

Phosphor Thermometry *Tutorial*



^{by} Mike Cates Steve Allison

What is a phosphor?

- A phosphor is a chemical material that, when stimulated by absorption of energy – often in the form of photons – will emit photons – usually at lower energy (longer wavelength) than the stimulating source.
- In appearance, a phosphor is usually a fine white or pastelcolored powder. There are two general types of phosphors: organic and inorganic. This presentation deals with inorganic. The majority of thermometry applications in our experience have used inorganic phosphors. Organic fluorescing materials may have advantages in certain situations.



What is a phosphor? (continued)

- Inorganic phosphors consist of:
 - Host material: e.g., oxide, garnet, sulfide, oxysulfide, vanadate, germanate, etc.
 - Activator material (aka dopant or impurity): usually rare-earth or transition metal elements.
 - An advantage of these dopants is that, typically, the emission consists of narrow bands.



Typical phosphor characteristics

- Must survive hazardous chemical environments
- Cannot be water soluble
- Durable
- Easy to apply
- Not easily detected or noticed without specialized equipment
- There are a wide variety of ceramic phosphors which fit these characteristics.





K/PH 94-13

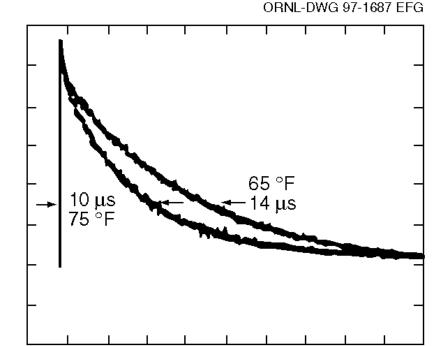
Background

- Phosphors became technologically and industrially important with the introduction of fluorescent lamps in 1938.
- Thermometry use suggested in German patent in 1938.
 First peer-reviewed article, to our knowledge, appeared in 1949.
- Between approximately 1950 to 1980, it was not widely used. Its most common use was for aerodynamics applications.
- Advances in lasers, microelectronics, and other supporting technologies enabled additional commercial as well as scientific uses.



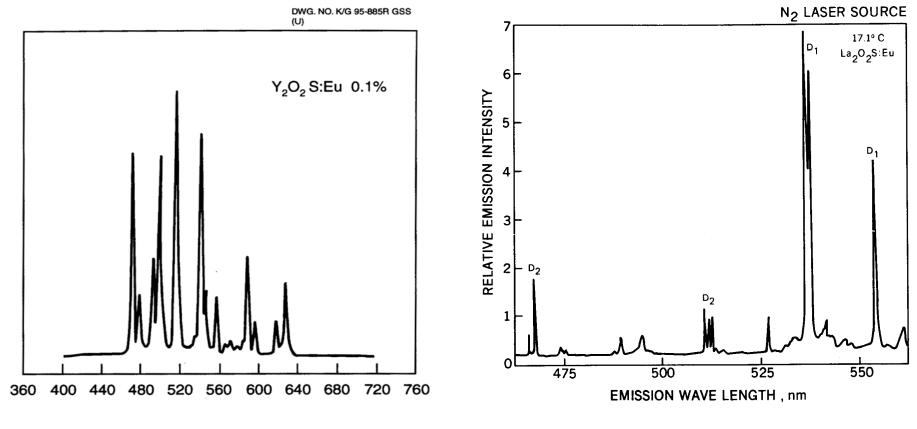
Various phosphor characteristics are affected by temperature

- 1. Decay Time
- 2. Line shift and broadening
- 3. Ratio of emission lines
- 4. Emission distribution
- 5. Absorption band width and position
- 6. Excitation band width and position





Typical fluorescence spectra for rare-earth doped phosphors





Factors that affect fluorescence

- Dopant (activator) concentration may change the phosphor emission spectrum. Dopant concentration that maximizes fluorescence varies with dopant and host. At high concentrations, the emission characteristic lifetime may vary from a simple single exponential. Rise times are also affected by dopant concentration.
- Characteristic size of phosphor particles affects intensity and lifetime of fluorescence when size is around 5 microns or less. For Y₂O₃:Eu, e.g., decay time increases from 440 to 600 microseconds when particle size decreases from 0.42 to 0.11 microns.



Factors that affect fluorescence (continued)

- **Impurities:** Deliberately added rare-earth impurities may either increase or degrade fluorescence efficiency, depending on how energy levels match. The literature contains information on which pairings favor enhancement.
- Magnetic Field: At least one tesla is usually required to observe a change in fluorescence spectra and the material must be very cold, say 20 K.



