# Fluorescence-based thermometry with phosphors

- Oak Ridge National Laboratory
- Engineering Science and Technology Division

# Outline

- List some past applications
- Discuss temperature dependence
- Survey applications

# History of Fluorescence-Based Thermometry ORNL/LANL/SB

1. Application to Gas Centrifuges – low and high speeds 1984
2. Permanent Magnet Motor - high speed, low temp 1985
3. High Altitude Test Simulating Wind Tunnel stationary, medium temperature 1985
4. TVA Demonstrator unit stationary/ambient temp 1986
5. Sponsored two Students to do Phosphor Metrology 1987-1989
6. Burner Rig low speed, moderately high temperature 1987
7. Spin Pit high speed, moderate temperature 1987
8. New High Temperature Materials yags, orthophosphates 1988
9. Low temperature heat flux gauge tests 1988
10. Laboratory Imaging of Temperature Profiles ambient 1988
11. $CO_2$ Laser Beam Profile Measurement 1988

# History continued

12. Steam Plant Water-Wall Field Measurement 1989
13. Pratt Whitney Test – First-stage Turbine Stator Vanes 700 C 1989
14. Stress/Strain Measurement
15. Virginia Tech Turbo Fan Measurements 1990
16. YAG:Tb and YAG:Dy lab measurements to 1500 C 1990
17. Transient Thermometry 100 C/ms lab demo 1990
18. ATEGG test at Pratt Whitney 1100 C 1992
19. Falling Film LiBr Heat Pump liquid/phosphor flow 1992
20. Pressure sensitivity and sensor investigation 1993-1995
21. Combustion Engine Piston and Intake Valve moderate temperatures 1994-1995
22. High-resolution thermometry lab demo 10 mK at 1073K 1995

# History continued

22. Galvanneal Strip Thermometry slow moving/ 700 C 1995-1996
23. Light-emitting diode excitation begun 1997
24. New phosphor investigations for use with pressure sensitive paints. 1999
25. Spallation Neutron Source transient application 1999-2001
26. Microcantilever measurement 2002
27. NASA High Temperature 1700 C coating studies 2001-2003
28. PEM Fuel Cell stationary / low profile 2003 to the present
29. Triboluminescence investigations 2003 to the present

# 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 aerodynamic applications.

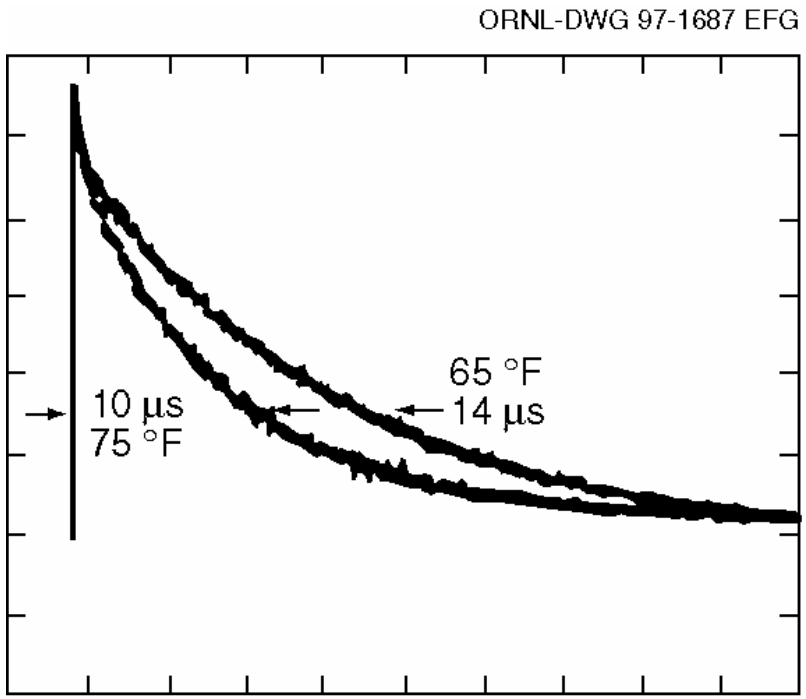
* Advances in lasers, microelectronics, and other supporting technologies enabled additional commercial as well as scientific uses.

# 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.

# 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
- 7. Rise time



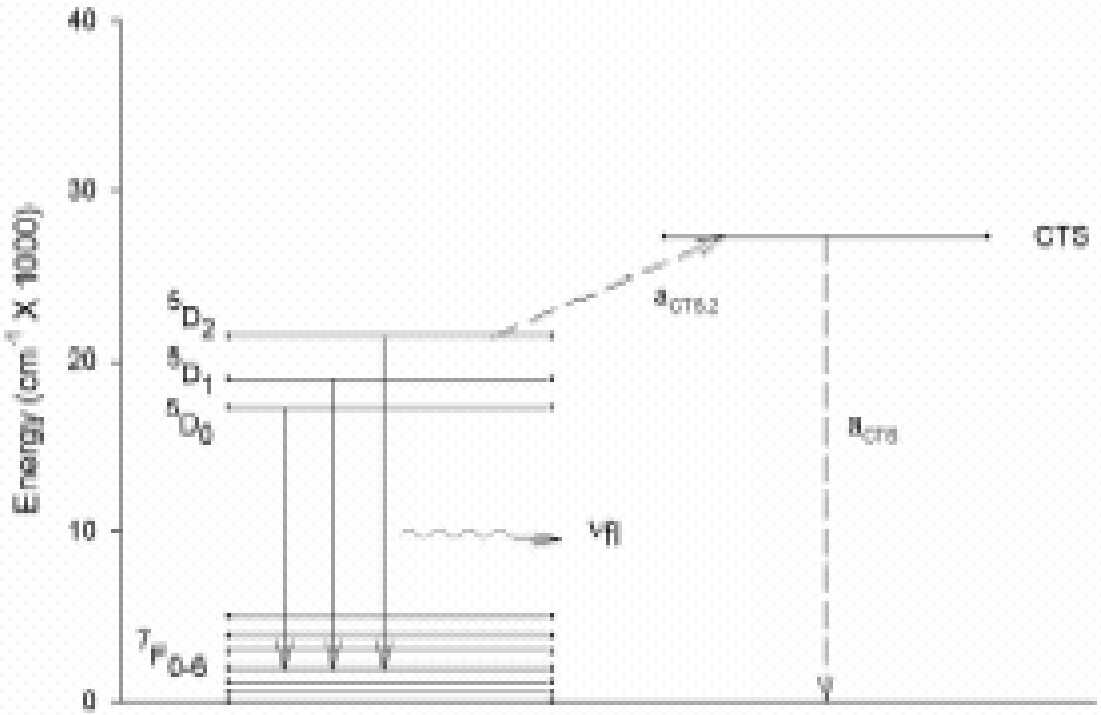
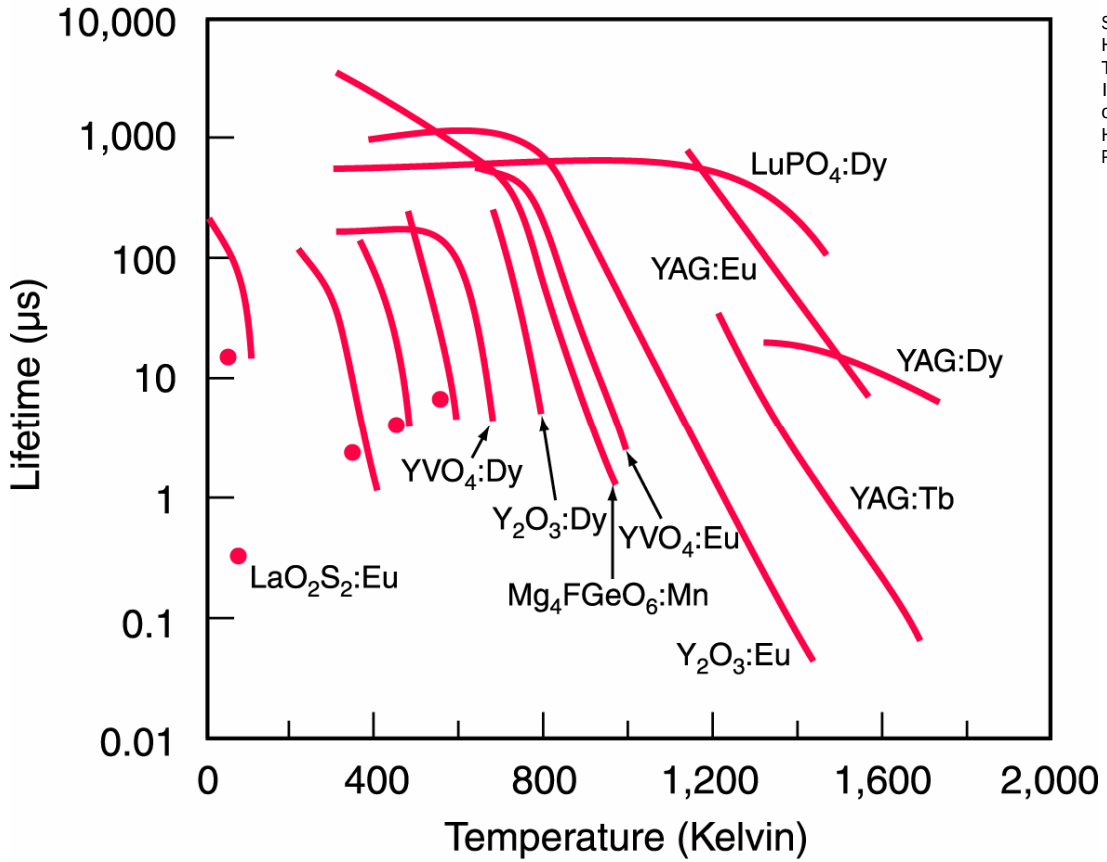



FIGURE 2. Energy level diagram for $Eu^{3+}$. The exact position of the charge transfer state (CTS) varies with host.

S. W. Allison, M. R. Cates, S. M. Goedeke, W. A. Hollerman, F. N. Womack, and G. T. Gillies, "Remote Thermography with Thermographic Phosphors: Instrumentation and Applications" a chapter in Handbook of Luminescence Display Material, and Devices, Edited by H. S. Nalwa, and L. S. Rohwer American Scientific Publishers Stevenson Ranch, CA 2003.

# Decay time vs temperature for selected phosphors

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




S. W. Allison, M. R. Cates, S. M. Goedeke, W. A. Hollerman, F. N. Womack, and G. T. Gillies, "Remote Thermography with Thermographic Phosphors: Instrumentation and Applications" a chapter in Handbook of Luminescence Display Material, and Devices, Edited by H. S. Nalwa, and L. S. Rohwer American Scientific Publishers Stevenson Ranch, CA 2003.

