A Survey of Thermally Sensitive Phosphors for Pressure Sensitive Paint Applications

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

ABSTRACT

We discuss selection and testing of thermally sensitive phosphors for use with pressure-sensitive paints (PSP's). These phosphors exhibit essentially no pressure dependence and therefore can provide an independent means for removing the temperature-dependent response of PSP's. The major selection criteria were 1) temperature sensitivity from ambient to 300 C, 2) a short decay time (important for rapidly moving surfaces), and 3) that the material be excitable by a blue light-emitting diode. The mechanisms which affect the temperature dependence are discussed. For example, as temperature is increased, some phosphors show an initial decrease in decay time followed by an increase then a subsequent decrease. This is explained by a thermalization process. Plots of decay time versus temperature for a variety of phosphors are presented. In summary, the most striking temperature dependence is found in rare-earth oxysulfide hosts with either europium or terbium as the activator, but no single one of them covers the entire temperature range. Several praesodymium-doped oxysulfide compounds come close to meeting the above criteria. Also, several cerium-activated compounds show promise, for instance YAG:Ce. It is characterized by bright, efficient emission, a short decay time (about 60 ns), but the temperature dependence does not begin until about 160 C.

INTRODUCTION

Pressure-sensitive paint (PSP) is justifiably receiving much attention since it enables pressure measurement in a variety of aerodynamic situations. This paper describes some experimental results aimed at selecting temperature-sensitive phosphor materials(1) to be used in conjunction with PSP's. The pressure dependence of phosphors is, for most aerodynamic applications, nil. On the other hand, many useful PSP's are both temperature as well as pressure dependent. Thus a TSP may, depending on experimental exigencies, be used to establish the temperature so that the pressure information may be extracted from the PSP.

At first glance, the instrumentation and methodologies for implementing pressure sensitive paints and thermal phosphors appear to be the identical. In both cases, a light source illuminates the fluorescing material and a detector(s) receives the induced emission. An optical configuration consisting of lenses, sometimes with the aid of fiberoptics, serves to direct the excitation light to the luminophor surface and to transport the resulting emission to suitable detectors. However, it has been determined that PSP instrumentation requirements are usually more stringent than the typical thermal phosphor application encounted by the authors and described in literature. This is due to need for imaging systems with high

resolution and coating uniformity.

Whereas in most cases phosphors are used for single point temperature measurements, PSP's are required for imaging of temperature and/or pressure. PSP applications require very uniform coatings, down to the pixel level, which is a few square microns. When the surface to be diagnosed is moving, the measurement requirements are even more stringent. Therefore, the phosphors selected for testing for this work were selected according to the following criteria:

1. The fluorescence decay time must be less than 10 microseconds.
2. The fluorescence should be excitable with a blue light emitting diode (LED).
3. The fluorescence spectrum should be different from the PSP.
4. The fluorescence of the phosphor should not excite the PSP to fluoresce.
5. It must be possible to apply a uniform thin coating of the phosphor in question.
6. The temperature range of interest is ambient to 300 C.

EXPERIMENTAL

A number of phosphors were initially characterized using a spectrophotometer to obtain fluorescence spectra and excitation spectra. Next, the decay time of selected ones were tested using either a blue light emitting diode or a nitrogen laser for excitation. A small sample of phosphor powder was placed on top of a cartridge heating element. The element is surrounded by ceramic brick. An optical fiber placed a few centimeters above the sample conveyed the fluorescence to a detector. For each desired emission band, an interference filter was used. A PC-based data acquisition system acquired, digitized, and analyzed the signal to estimate the lifetime (a.k.a. decay time).

DECAY TIME RESULTS

The results could not be fit onto one graph so the data has been separated into three separate figures, 1-3.