Decay time vs temperature for selected phosphors

DWG. NO. K/G 96-569 GSS (U)

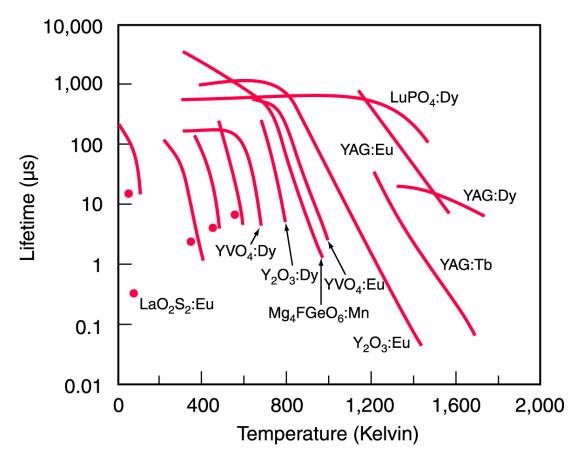
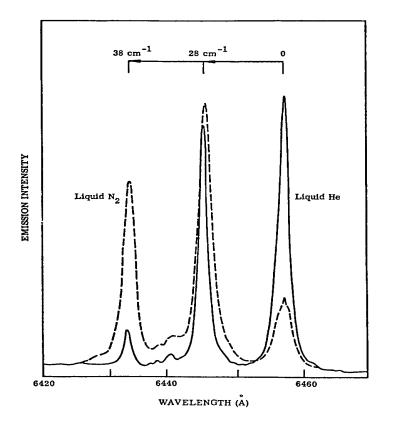


Figure 12. Lifetime versus temperature of selected phosphors.



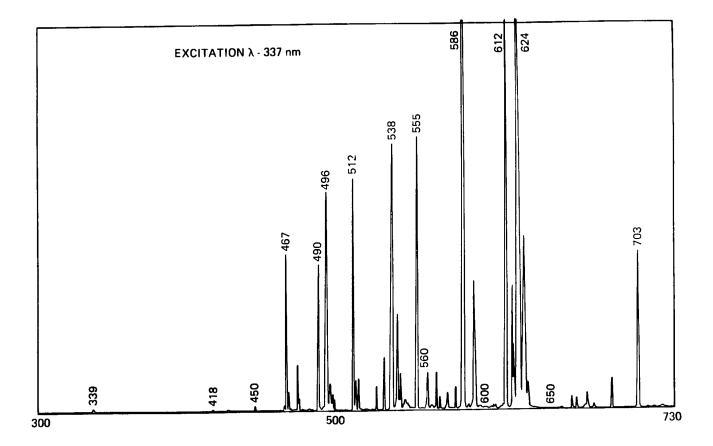
Intensities of emission bands are a function of temperature



 Change in intensity at cryogenic temperatures

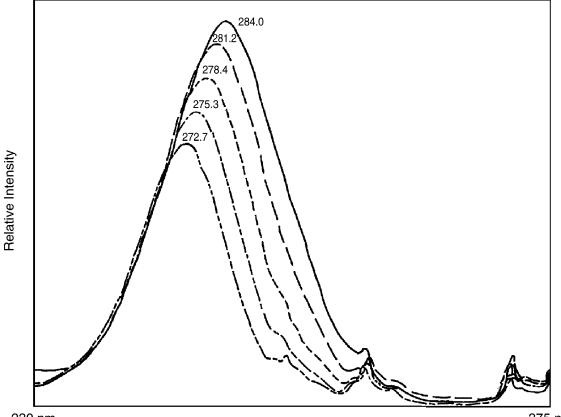


La₂O2S:Eu at low temperature





Temperature dependence of excitation $(Y_2O_3:Eu)$



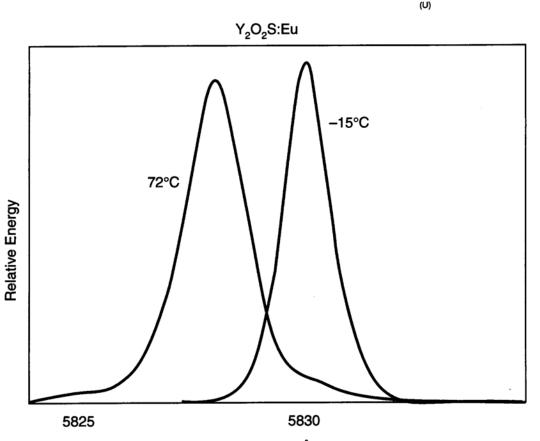
230 nm

375 nm



Temperature dependent line position and bandwidth

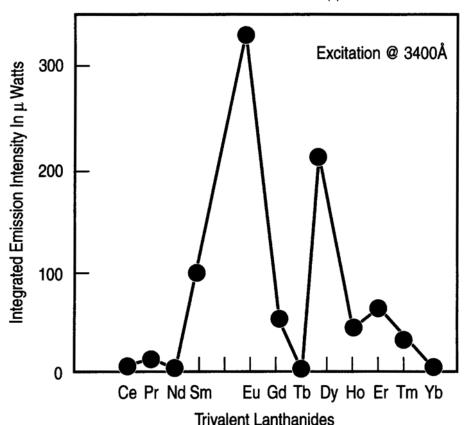
DWG. NO. K/G 95-888 GSS



Wavelength (Å)



