

# *Sub-Microsecond Decay Time Phosphors for Pressure Sensitive Paint Applications*

S. W. Allison, M. R. Cates, and D. L. Beshears  
Oak Ridge National Laboratory  
Oak Ridge, TN. 37831-8058

## **KEYWORDS**

Pressure sensitive paint, PSP, phosphor thermometry, TSP, sensing

## **INTRODUCTION**

The purpose of the effort described here is to identify and characterize thermally sensitive phosphors of potential use to pressure-sensitive paint (PSP) applications. Some PSPs show a pronounced dependence on both temperature and pressure. Pressure dependence of a phosphor is negligible. Thus a phosphor can unambiguously indicate temperature. A suitable combination of a PSP and a phosphor can therefore potentially provide for both pressure and temperature measurement.

A short decay time is one of the major requirements for applications with PSPs when the application involves imaging of high speed moving surfaces. Reference 1 states "The decay time of the  $\text{Ce}^{3+}$  emission is  $10^{-7}$  to  $10^{-8}$  s, the shortest in observed lanthanide ions." For this reason, the research efforts in this lab in the past year have concerned cerium-doped phosphors. Such phosphors are commercially available. They are typically used where the short decay time is advantageous such as for flying spot scanners and beam-index type cathode-ray tubes.

Another essential requirement for the present effort is to find phosphors that can be used to measure temperature in the ambient to 300 C range. To cover this range, more than one phosphor is needed. Typically, a phosphor decay time will be constant at low temperature. As temperature is raised, at some value, the decay time will begin to decrease due to incipient quenching of the fluorescence. This temperature is termed the quenching temperature. The phosphor can be used to sense temperature from the quenching temperature and higher until the signal becomes too dim or the decay time is too short for the measurement system that is used.

Presented here are results for several cerium-doped compounds that, in combination, allow for temperature measurement from below ambient to at least 300 C. In addition, two other materials,  $\text{ZnS:Ag}$  and  $\text{Gd}_2\text{O}_2\text{S:Pr,Ce}$ , also exhibited interesting and possibly useful characteristics.

## **EXPERIMENTAL**

For the characterizations, a phosphor powder sample, a fraction of a gram, is placed on the end of a silver-coated diffusion-pump heating element. The element sits in a ceramic housing. A quartz window is placed on top of the phosphor sample. A single 1-mm core diameter optical fiber delivers light from either a nitrogen laser or a blue LED. All the results plotted are for nitrogen laser excitation at 337 nm. Quite often the fluorescence was so bright when using the laser that a high degree of attenuation was required to prevent saturation of the detector, a photomultiplier. Saturation is indicated by a nonlinear response of the PMT. A suitable bandpass filter in front of the PMT allows only the desired fluorescence band to be

detected. The frequency response of the system was such that the minimum decay time that could be measured with the setup was between 5 and 10 ns, depending on specific cables and arrangement used.

## RESULTS

As noted in the previous proceedings to this conference (references 2 and 3), the emission of YAG:Ce is broad, ranging from the blue to the red. Emission near the peak at 510 nm was monitored to determine decay time. (The decay time was independent of emission wavelength). Figure 1 shows the results for three yttrium aluminum garnet phosphors, all doped with cerium. The formula for YAG is  $Y_3(Ga_xAl_{1-x})_5O_{12}$ . The difference between the formulations is the substitution of gallium, Ga, for aluminum, Al. Increasing the ratio of Ga to Al lowers the quenching temperature. The sample with no gallium showed the highest quenching temperature, just under 200 C. For the sample where X, the fraction of Ga, is 0.5, the quenching temperature is just above ambient, about 50 C. For the case of X = 0.75, the quenching temperature is somewhat below room temperature, lower than achievable with the existing setup. Overall, the results seem to indicate that the quenching temperature, and hence the range in temperature over which a phosphor may function, may be controlled by specification of the Ga to Al ratio.

Another means of controlling the temperature dependence is to substitute gadolinium, Gd, for yttrium, Y, in the host matrix. Figure 2 shows the effect, lowering the threshold for temperature dependence by about 20 C. This is thought to be due to the fact that Gd has a larger ionic radius than Y. If such is the case, substitution of lanthanum, La, would lower the threshold by another 20 C. A sample is available for testing in the future. The flattening of the curve above 130 C is likely due to the system's limiting time response.

The most striking temperature dependence was observed for  $Y_2SiO_5:Ce$ . This is seen in Figure 3 where the decay time versus temperature curve is compared with YAG:Ce. The decrease in slope at the highest temperatures is likely due to the system time response limitations. The quenching temperature is about 50 C. The emission is mainly in the blue and efforts to excite fluorescence using a blue light emitting diode were unsuccessful. It has a broad absorption band in the near ultraviolet.  $Gd_2SiO_5:Ce$  and  $La_2SiO_5:Ce$  are compounds that will be tested at a future date. The gadolinium silicate absorption and emission characteristics are similar to yttrium silicate. Interestingly, for the lanthanum material, the emission is peaked at 390 nm. It has a broad absorption band that extends from 260 to 330 nm.