**Figure 12. Lifetime versus temperature of selected phosphors.**

# From first publication 1983

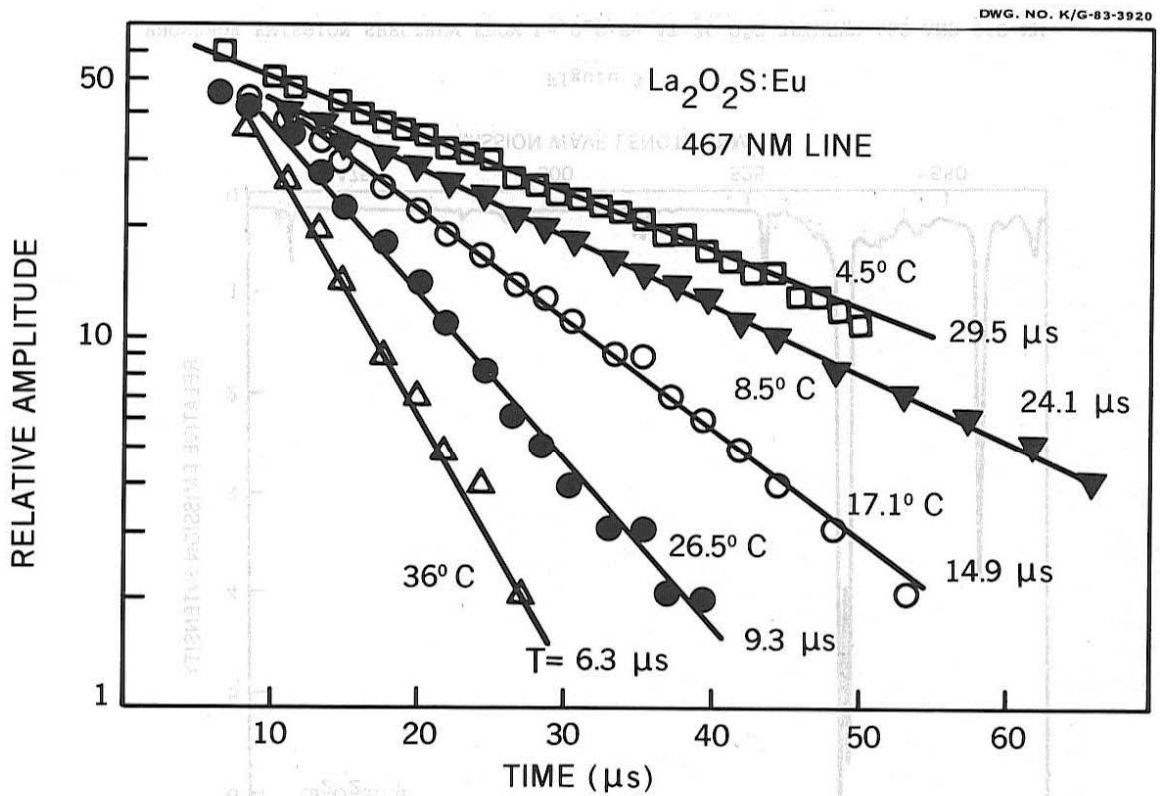


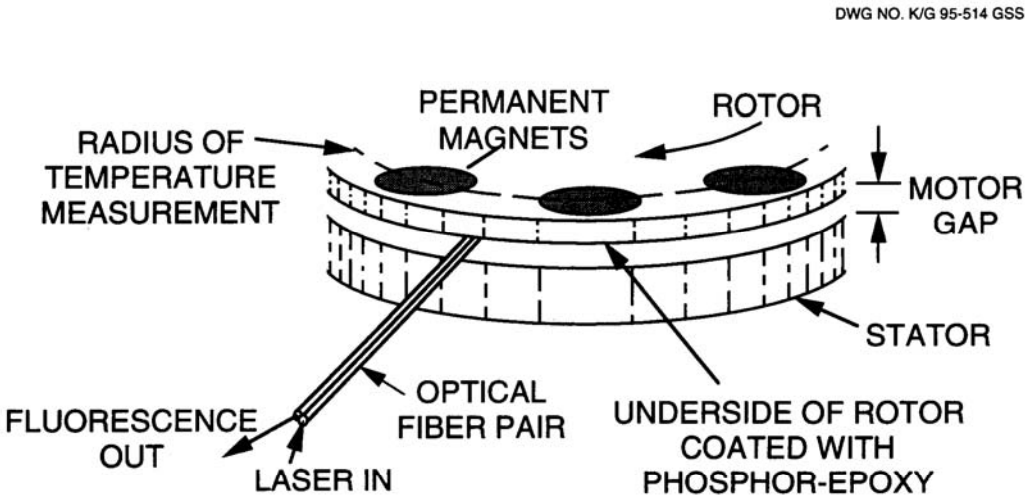

Figure 4

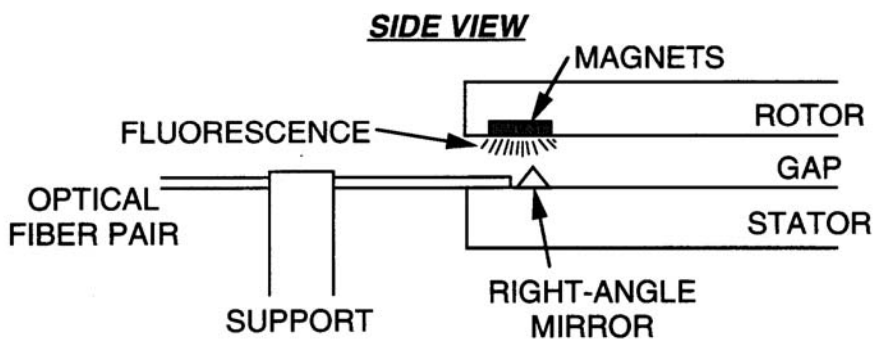
PHOSPHOR DECAY DATA AT VARIOUS TEMPERATURES FOR THE 467 NM LINE



Cates, M. R., Allison, S. W. et al., *Remote Thermometry of Moving Surfaces by Laser-Induced Fluorescence of Bonded Phosphor*, Proceedings of the Laser Institute of America, **39**, pp. 50-56, 1984. (also Martin Marietta Energy Systems Report K/TS-11,232, 1983.)

# Permanent magnet motor




Allison, S. W., Gillies, G. T., Cates, M. R., and Noel, B. W., *Method for Monitoring Permanent Magnet Motor Heating with Thermographic Phosphors*, IEEE J. of Inst. and Control, Vol. 37, No. 4, pp 637-641, 1988.

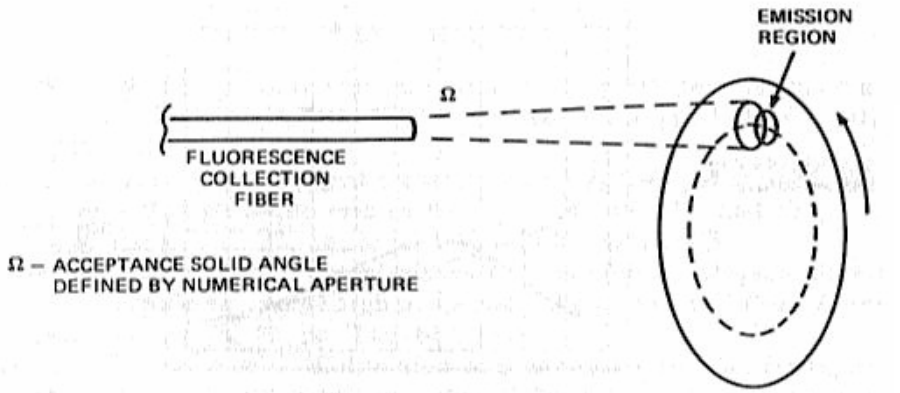
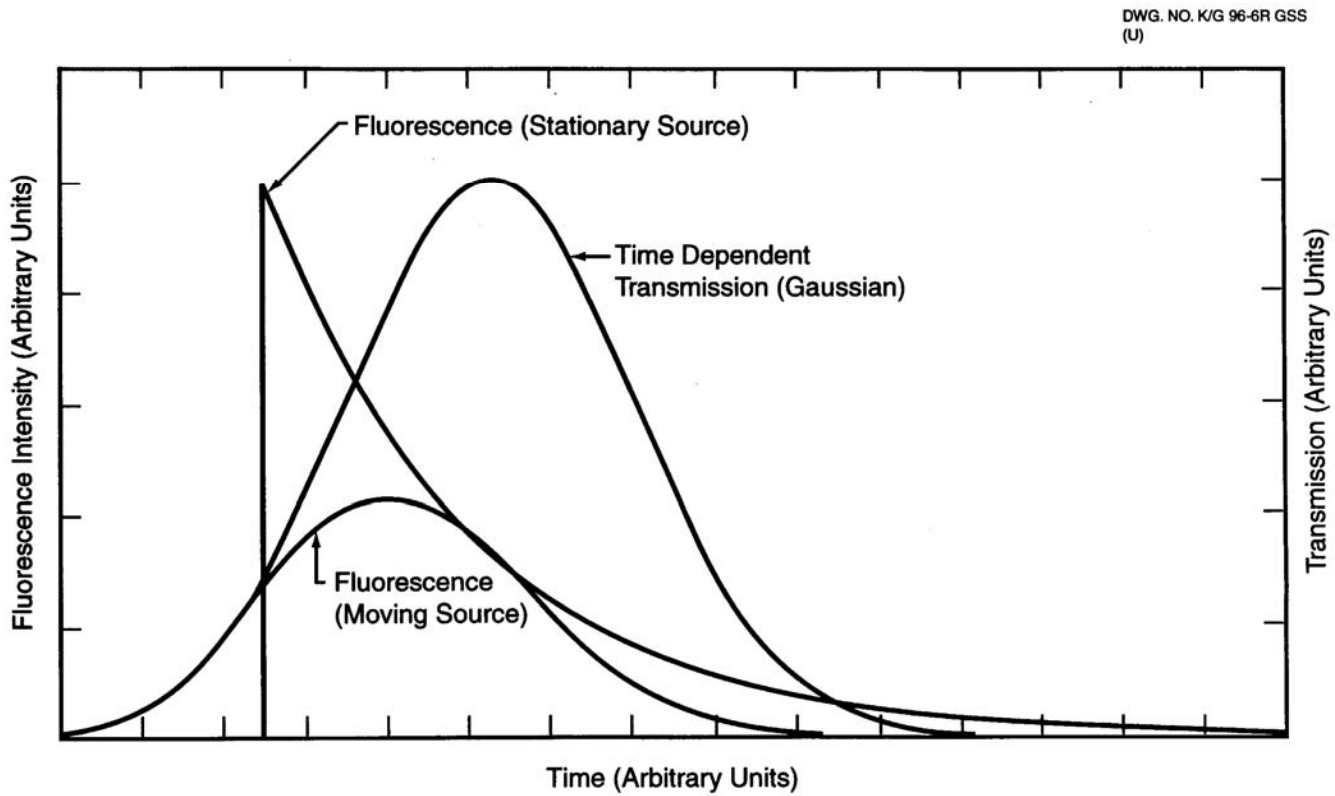



Fig. 4. The rotation of the rotor causes the fluorescing spot to move with respect to the fluorescence collection fiber's input aperture.

Take ratio of temperature independent emission line for stationary and moving. Normalize the temperature dependent signal with this.




Allison, S. W., Gillies, G. T., Cates, M. R., and Noel, B. W., *Method for Monitoring Permanent Magnet Motor Heating with Thermographic Phosphors*, IEEE J. of Inst. and Control, Vol. 37, No. 4, pp 637-641, 1988.