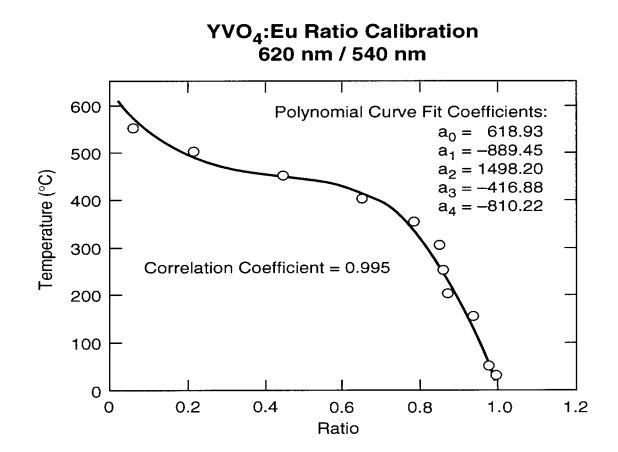
Emission intensity versus rare-earth dopant in YVO₄



DWG. NO. K/G 95-877R2 GSS (U)

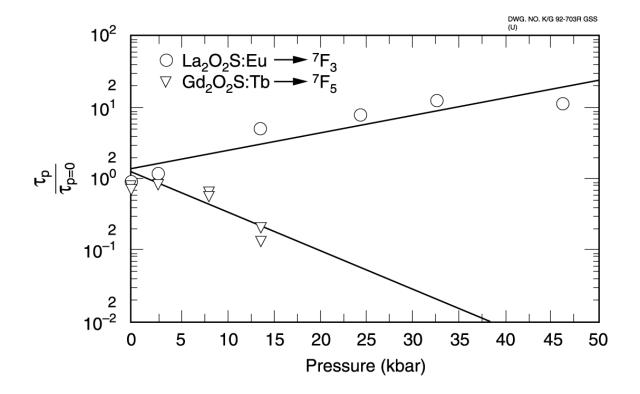


Example of ratio data





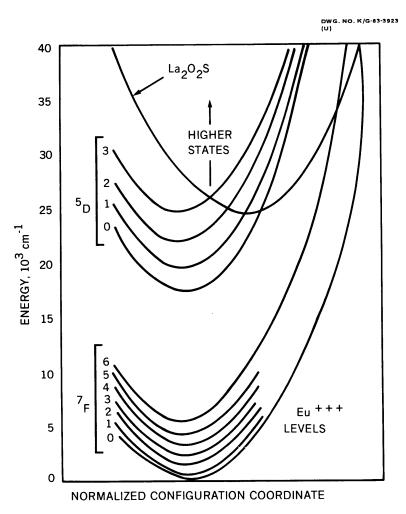
Pressure dependence of two pressure-sensitive phosphors



 Pressure vs decay time for La₂O₂S:Eu (top curve) and Gd₂O₂S:Tb (lower curve)



Origin of temperature dependence



Charge Transfer
 State Model

OAK RIDGE NATIONAL LABORATORY

U.S. DEPARTMENT OF ENERGY



Model of temperature and pressure dependence

$$\tan := \left[a_1 + a_2 \cdot \left[\exp \left[\frac{-(P \cdot q + Ects) \cdot h \cdot c}{k \cdot T} \right] \right] \right]^{-1}$$

A model was developed, resulting in the equation above, that predicts the decay time, tau, versus both pressure and temperature for La_2O_2S :Eu. Three of the parameters, a_1 , a_2 , and Ects; are obtained from fitting to temperature vs decay time data. The reciprocal of the low temperature decay time, a_1 , is 6369 sec⁻¹. The transfer rate ratio, a_2 , from the excited 5D_2 emitting state is 10¹²; and Ects = 3370 cm⁻¹ is the effective energy difference between the ${}^{5}D_{2}$ state and the charge transfer state. k is the Boltzmann constant, h is Planck's constant, and c the speed of light. T is the temperature in Kelvin. P is the pressure in psi. q is obtained empirically, it is the slope of the pressure versus decay time curve. Here $q = 2.73 * 10^{-3}$ psi⁻¹ * (cm⁻¹)⁻¹.

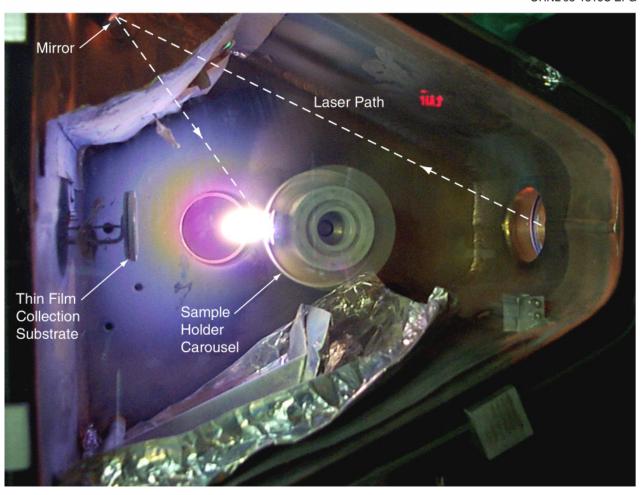


Phosphor selection criteria

- 1. Temperature Range of Application
- 2. Chemical compatibility
- 3. Target stationary or moving
- 4. Measurement Method used: decay time or ratio
- 5. Surface preparation considerations
- 6. Imaging or point measurements required