Two phosphors were surveyed whose emission intensity increased with temperature. These were ZnS:Ag and  $Gd_2O_2S:Pr,Ce$ . The luminescence from the latter appears light green and the former white. It should be noted that this intensity increase occurs for 337 nm excitation. Excitation at other wavelengths may not necessarily produce the same results. The emission at 514 nm for the two phosphors was not a single exponential decay. Also, there was no means to integrate the signal. Thus, as an indicator of temperature dependence, the intensity at a time 1 microsecond after excitation is plotted as a function of temperature. Figure 4 shows the intensity of ZnS:Ag increasing rapidly from ambient to about 100 C, then falling off above 200 C. Around 400 C the material appeared to react with the air and/or heating element. The emission from the Pr,Ce compound rises to a peak at about 220 C and decreases above that. Their respective decay appears to be a few microseconds at room temperature. The nonexponentiality of the decay made it difficult to determine the temporal characteristics precisely though more analysis could produce useful lifetime information.

## CONCLUSIONS

The results suggest that garnet phosphors can be engineered to function thermographically over desired temperature ranges by adjusting gallium content. Substituting gadolinium for the yttrium in the host

matrix also has an effect but it is not as large. A silicate phosphor showed the greatest temperature dependence though it could not be excited to fluoresce by a blue LED. All the garnet phosphors could be excited with such a blue source. Two phosphors tested showed an increase in intensity with temperature. Other garnet and silicate materials as mentioned above will be tested in the future. In addition, some perovskite phosphors, such as  $\text{GdAlO}_3:\text{Ce}$ , will also be investigated.

This work was performed under subcontract ERD-94-YA340 with ISSI, Inc. The authors are grateful to Dr. Larry Goss of ISSI and Kelly Navarra of Wright Laboratory for their support of this project

The Oak Ridge National Laboratory is operated for the U. S. Department of Energy by UT-Battelle, LLC. under contract DE-AC05-00OR22725.

#### REFERENCES

1. Phosphor Handbook, S. Shionoya and W. M. Yen, eds., p. 187, CRC Press, 1999.
2. S. W. Allison M. R. Cates, and D. L. Beshears, "Excitation of Thermographic Phosphors with a Blue LED," Proceedings of the 45<sup>th</sup> International Instrumentation Symposium, published by the Instrument Society of America, pp. 243-252, 1999.
3. S. W. Allison, M. R. Cates, and D. L. Beshears, AA Survey of Thermally Sensitive Phosphors for Pressure Sensitive Paint Applications@Published in the Proceedings of the ISA 46<sup>th</sup> Annual, May 2000.

**The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. DE-AC05-00OR22725. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.**

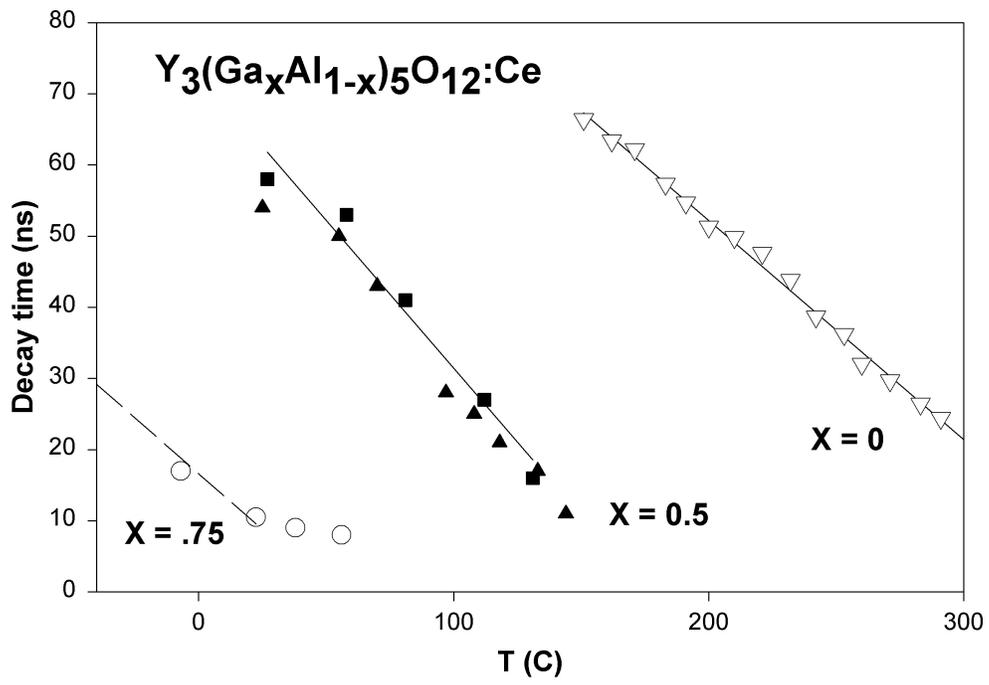


Figure 1. Decay time change with temperature for different gallium/aluminum ratios of YAG.