At the onset of this work it was thought that cerium-activated phosphors may be attractive since the decay time in some materials in our experience is known to be short. Figure 1 shows results for several yttria-host Ce phosphors. Other yttria-based phosphors are depicted as well. The only one of these to exhibit a short decay time is YAG:Ce. The emission is very bright and efficiently excitable with a blue LED(2). The decay at ambient is about 60 ns. The decay time becomes temperature dependent at about 150 C. Therefore, it will successfully function as a TSP from 150-300 C. All the other materials in this graph show long decay times. $YAlO_3$:Ce emission is long and actually increases with temperature. A curious feature is that the 510 nm band of emission from $Y_3(Al,Ga)_5O_{12}$:Ce appears to decrease from about 7 µs at ambient to 4 µs at 100 C followed by an apparent increase in decay time. It is 50 µs at 200 C. This is apparently due to thermalization, i.e. the state is being thermally excited from another state. The decay time algorithm (which assumes single exponential decay) had difficulty discriminating between the two states in the 100 to 200 C region. Also shown in the figure is the thermal quenching curve for La_2O_2S:Eu. This material exhibits the most striking temperature dependence, albeit, the decay times are too long. For reference purposes, the thermal quenching curve of YAG:Cr is also shown here. As indicated, the decay time is ten times longer. Whereas the slope of the lifetime versus temperature curve is not great, it is nonetheless a useful temperature sensor in this temperature range. It serves to illustrate

for comparison purposes the degree of temperature dependence that is useful.

Figure 2 shows results for a variety of oxysulfide phosphors. Based on previous experience, this class of phosphor shows pronounced temperature dependence for some emission lines and activators. Of note in this graph is Gd_2O_2S:Pr,Ce,F. The 510 nm emission band shows a temperature dependence over a wide range. The decay time is fairly long at ambient; but, it is short but still detectable in the 200 to 300 C range. Thus it may have utility for use with pressure sensitive paints. It is clear that other emission bands from this phosphor and the other phosphors depicted do not meet the above mentioned criteria.

Figure 3 shows the results for several yttrium oxysulfide phosphors. All have decay times longer than desired. Several terbium phosphors exhibit striking temperature dependence, a property that could be useful in certain situations. The 510 nm band of Y_2O_2S:Pr is very stable and constant over a wide temperature range, ambient to 150 C. Above that the decay times are moderately short.

SPECTRAL DATA

The excitation spectrum and emission spectrum of several phosphors have been compared with a pressure sensitive paint marketed by Innovative Scientific Solutions, Inc. The Pt(TfPP)-FIB-Based PSP is described in detail in company literature.

Figure 4 shows the emission spectrum of YAG:Ce. A significant fraction of the emission falls at a shorter wavelength than the PSP emission. This is a very bright phosphor however, and care should be taken that in a PSP-YAG:Ce mixture, the detected emission above 600 nm is due to the PSP rather than due to the red-end of the YAG:Ce emission band.

Figure 5 shows the emission spectrum of Y_2O_2S:Pr in relation to the PSP excitation and emission. The excitations are well separated; and, the main emission band at about 510 nm is well removed from that of the PSP. There are some weak bands of the Pr phosphor that are present under the PSP envelope but this can be discriminated against by use of narrowband filters and the fact that the decay times are significantly different. It may be noted that it does not appear that a blue LED would efficiently excite this phosphor. Typically, blue LED output would be no shorter than 380 nm. Even though the absorption bands in this region are weak, nevertheless, significant fluorescence is produced by a blue LED.

Figure 6 shows the emission spectrum of Gd_2O_2S:Tb (0.001%) in relation to the PSP. This is a low concentration and the emission is weak. For this phosphor host and activator, low concentrations tend to enhance the blue emission at the expense of the green emission. There are a number of lines between 390 and 500 nm which would be essentially quenched at higher Tb concentrations. It is also known that the blue lines are temperature dependent at lower temperatures than the green. The emission is sufficiently different from the PSP emission band.