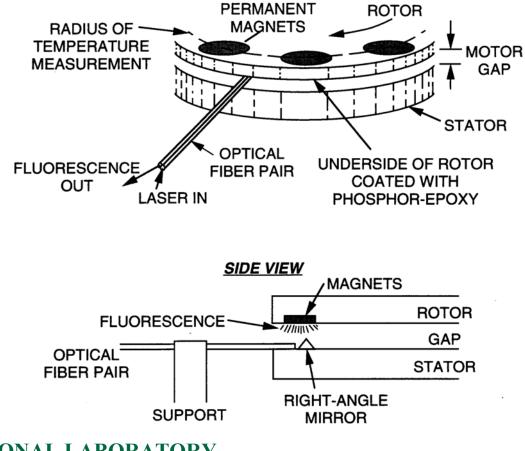
Pulsed laser deposition (PLD) can be used to apply phosphor coatings





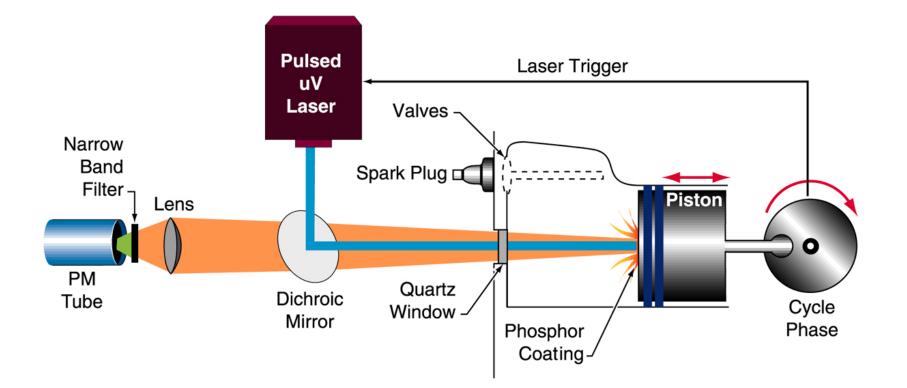
Permanent magnet motor

DWG NO. K/G 95-514 GSS





Set-up for piston measurement



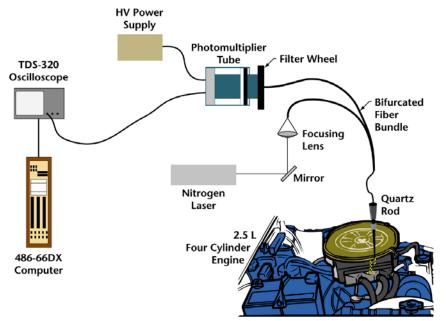


Fluorescing piston





Intake valve setup



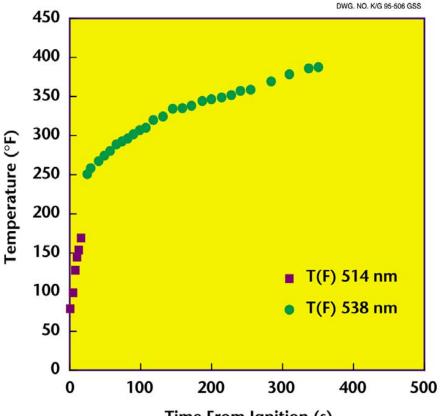
DWG. NO. K/G 95-508R GSS





Intake valve results

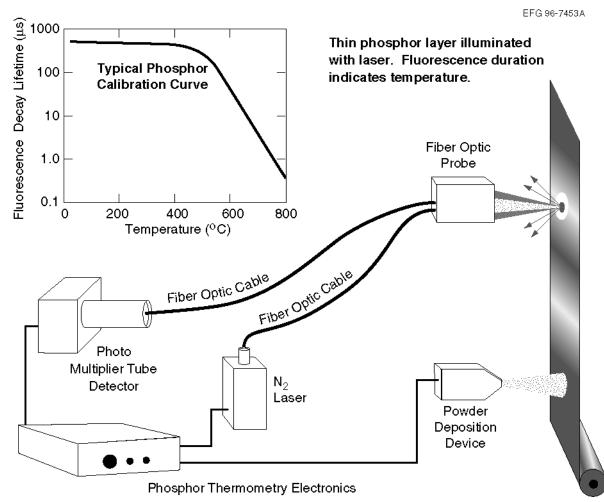




Time From Ignition (s)