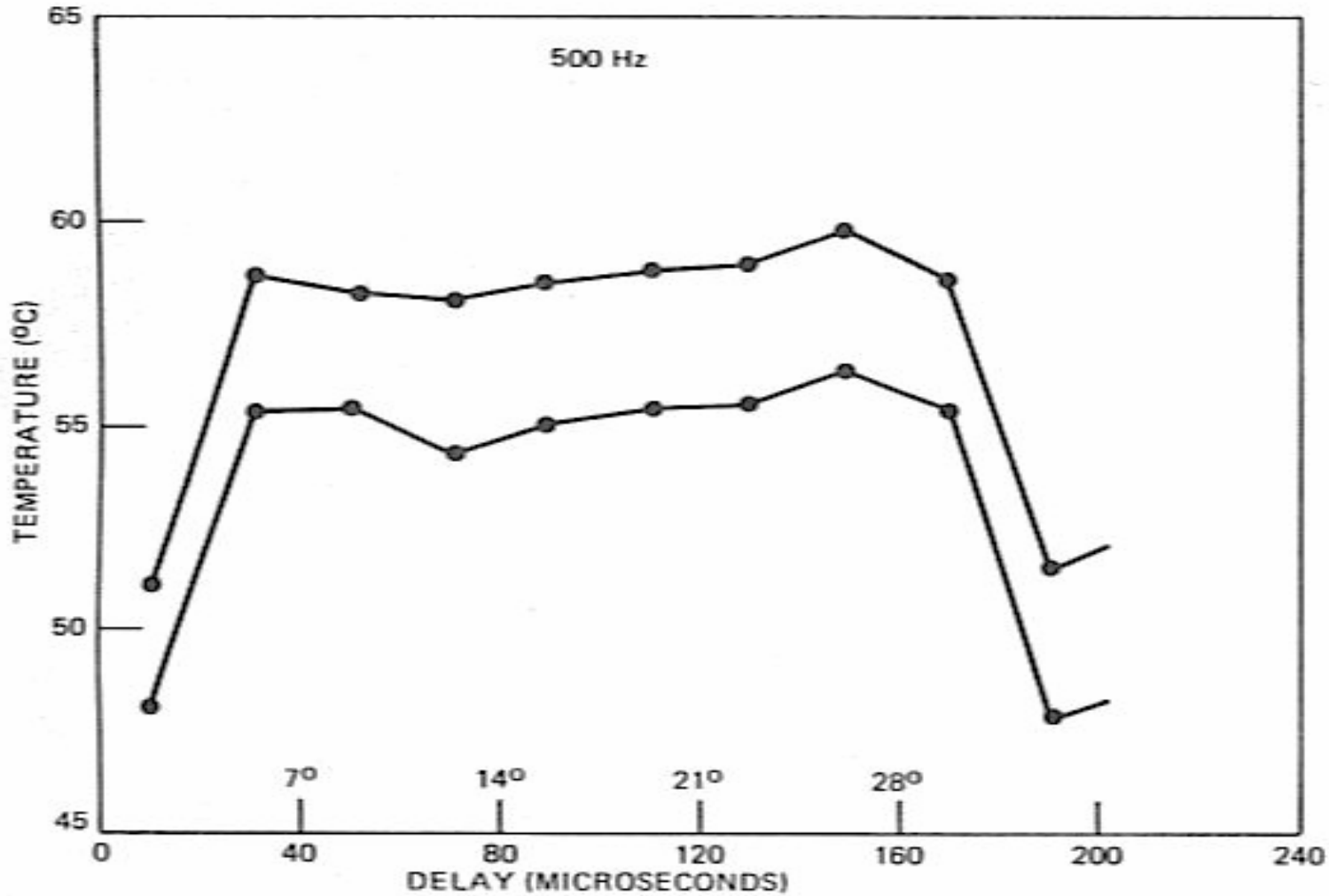
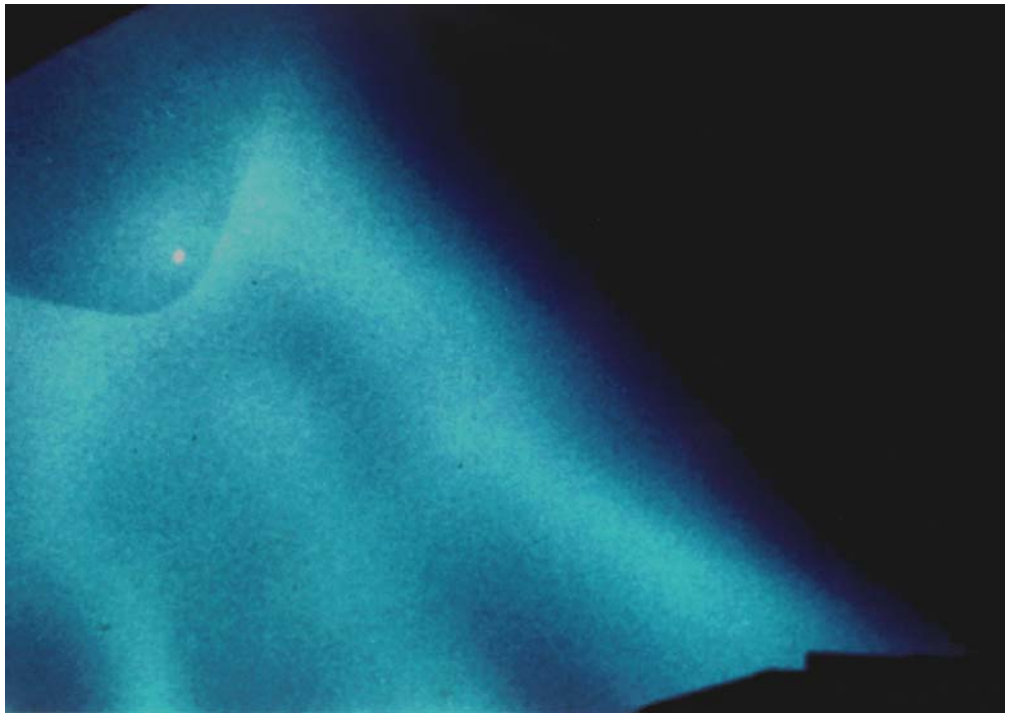
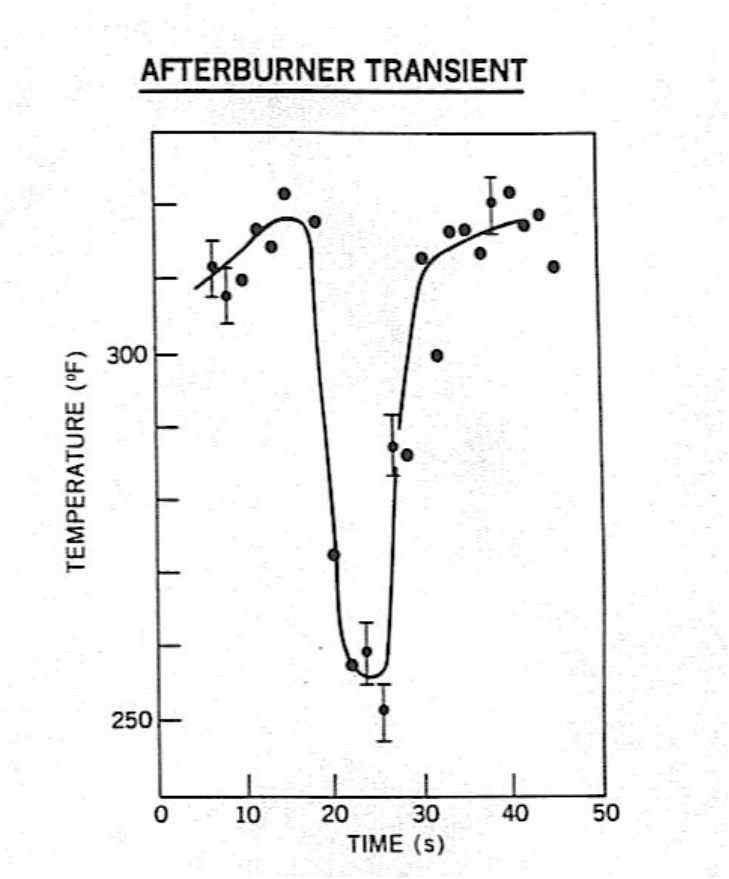



Fig. 8. Temperature distribution across the surface of one of the permanent-magnets on the rotor.

Allison, S. W., Gillies, G. T., Cates, M. R., and Noel, B. W., *Method for Monitoring Permanent Magnet Motor Heating with Thermographic Phosphors*, IEEE J. of Inst. and Control, Vol. 37, No. 4, pp 637-641, 1988.

# Phosphor emission in afterburner flame






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

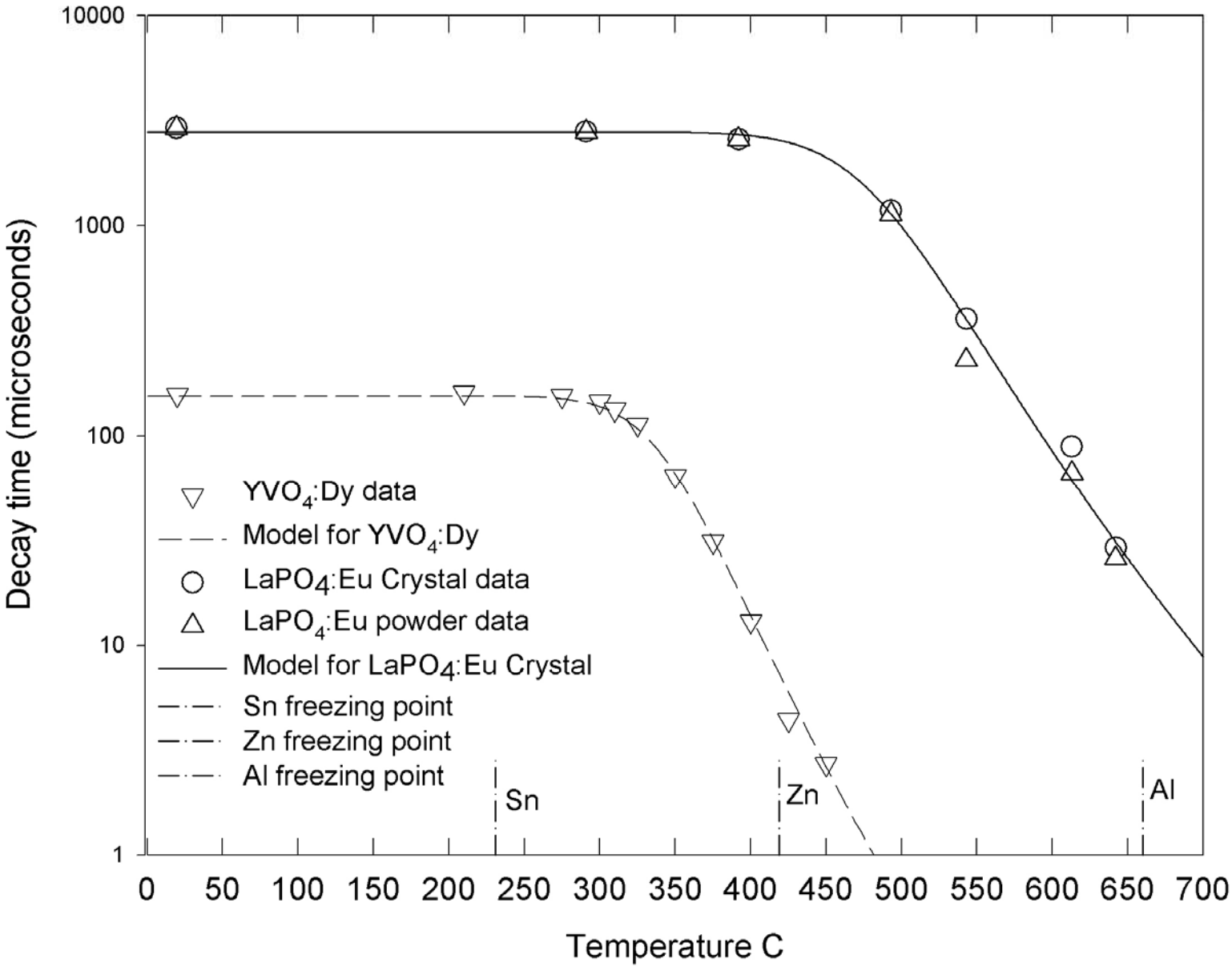
Allison, S. W., Cates, M. R., Scudiere, M. B., Bentley, H. T., Borella, H. M., and Marshall, B. R., *Remote Thermometry in a Combustion Environment using the Phosphor Technique*, Proc. of SPIE Conf. on Flow Visualization and Aero-Optics in Simulated Environments, Vol. 788, pp. 90-99, 1987.

