature of 600 °C. A Y_2O_3:Eu paint was sprayed on one side of two different ceramic substrates. One sample was cured at room temperature. The second sample was cured by heating to 600 °C for 60 minutes. Both cured samples were then heated to 1,200 °C for 60 minutes. Results from the comparison can be found in Figure 4. Notice the spectra for the room temperature and 600°C cures are statistically identical. Curing temperature does not appear to affect the emission spectrum for the Y_2O_3:Eu paint.

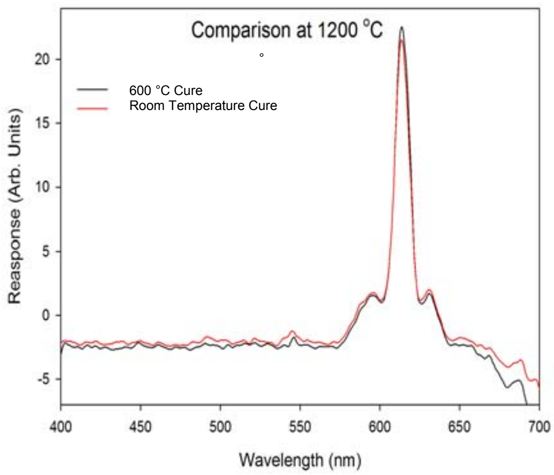

Figure 4. Comparison of fluorescence spectra for different curing temperatures

Magnesium Dioxide

During visual inspection with a UV light, the orange fluorescence color appeared to change slightly for paint mixture three after heating to temperatures larger than 1,300 °C. Remember the paint mixture three contains no MgO_2. Conversely, paint mixture four was mostly intact and emitted orange fluorescence to temperatures as large as 1,400 °C. No shift in fluorescence color was observed at any temperature for paint mixture four containing MgO_2. A more careful analysis was then completed measuring the fluorescence intensity and peak wavelength as a function of temperature.

Plots of light emission amplitude and peak wavelength versus temperature for paint mixtures three and four are shown in Figure 5. The light amplitude is taken from the emission spectra. The 612 nm emission peak from Y_2O_3:Eu was used to compare drift of the spectral emission as a function of temperature. For mixture three (no MgO_2), the fluorescence amplitude increases after a minimum and peak amplitude decreases above a temperature of 1,300 °C. This is in complete contrast to mixture four (MgO_2) where the amplitude decreases monotonically and the peak wavelength is constant. It is quite apparent that the MgO_2 is affecting the fluorescence properties of the Y_2O_3:Eu paint. Additional research is needed to quantify these results.

(a) Paint Mixture Three (No MgO_2) **(b) Paint Mixture Four (MgO_2)**

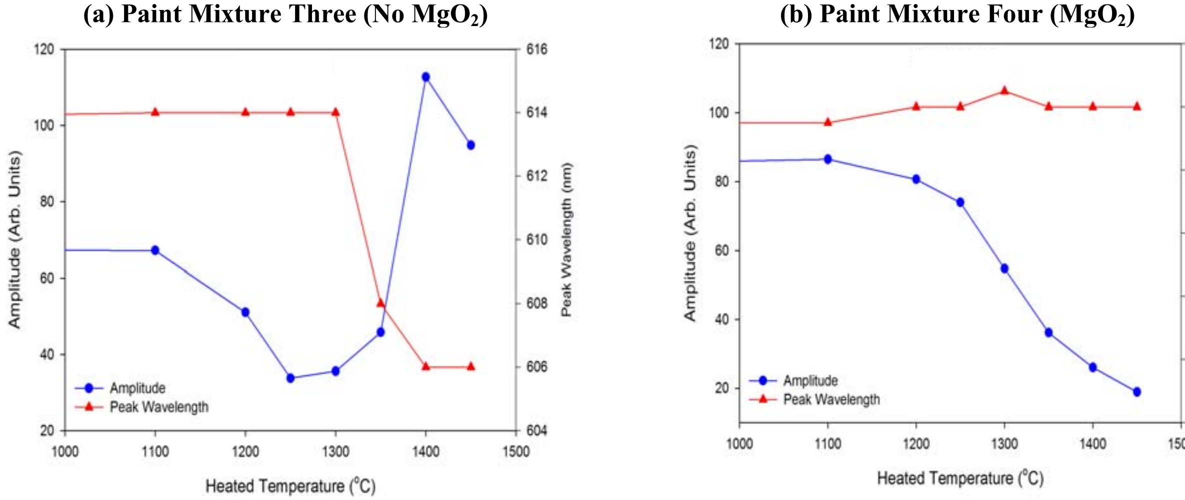

Figure 5. Light amplitude and peak wavelength as functions of temperature for mixtures Three and Four

CONCLUSIONS

Phosphors are materials doped with trace elements that give off visible light when suitably excited. Many of them are ceramics that can withstand high temperatures. The fluorescence characteristics of phosphor coatings allow them to be used as thermometers. 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 functioning at high temperatures such as those present during combustion.

Results from this research indicate that LRC is a durable binder for high temperature applications to about 1,400 °C. Both Y_2O_3:Eu and YVO_4:Eu continue to emit fluorescence after heating to 1,400 °C. It is likely that the introduction of the MgO_2 powder helped prevent the wavelength and intensity changes that started around 1,300 °C.

The LRC-based phosphor paint was found to survive heating to almost 1,500 °C, which approaches the maximum value of 1,600 °C as measured by the authors for other binder and phosphor paints[8,10]. While both of these temperature benchmarks are impressive, they still fall short of the maximum calibrated phosphor temperature measurement of 1700 °C[11]. Additional research is needed to quantify these results.

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