Figure 7 depicts the emission spectrum of YAG:Cr. This is the one phosphor with emission to the red of the PSP. Its decay time is extremely long so it is not applicable to applications with motion. It is easily excited with a blue LED, however, and may be an excellent choice for stationary imaging. It covers a wide range. The authors have calibrated a sample from ambient to about 700 C. It may also be useful at temperatures significantly below ambient.

All these phosphors are currently commercially available.

CONCLUSIONS

At present the phosphors which show the most promise for PSP applications are activated with Ce or Pr. YAG:Ce emission has a short decay time, 60 ns at ambient, and it decreases as a function of temperature between 150 and 300 C. The decay time of Gd_2O_2S:Pr,Ce,F at 510 nm is temperature dependent from about 50 to 300 C and the decay time varies from about 3 µs to 30 ns over that region. Future work will investigate whether or not a deliberately added impurity can improve the performance of these phosphors by lowering the temperature at which quenching begins. Other classes of phosphors may be tested such as the zinc sulfides and zinc selenides. Coating issues should be addressed for all these materials and will be the subject of future effort.

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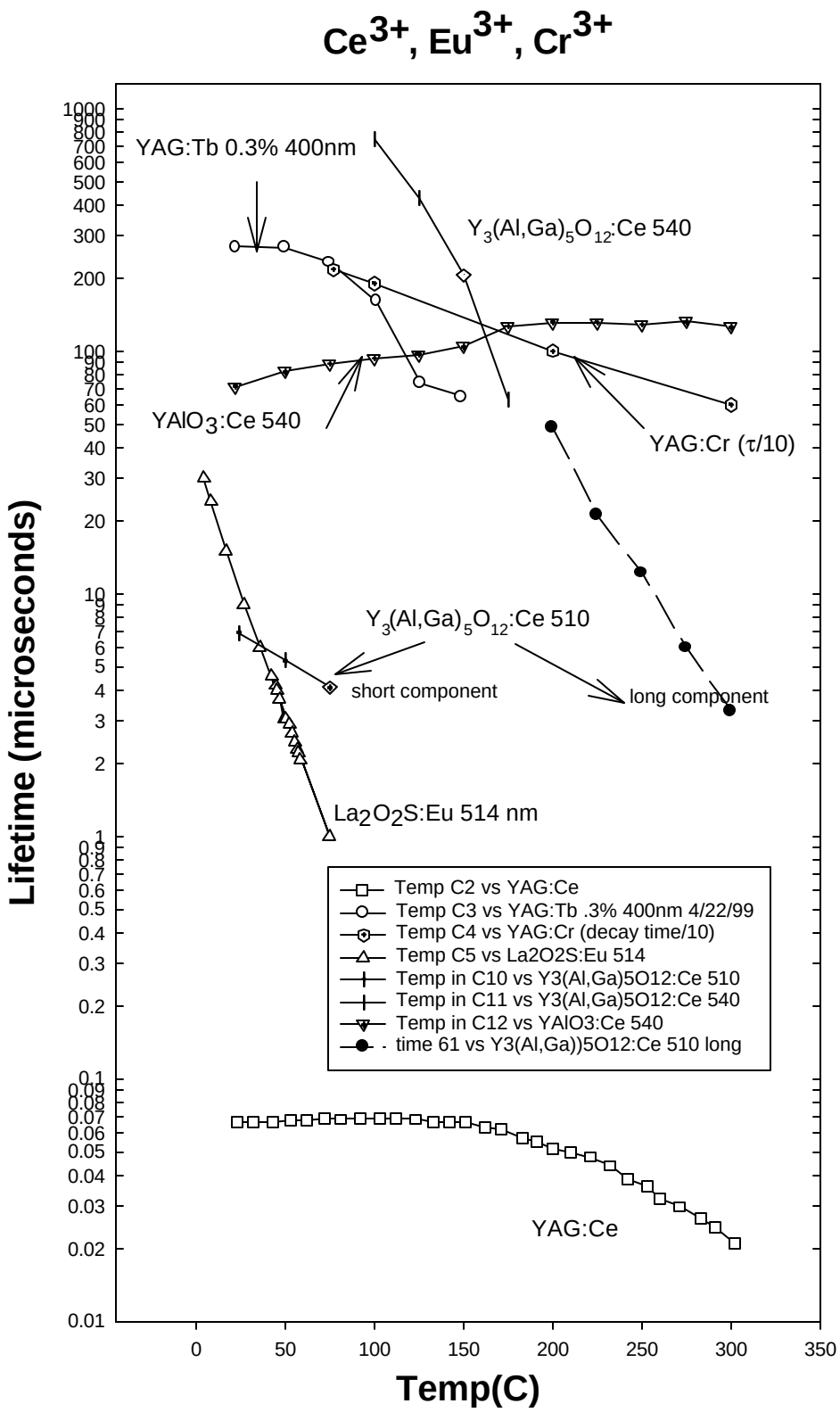