# Model of temperature

$$tau = \frac{1}{a_1 + a_2 \exp\left(-\frac{E}{kT}\right)}$$

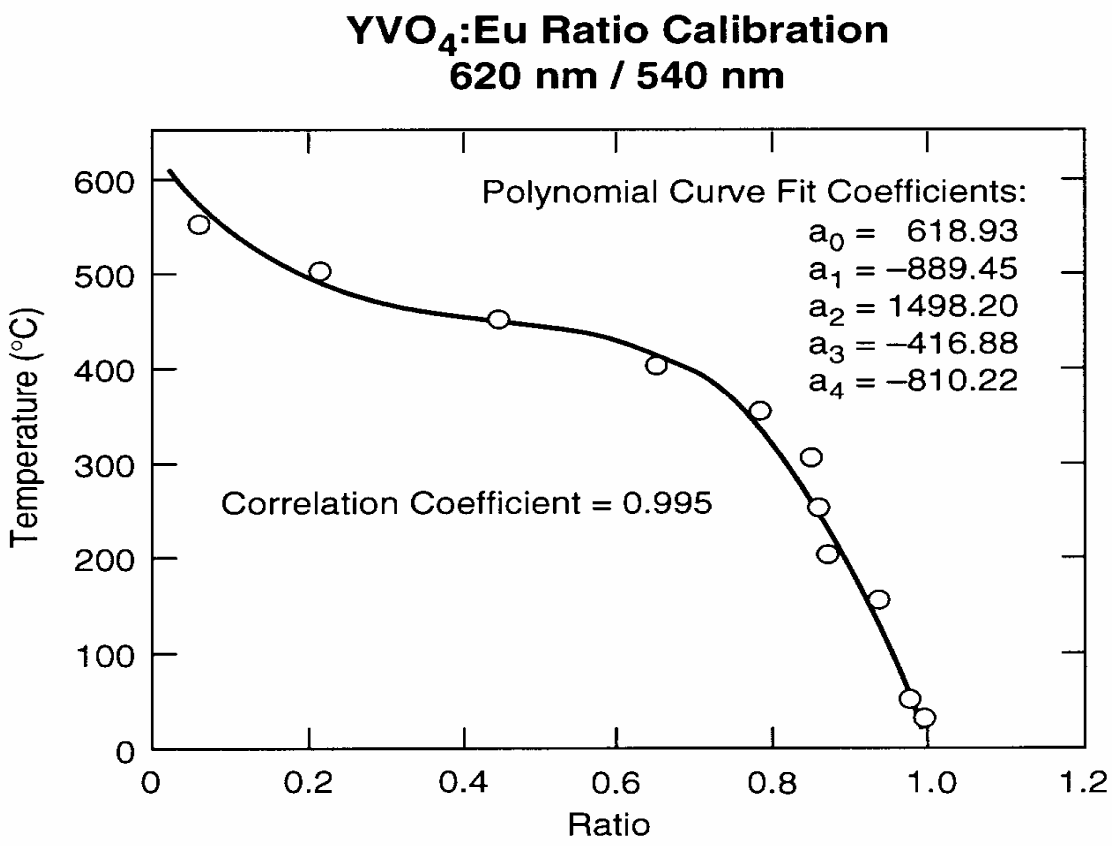
- A model was developed, resulting in the equation above, that predicts the decay time, tau, versus both pressure and temperature for $La_2O_2S$:Eu. Three of the parameters, $a_1$, $a_2$, and Ects; are obtained from fitting to temperature vs decay time data. The reciprocal of the low temperature decay time, $a_1$, is 6369 $sec^{-1}$. The transfer rate ratio, $a_2$, from the excited $^5D_2$ emitting state is $10^{12}$; and Ects = 3370 $cm^{-1}$ is the effective energy difference between the $^5D_2$ 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 = $2.73 * 10^{-3}$ $psi^{-1} * (cm^{-1})^{-1}$.

S. W. Allison, D. Beshears, M. R. Cates, and G. T. Gillies, "A Wide-Range Phosphor Thermometry Technique," to be published in the Proceedings of the Instrument Society of America's 44th International Symposium on Instrumentation, 1998.




Allison, S.W., M.R. Cates and G.T. Gillies 2002. "PHOSPHOR THERMOMETRY TECHNIQUES FOR THE REALIZATION OF THERMAL STANDARDS," *roceedings of the 48th International Instrumentation Conference, San Diego, CA USA, ISA, ISA, San Diego, CA USA, 05/05/2002-05/09/2002.*

# Example of ratio data




S. W. Allison,et.al., “A Wide-Range Phosphor Thermometry Technique,” Proceedings of the ISA’s 44th International Instrumentation Symposium, 1998. ISBN: 1-55617-663-5

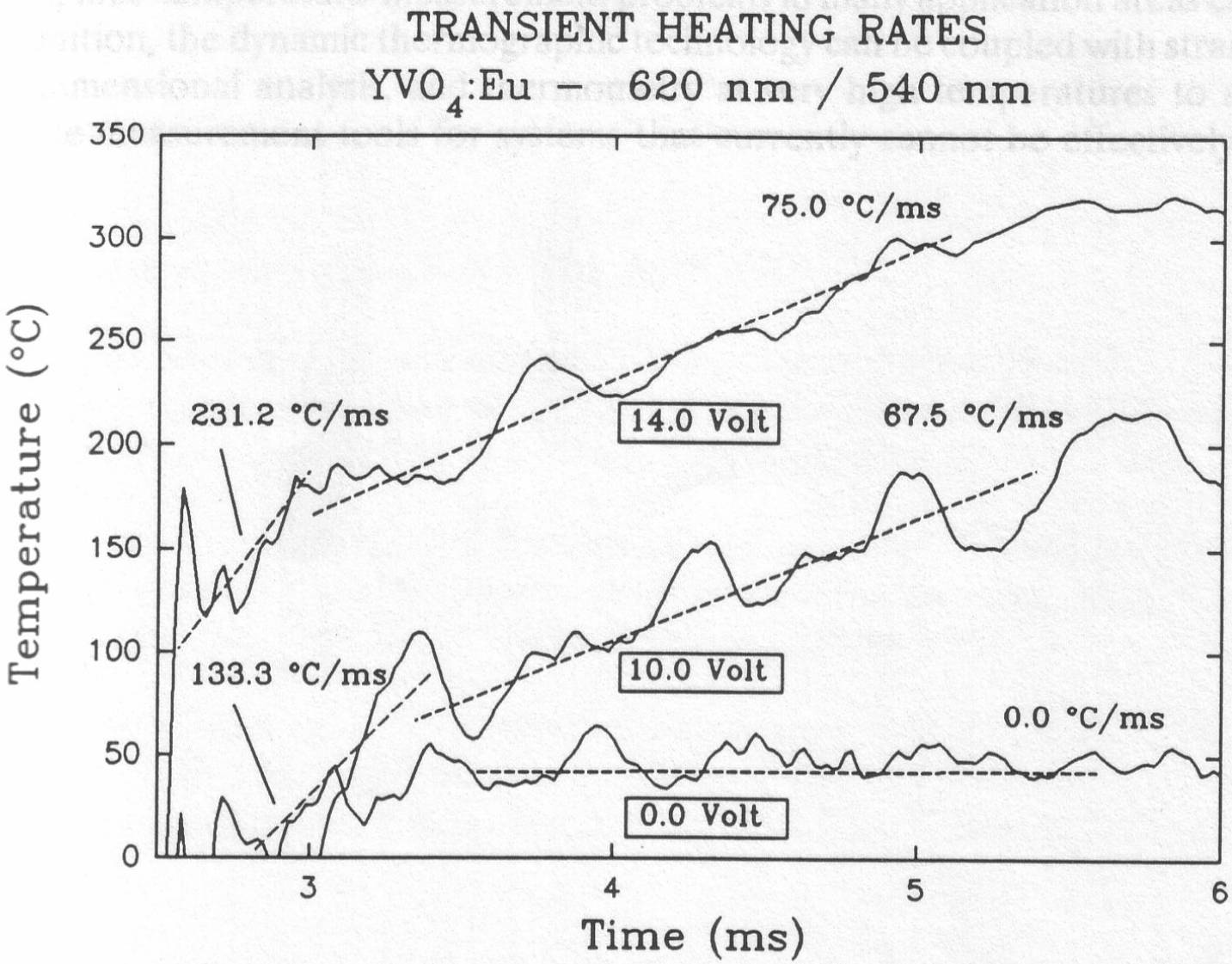
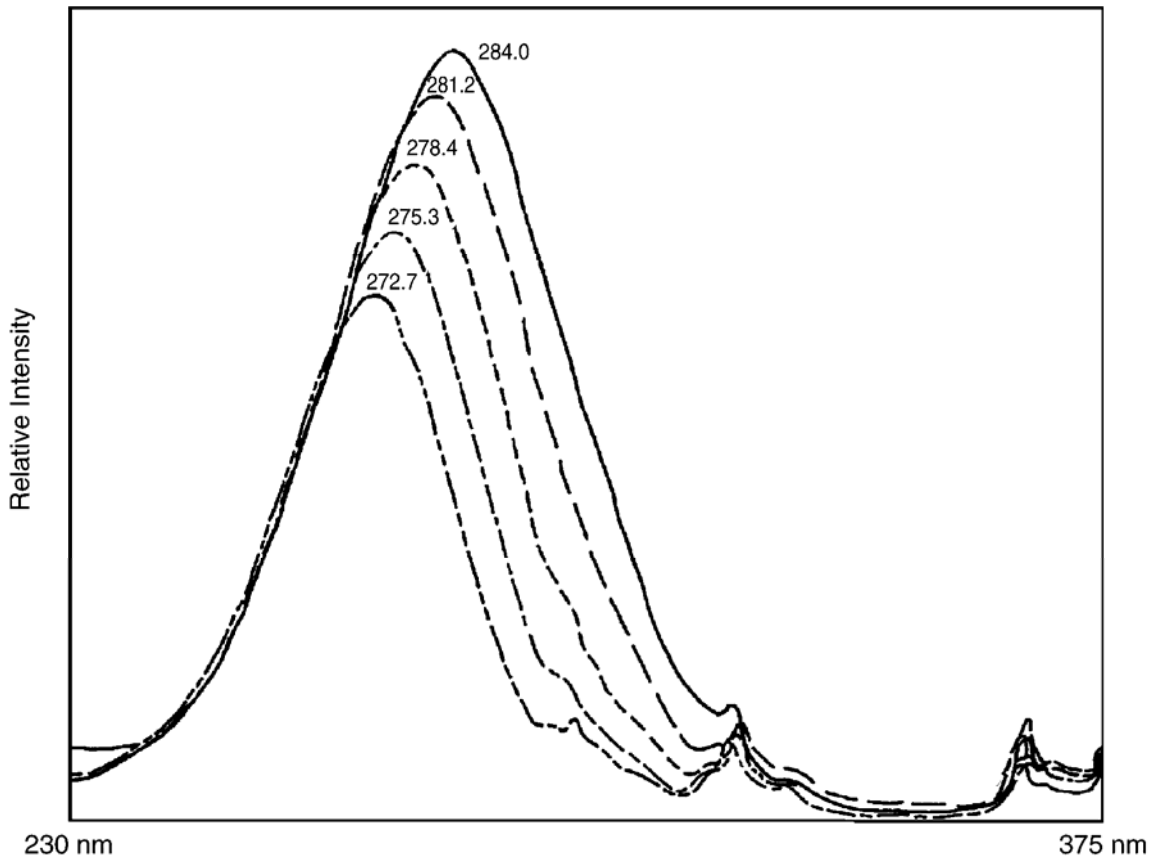