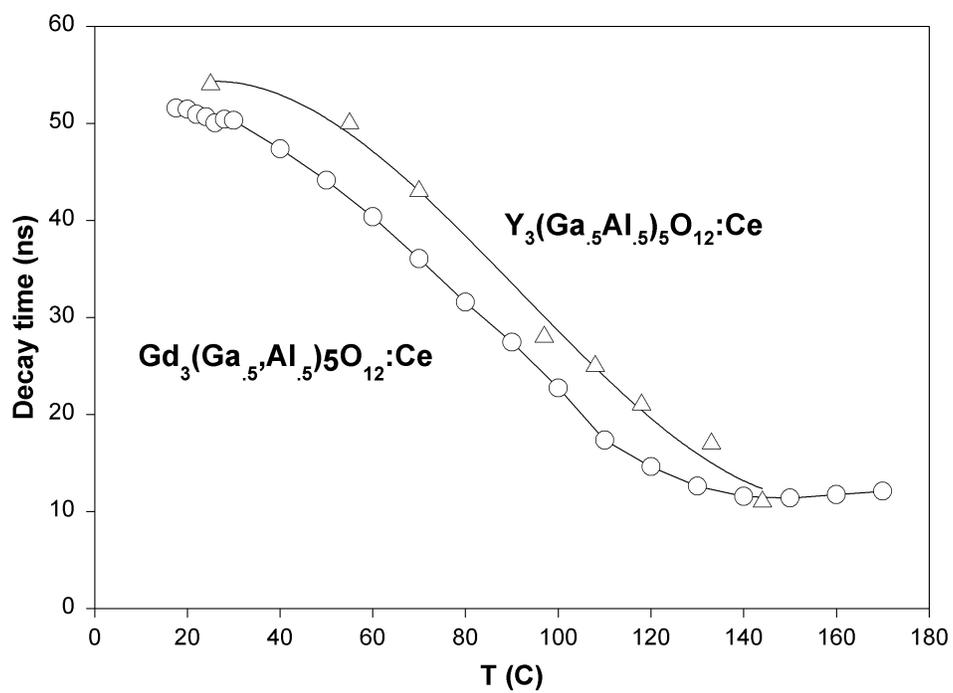


Figure 2. Decay time versus temperature for yttrium and gadolinium garnets.