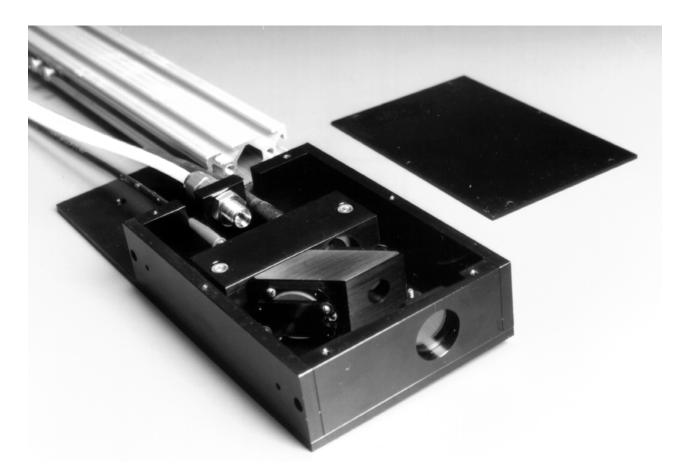


Galvanneal steel temperature





Optics for galvanneal steel





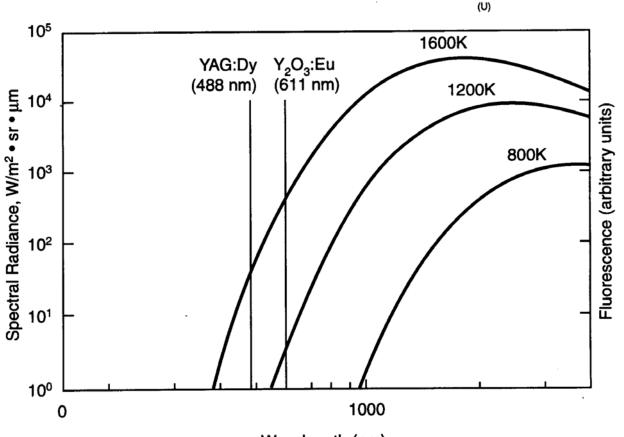
Phosphor emission in afterburner flame



 Afterburner flame impinging on a variable-area extractor. The white spot is phosphor luminescence.



Blackbody vs fluorescence emission



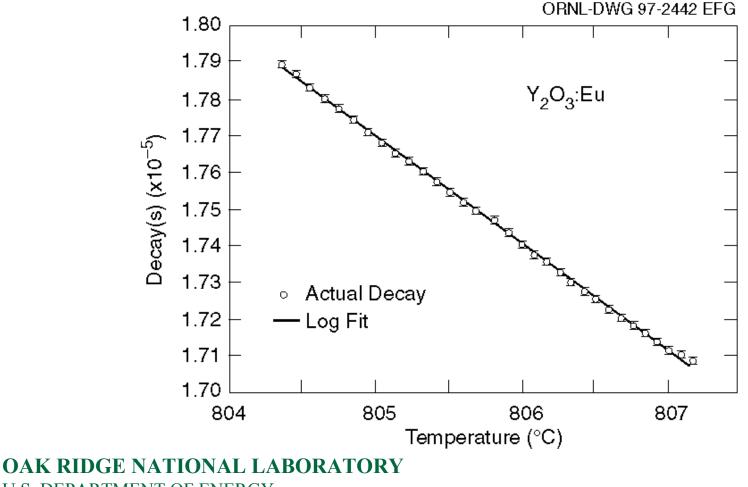
Wavelength (nm)

OAK RIDGE NATIONAL LABORATORY U.S. DEPARTMENT OF ENERGY



DWG, NO, K/G 95-889R GSS

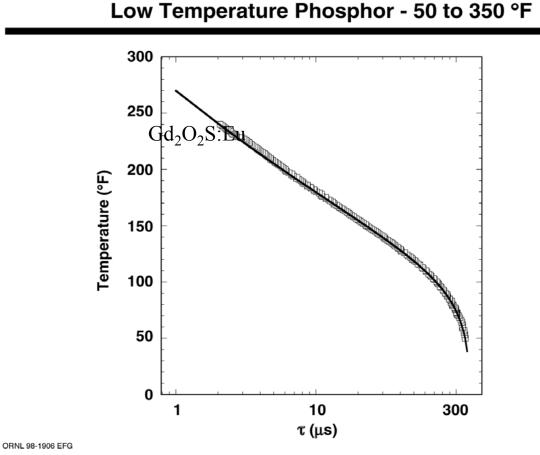
Precision limits are <10 mK for some phosphors and conditions