Fig. 11. Representative heating rates for 0-, 10-, and 14-V heating transients.

S. W. Allison,et.al., "A Wide-Range Phosphor Thermometry Technique," Proceedings of the ISA's 44th International Instrumentation Symposium, 1998. ISBN: 1-55617-663-5

# Temperature dependence of excitation ($Y_2O_3$:Eu)




S. W. Allison,et.al., “A Wide-Range Phosphor Thermometry Technique,” Proceedings of the ISA’s 44th International Instrumentation Symposium, 1998. ISBN: 1-55617-663-5

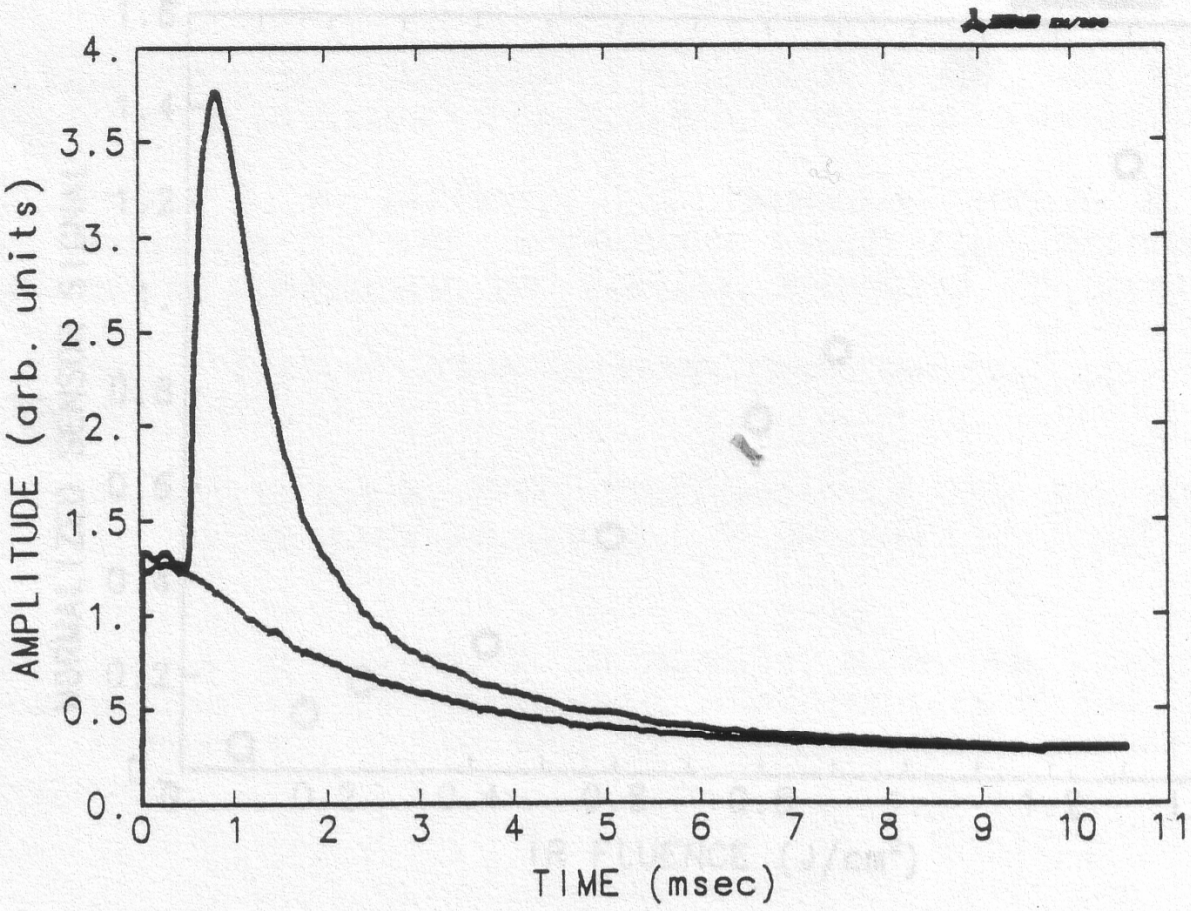
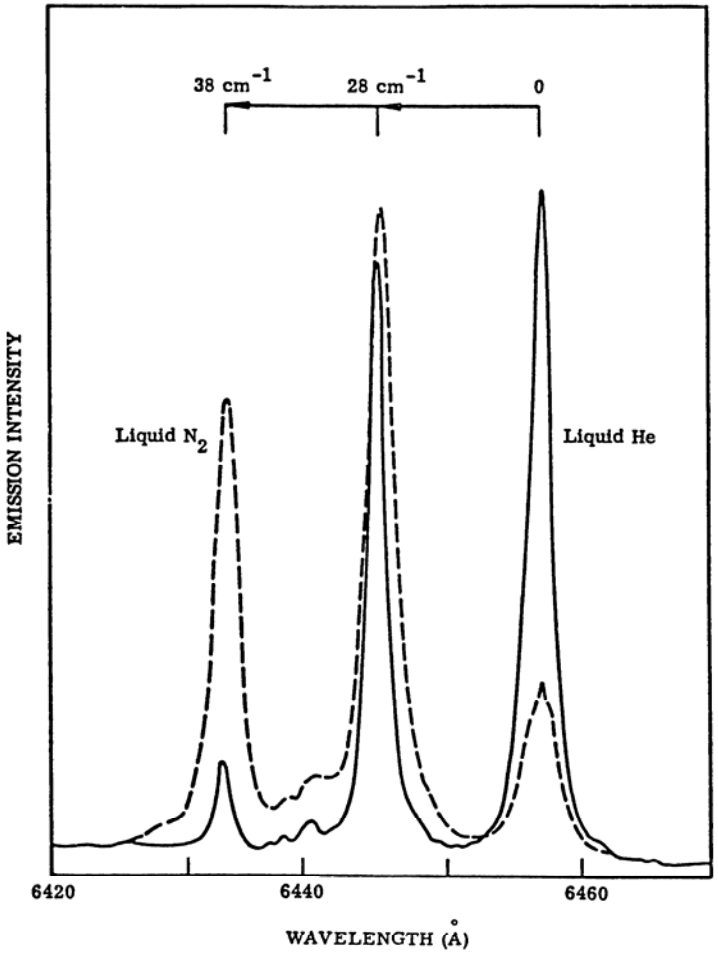



Fig. 7. UV-excited $YVO_4$:Dy sensor luminescence at 575 nm x 10 nm in the presence (top) and absence (bottom) of the $CO_2$ laser pulse.

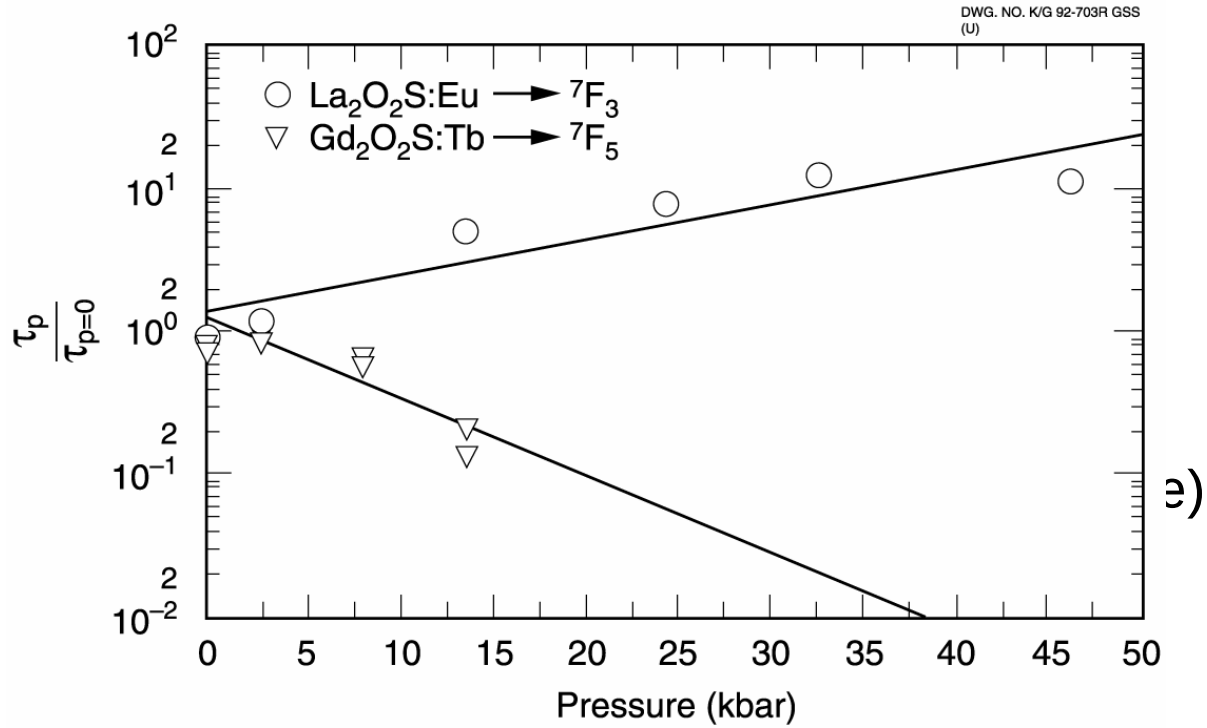
Turley, W. D., et al *A Fiber Optic Detection System for Determination of an Infrared Beam Spectrum in an Adverse Environment*, Chemical Biochemical, and Environmental Fiber Sensors, Proceedings, SPIE, Vol. 1172, September 6-7, 1989.