Figure 1. YAG and yttrium based phosphors.

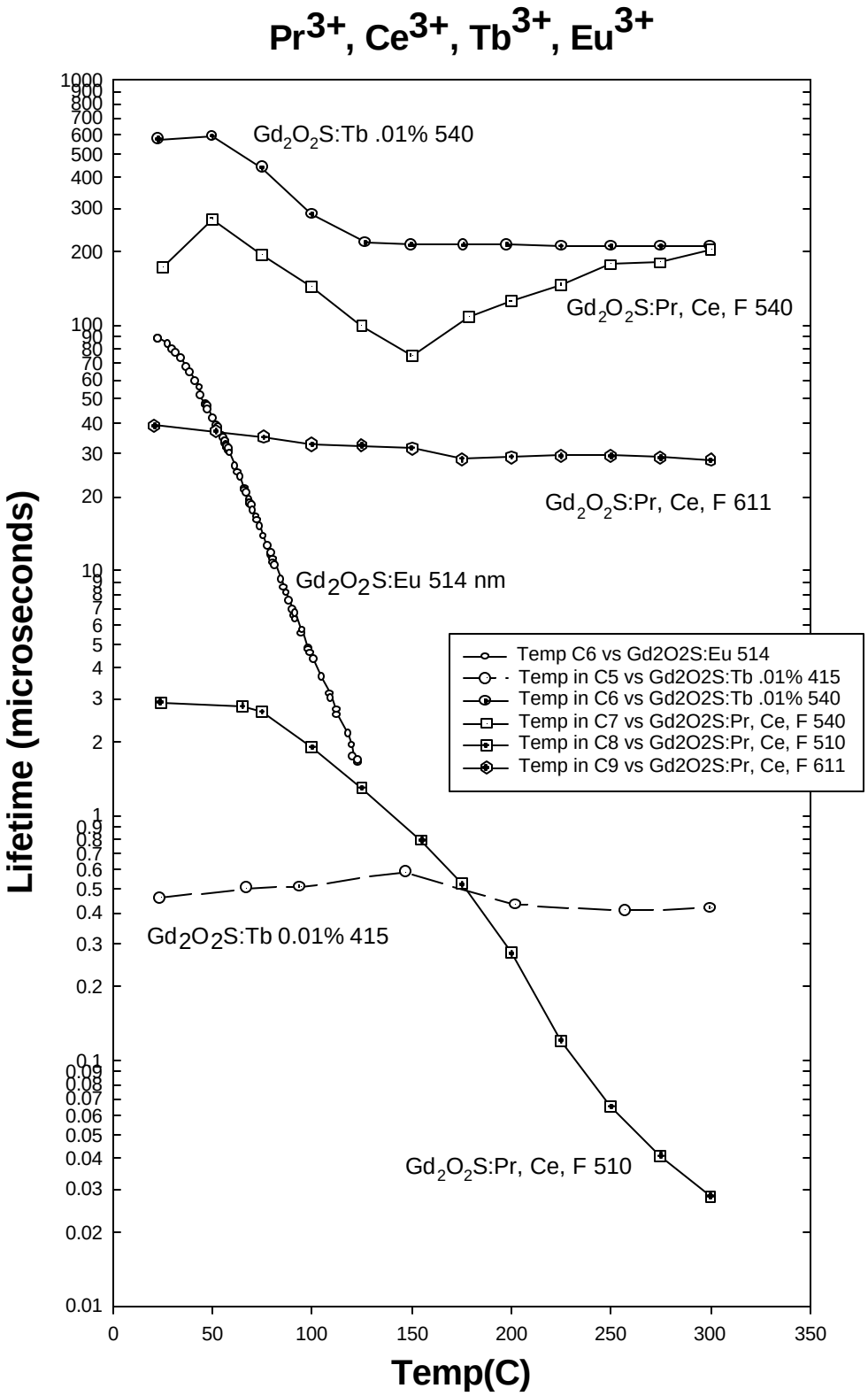

Figure 2. Gd_2O_2S-based phosphors.