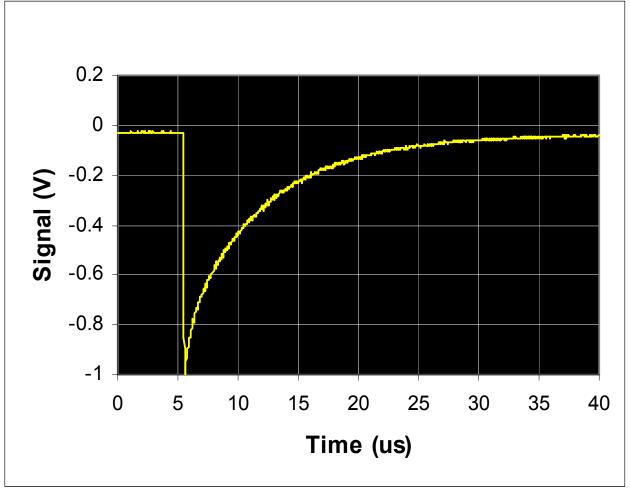
U.S. DEPARTMENT OF ENERGY

Low-temperature response



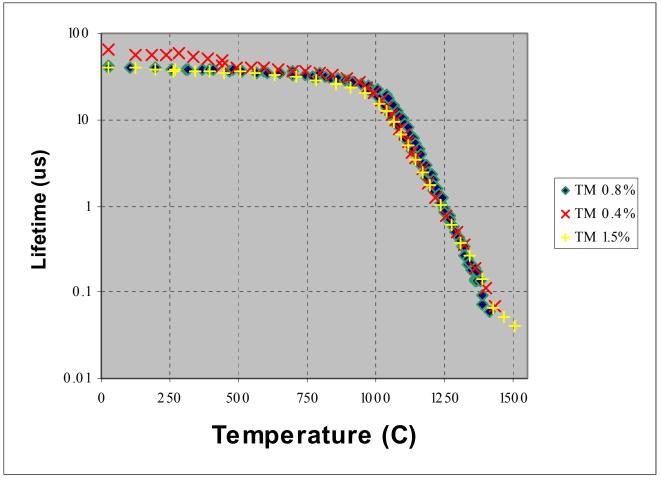


Averaged signal data of 460-nm emission from YAG:Tm at 1092 C



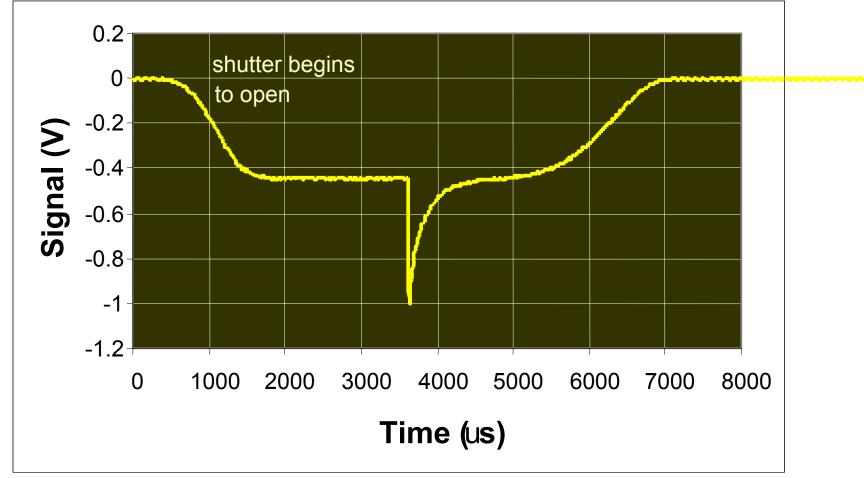


YAG:Tm temperature response



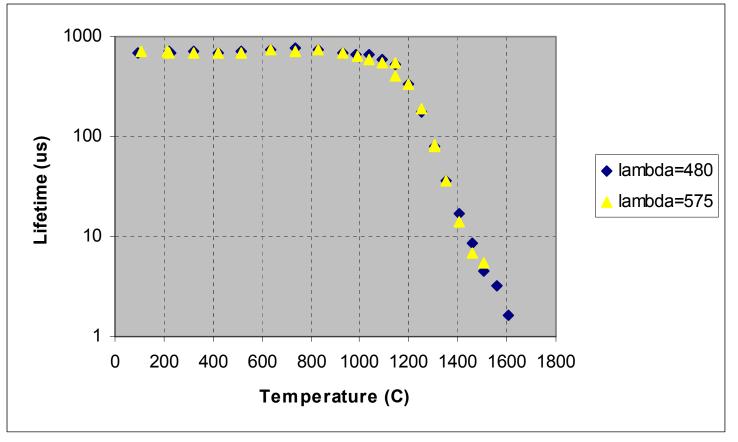


YAG:Dy 453-nm emission on blackbody background at 1306 C



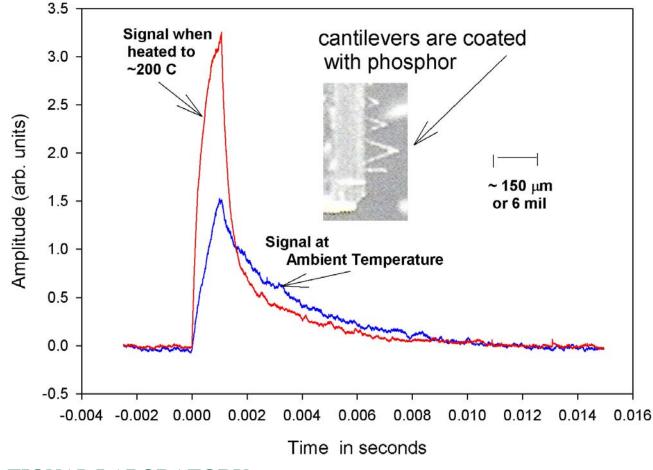


YAG:Dy temperature response





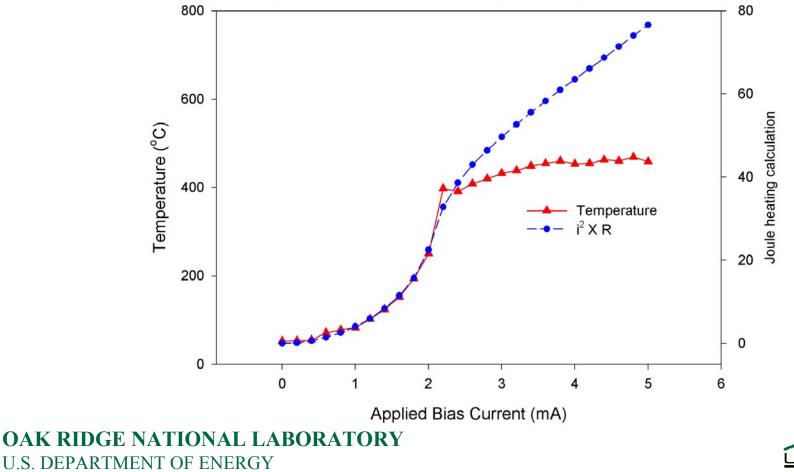