# Intensities of emission bands are a function of temperature




- Change in intensity at cryogenic temperatures

# Pressure dependence of two pressure-sensitive phosphors

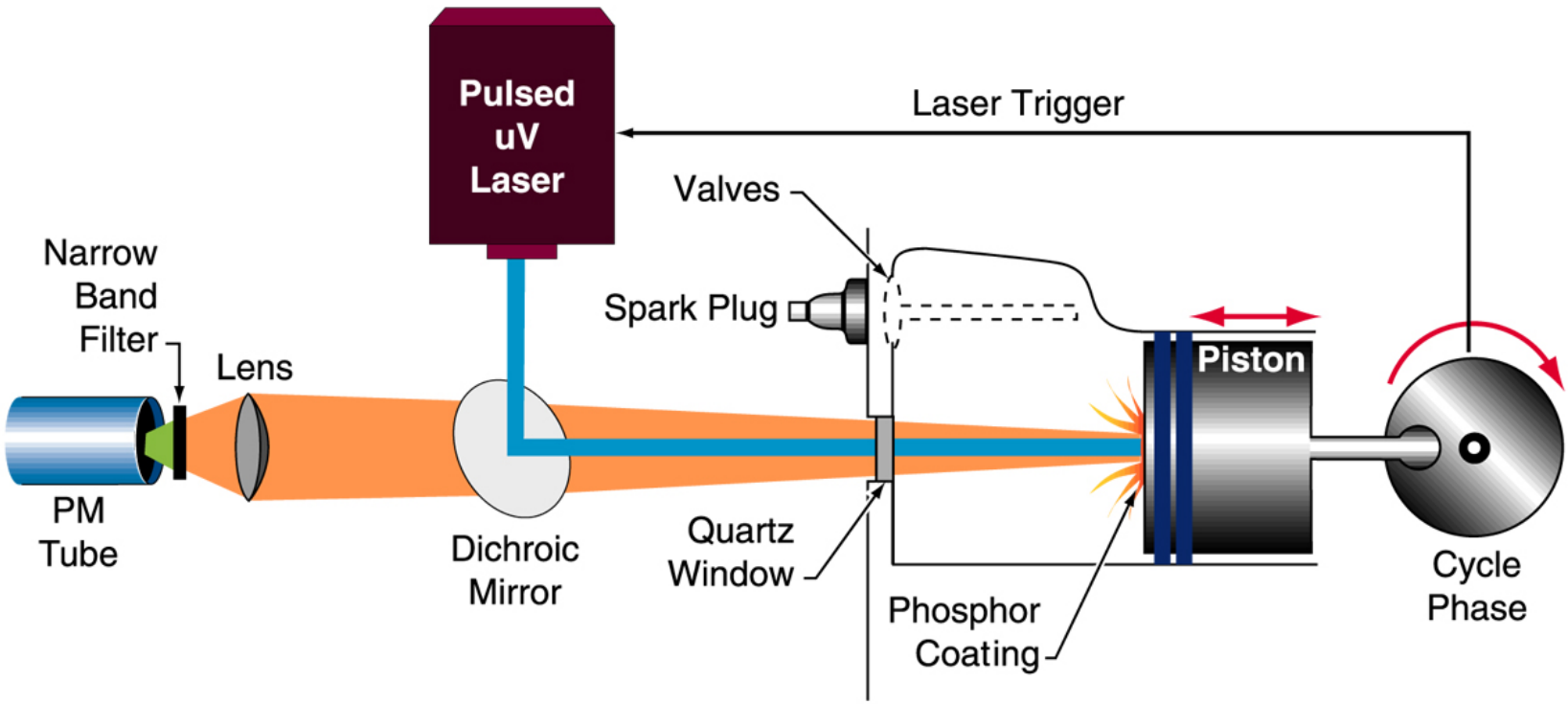


# Phosphor selection criteria

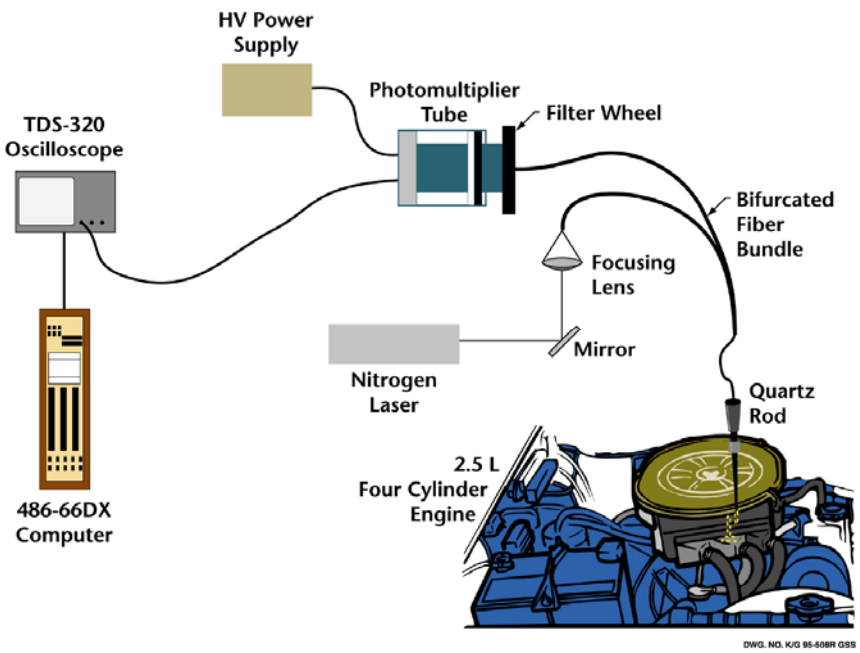
- 1. Temperature Range of Application
- 2. Chemical compatibility
- 3. Target stationary or moving
- 4. Measurement Method used: decay time or ratio
- 5. Surface preparation considerations
- 6. Imaging or point measurements required