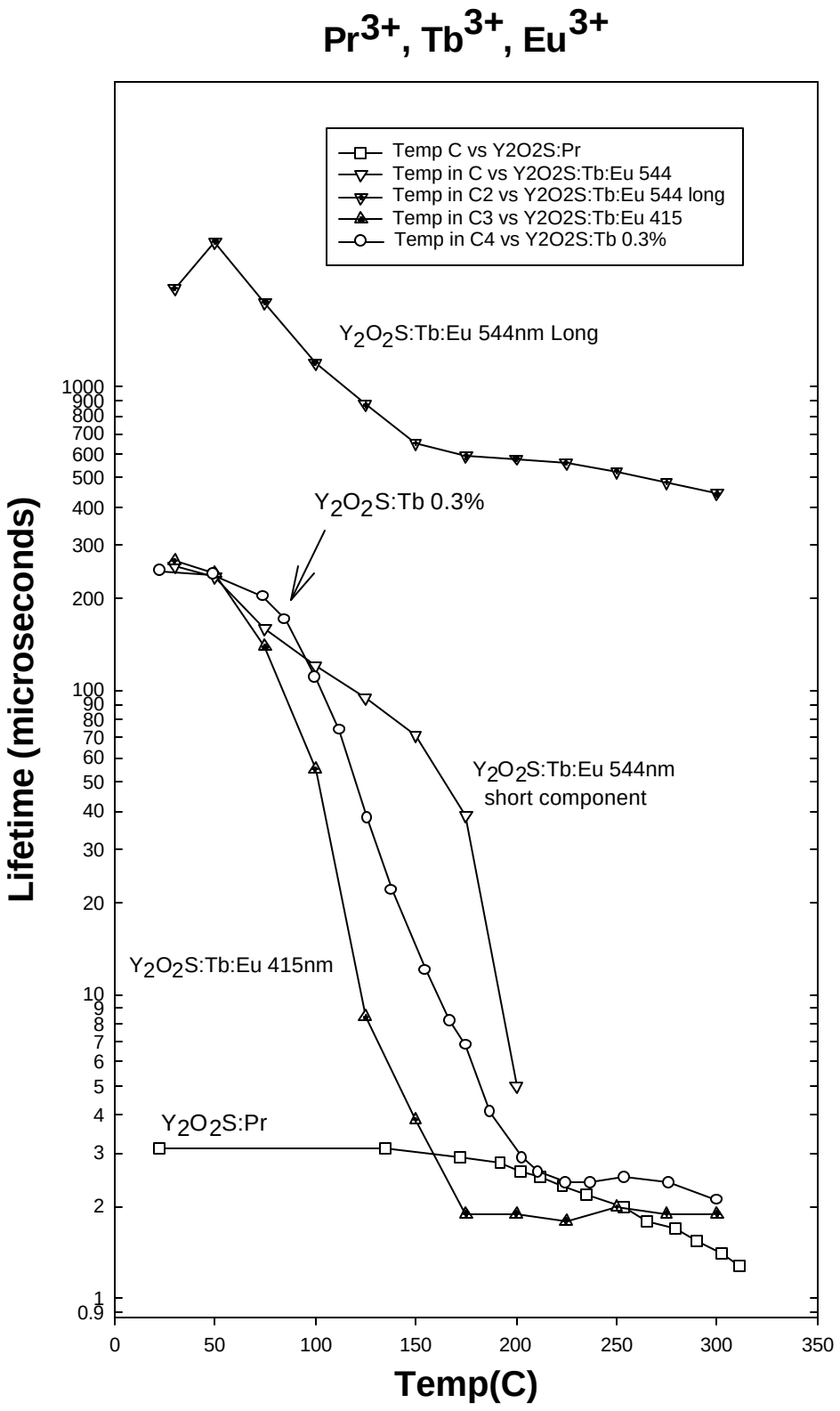

Figure 3. Y_2O_2S-based phosphors.

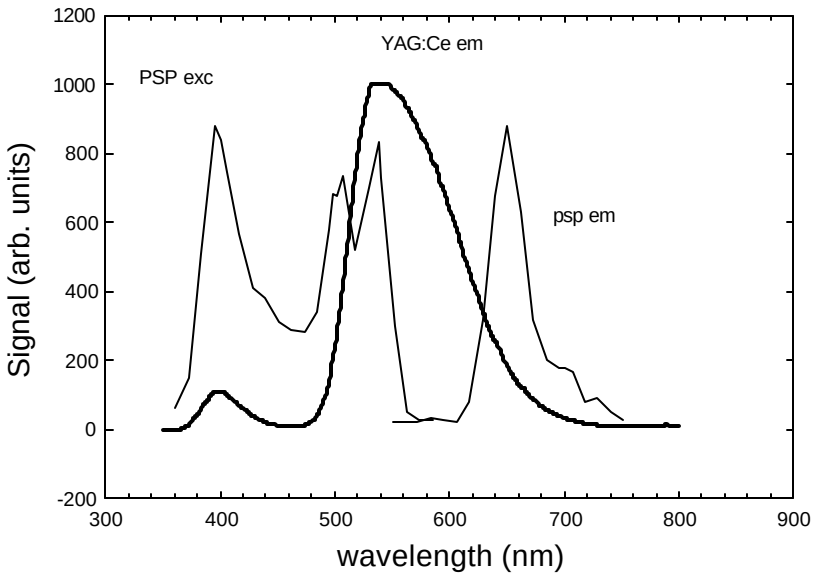