Fluorescent lifetimes change when cantilever is heated





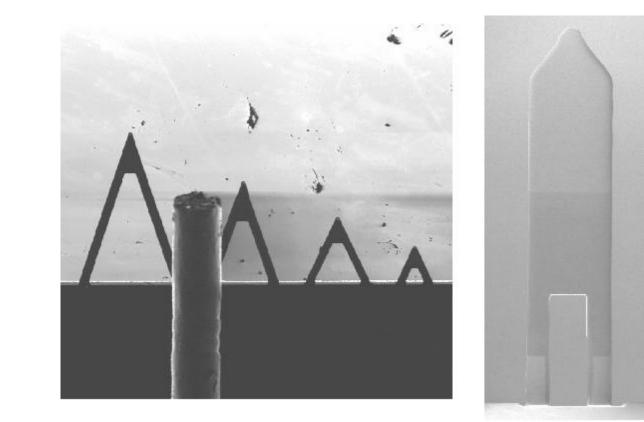
Measured energy compared with measured temperature in a micro-cantilever

Variation in Temperature and Joule heating with Applied Bias Current 1-10-02





Micro-cantilevers



(a)

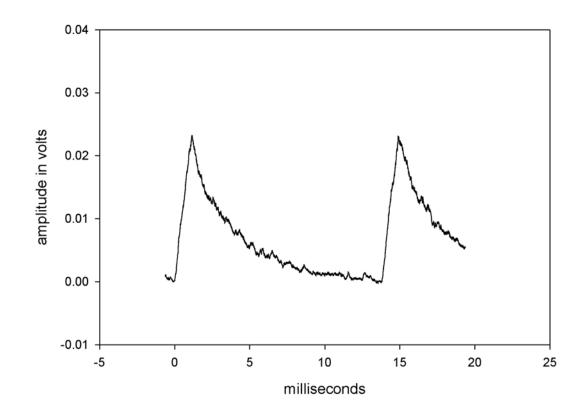
(b)





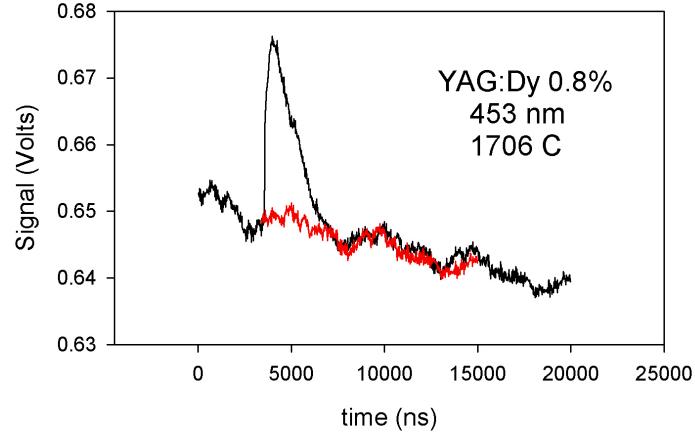
LED-induced fluorescence from a micro-cantilever

fluorescence from microcantilever coated with phosphor (excited with ~2 ms duration square wave pulse from blue LED)