# Fluorescing piston

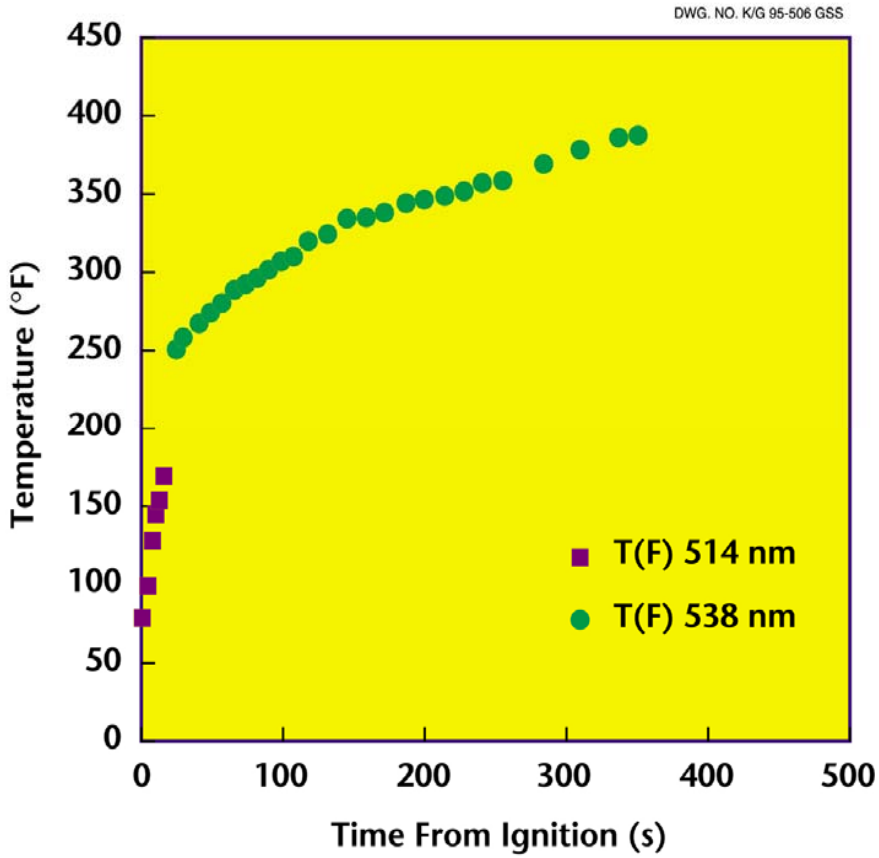
# Set-up for piston measurement



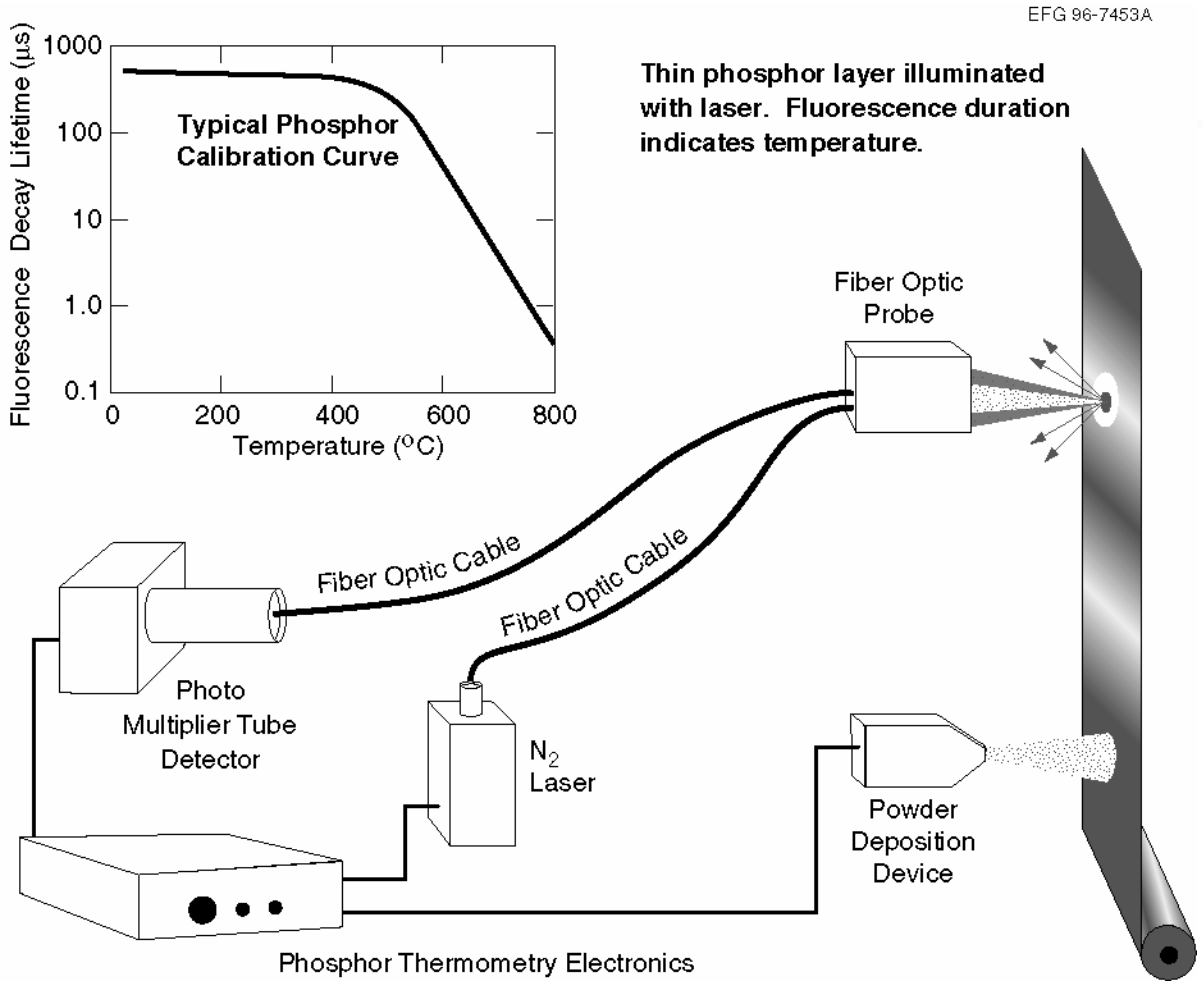
# Intake valve setup



# Intake valve results

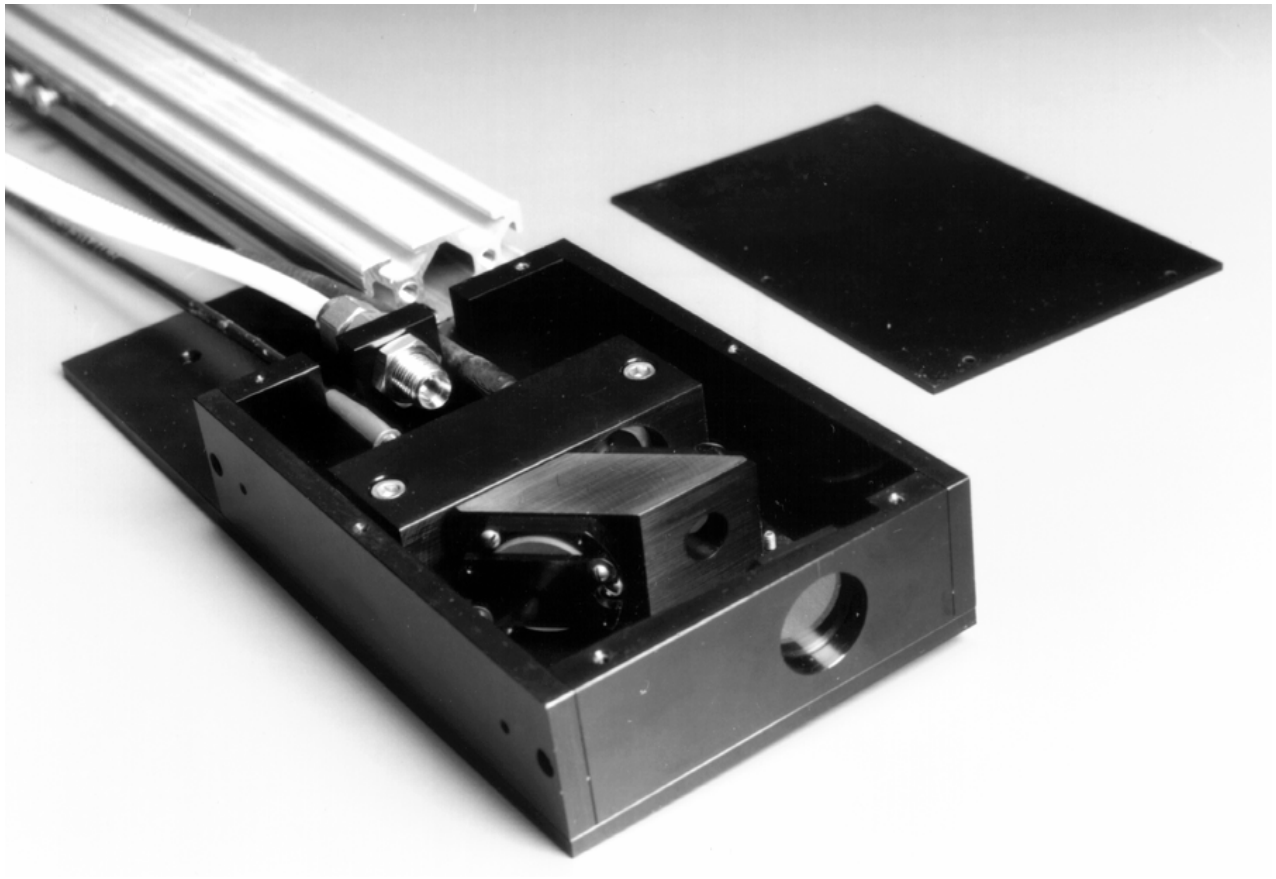


# Galvanneal steel temperature



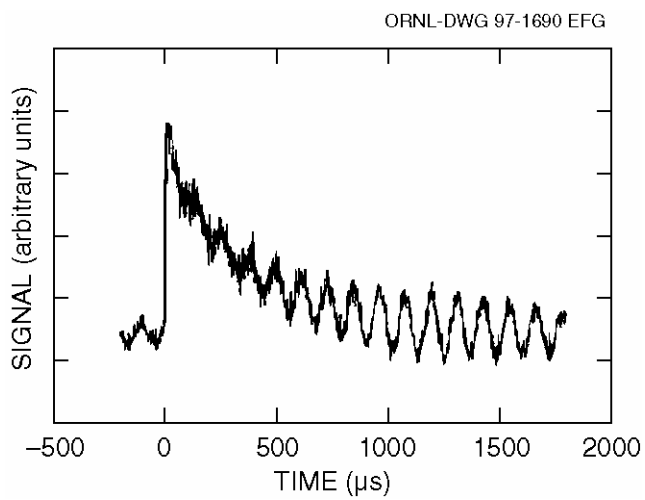

W. W. Manges, S. W. Allison, J. R. Vehec, *Galvanneal thermometry with a thermographic phosphor system*, Iron and Steel Engineer Vol. 74(12), pp. 33-36, Dec. 1997.

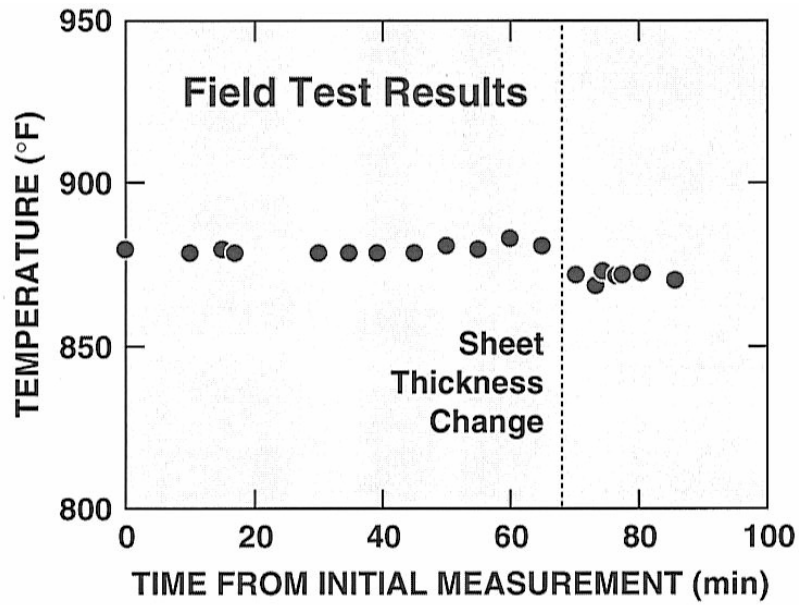
# Optics for galvanneal steel



W. W. Manges, S. W. Allison, J. R. Vehec, *Galvanneal thermometry with a thermographic phosphor system*, Iron and Steel Engineer Vol. 74(12), pp. 33-36, Dec. 1997.

# Signal and results – galvanneal project

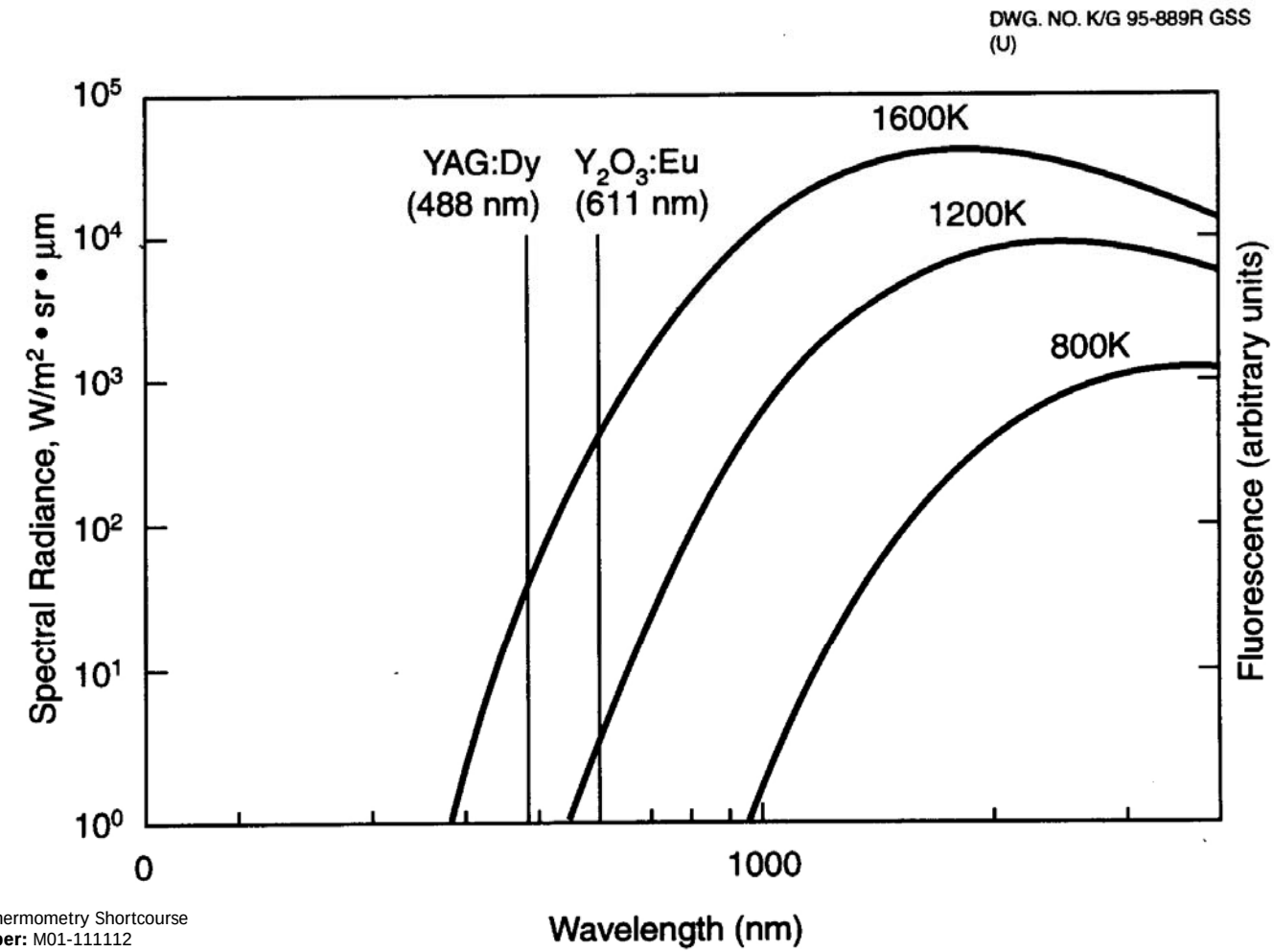



RF pickup – the reason we eventually incorporated optical fiber

W. W. Manges, S. W. Allison, J. R. Vehec, *Galvanneal thermometry with a thermographic phosphor system*, Iron and Steel Engineer Vol. 74(12), pp. 33-36, Dec. 1997.