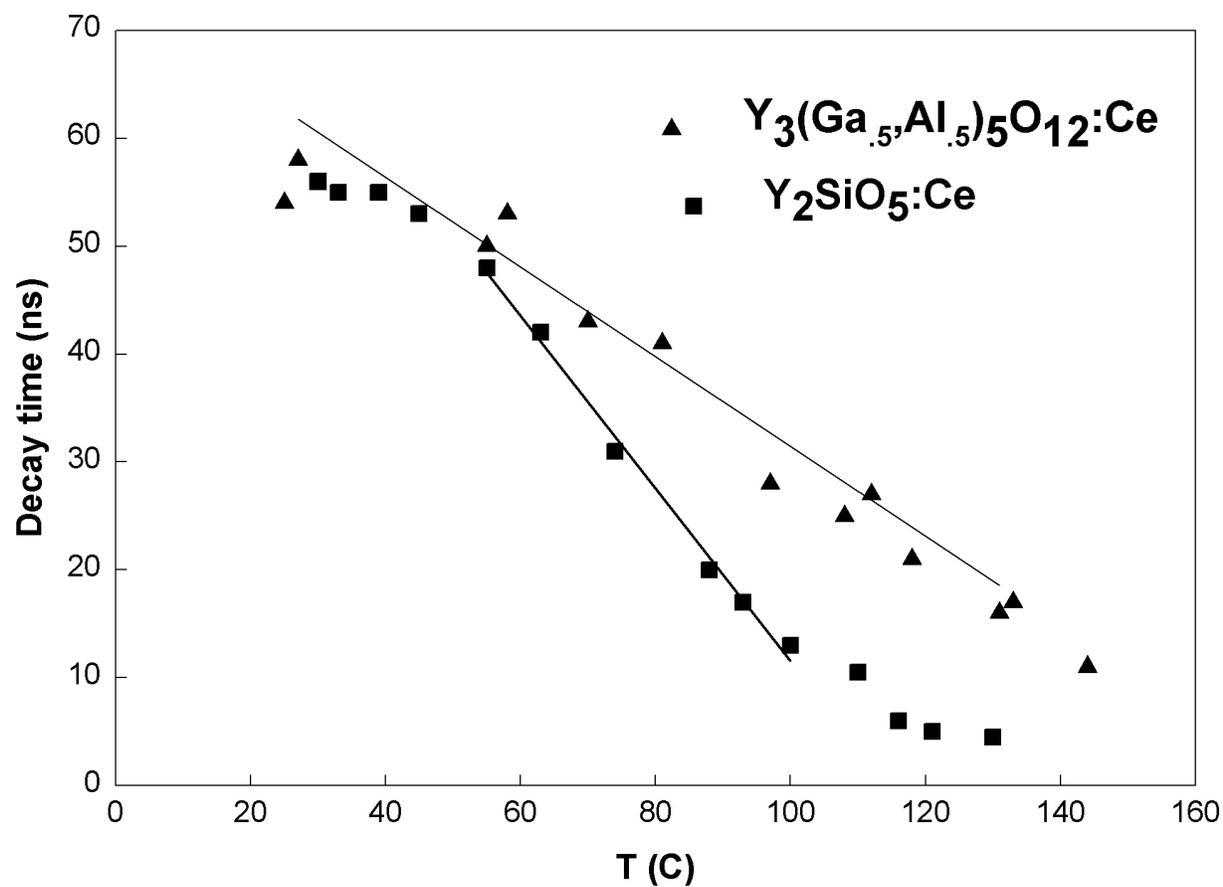
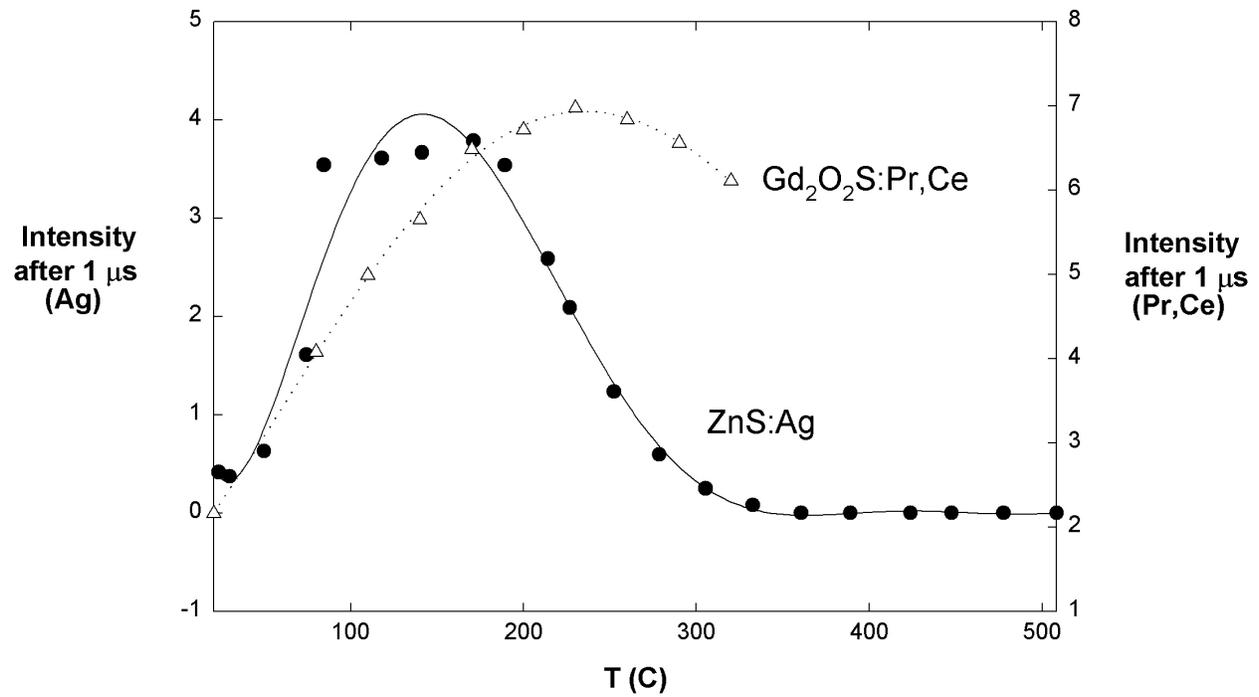


Figure 3. Comparison of yttrium silicate and yttrium garnet phosphors.



**Figure 4. Emission intensity increase with temperature and subsequent decrease for Ag and Pr,Ce doped phosphors.**