Figure 4. YAG:Ce and PSP spectra.

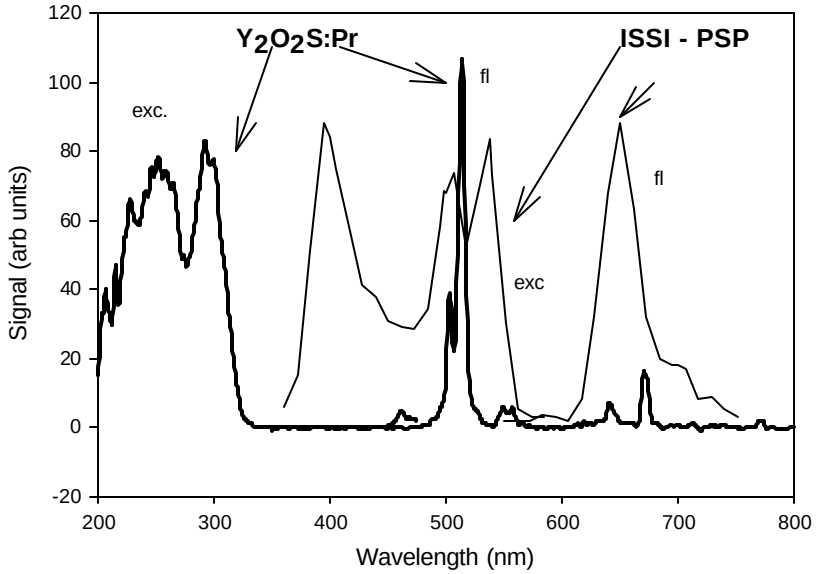

Figure 5. Y_2O_2S:Pr and PSP spectra.