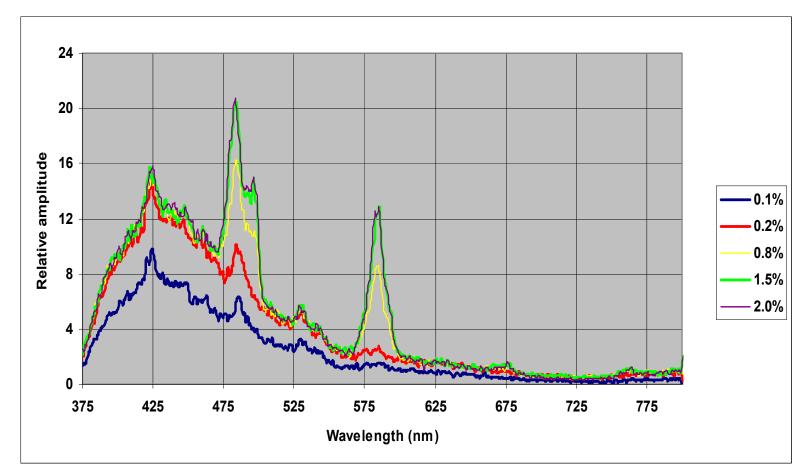


Signal & background at 1706 C



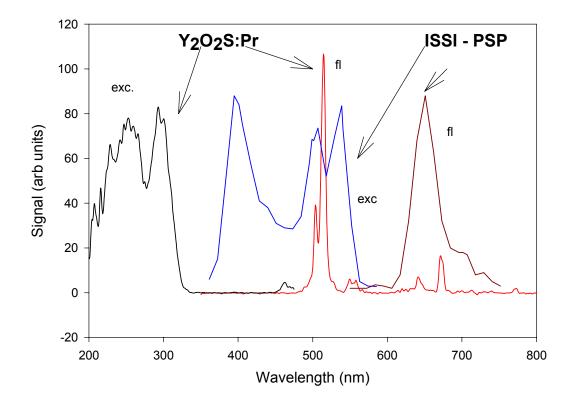


YAG:Dy emission strengths vary with dopant concentration





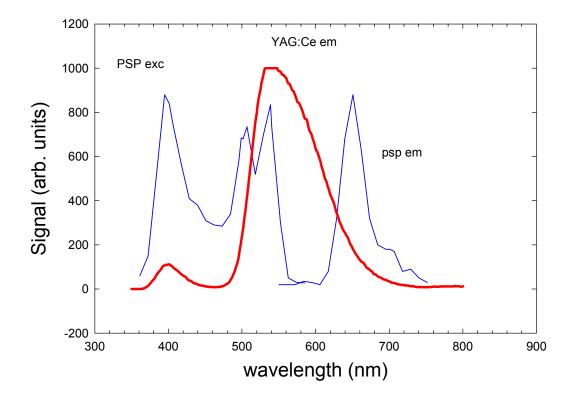
Emission bands of Y₂O₂S:Pr and pressure sensitive paint (PSP)





Emission bands: YAG:Ce and PSP

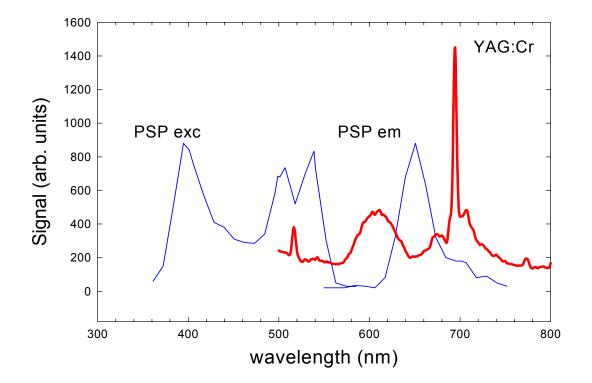
YAG:Ce and PSP





Emission bands: YAG:Cr and PSP

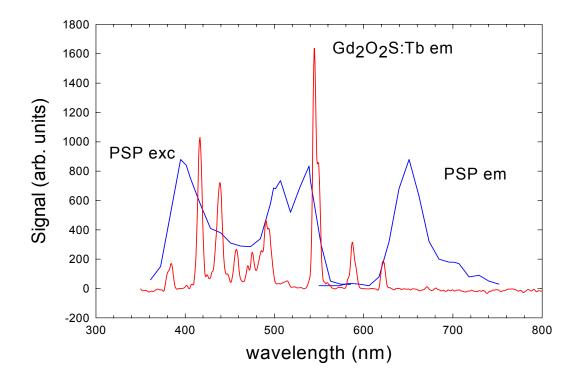
YAG:Cr and PSP





Emission bands: Gd₂O₂S:Tb

Gd₂O₂S:Tb (low Tb concentration) and PSP





Bibliography of phosphor chemistry and physics

- K. T. V. Grattan and Z. Y. Zhang, *Fiber Optic Fluorescence Thermometry*, Chapman & Hall, London (1995). (New Edition planned)
- G. Blasse and B. C. Grabmaier, *Luminescent Materials*. Springer Verlag, New York (1994).
- R. C. Ropp, *Luminescence and the Solid State*, Studies in Inorganic Chemistry, Vol. 12, Elsevier, Amsterdam (1991).
- S. W. Allison and G. T. Gillies, *Remote Thermometry with Thermographic Phoshpors: Instrumentation and Applications*, Review of Scientific Instruments, 68(7), 1997.
- R. C. Ropp, *The Chemistry of Artificial Lighting Devices: Lamps, Phosphors and Cathode Ray Tubes*, Studies in Inorganic Chemistry, Vol. 17 (Elsevier, Amsterdam, 1993).
- Handbook of Phosphors, ed. By S. Shionoya and W. M. Yen, CRC Press, NY. 1999.