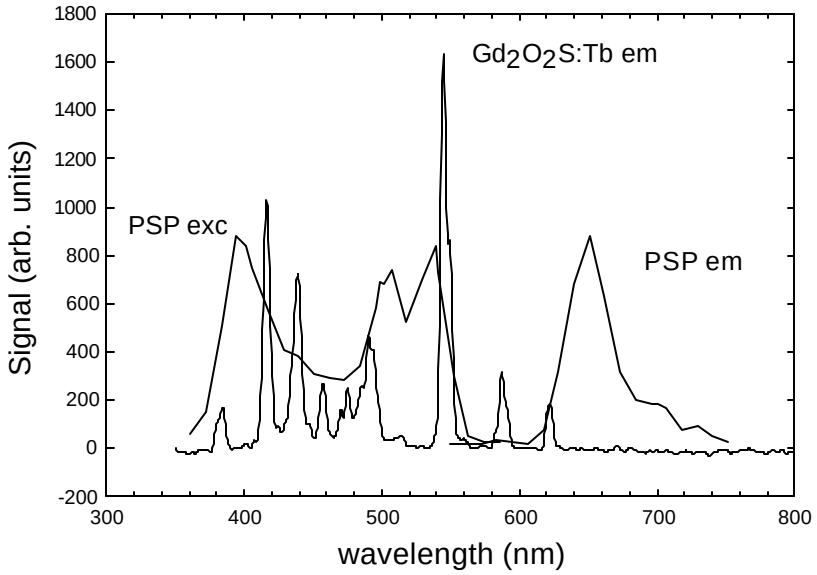

Figure 6. Gd_2O_2S:Tb and PSP spectra.

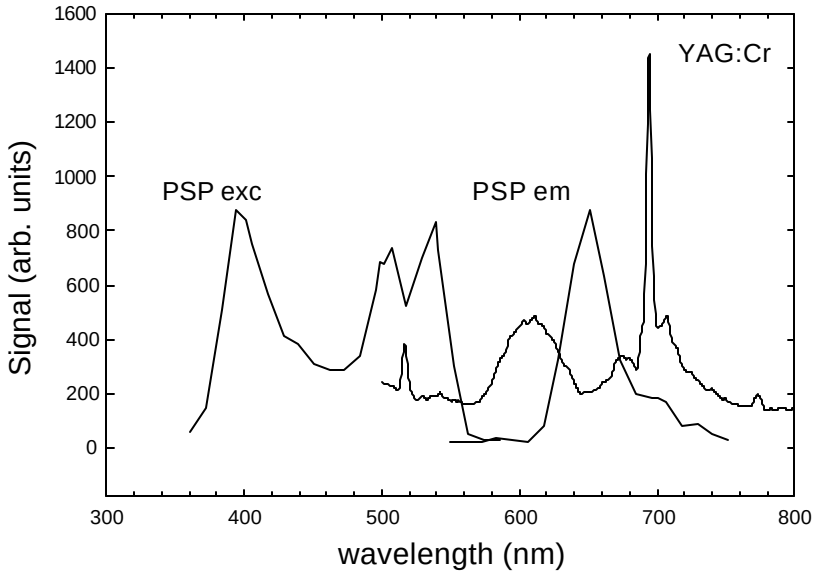

Figure 7. YAG:Cr and PSP spectra.