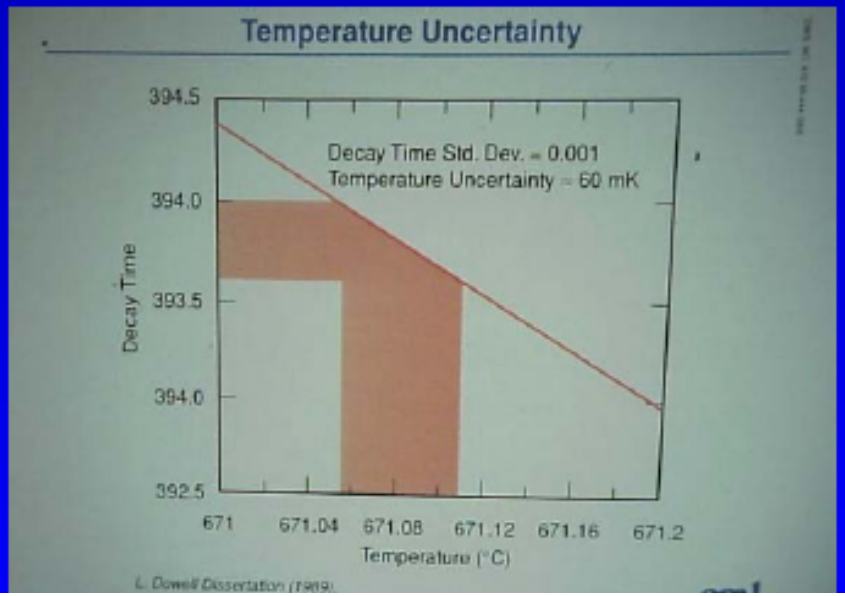
# Blackbody vs fluorescence emission



# RESULTS

| Temperature (K) | SNR | $\beta$ | $\tau$ (ms) |
|---|---|---|---|
| 300 | 5690:1 | 2.693138±0.000247 | 0.930108±0.000140 |
| 666 | 4040:1 | 2.795084±0.000354 | 0.896184±0.000157 |
| 765 | 3780:1 | 2.848691±0.000382 | 0.879319±0.000158 |
| 865 | 6860:1 | 1.453592±0.000157 | 0.688964±0.000224 |
| 965 | 3110:1 | 0.930440±0.000306 | 0.270189±0.000187 |
| 1064 | 330:1 | 1.233660±0.003112 | 0.040672±0.000178 |

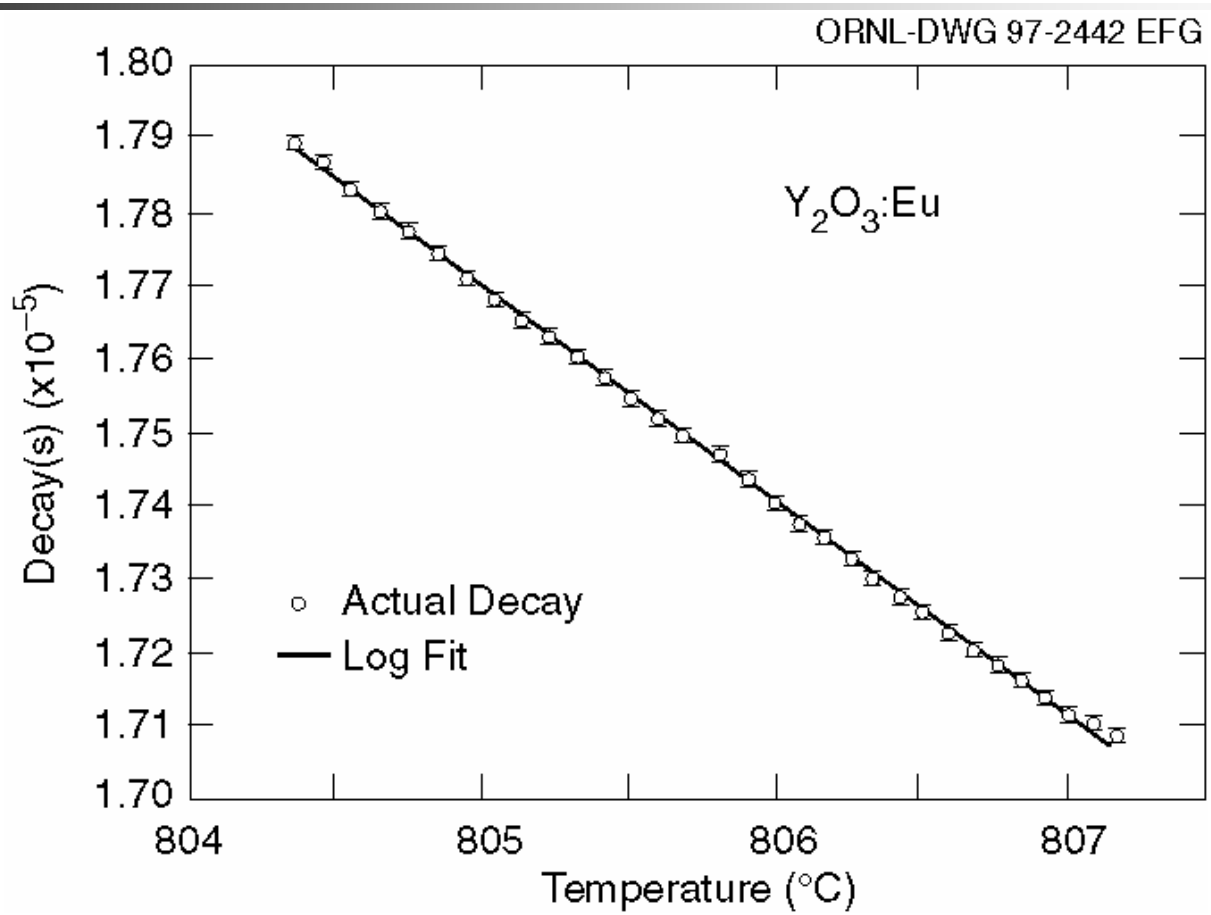
Table IV-IIIb. 1% Eu:$Y_2O_3$ 611 nm lifetime with excitation near 466 nm.




L. J. Dowell, M.Sc. Thesis, U.Va. May 1987, 299 pp.

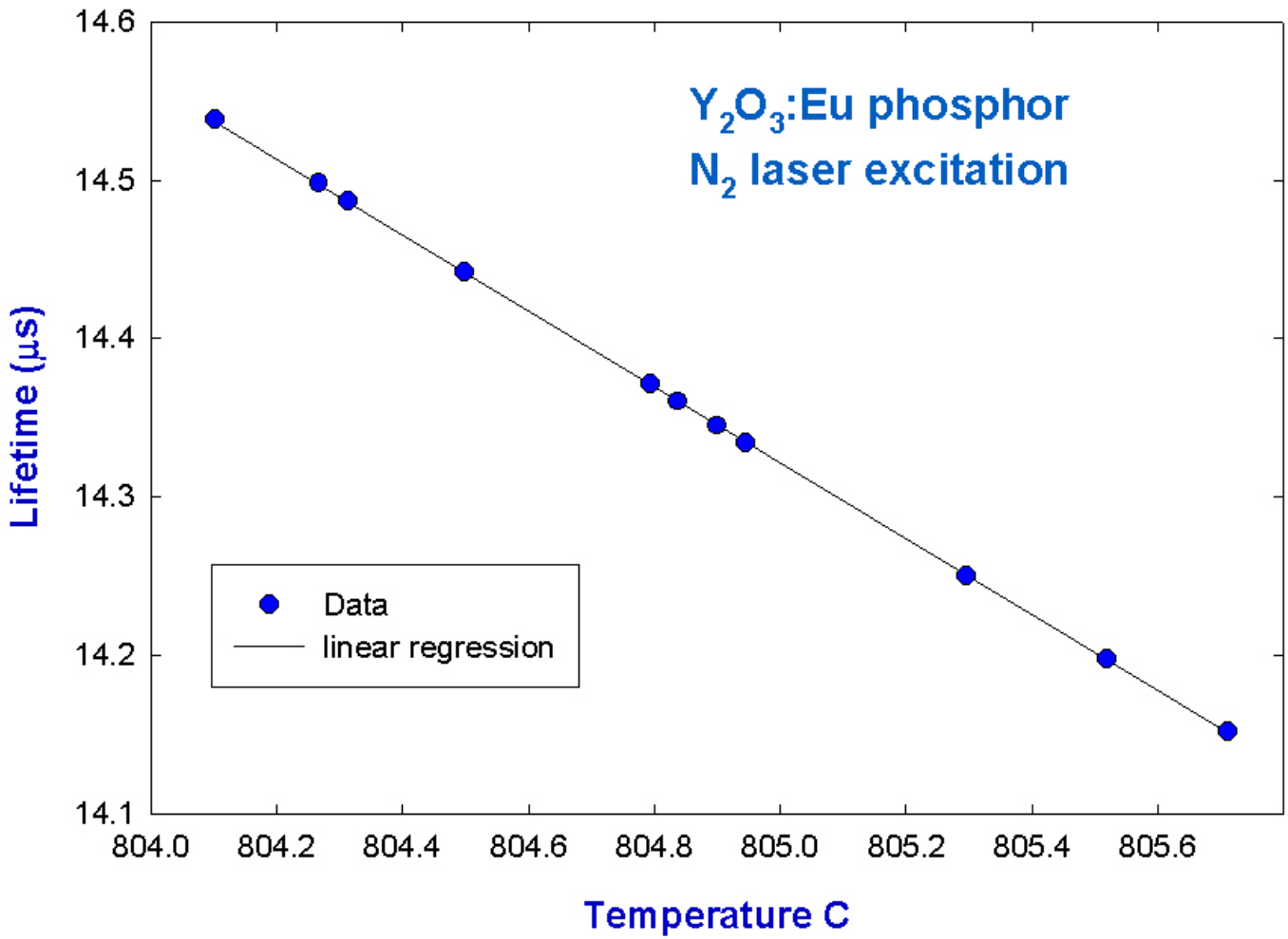
L. J. Dowell, Ph.D. Dissertation, U.Va., May 1989, 153 pp.

# Precision limits are <10 mK for some phosphors and conditions



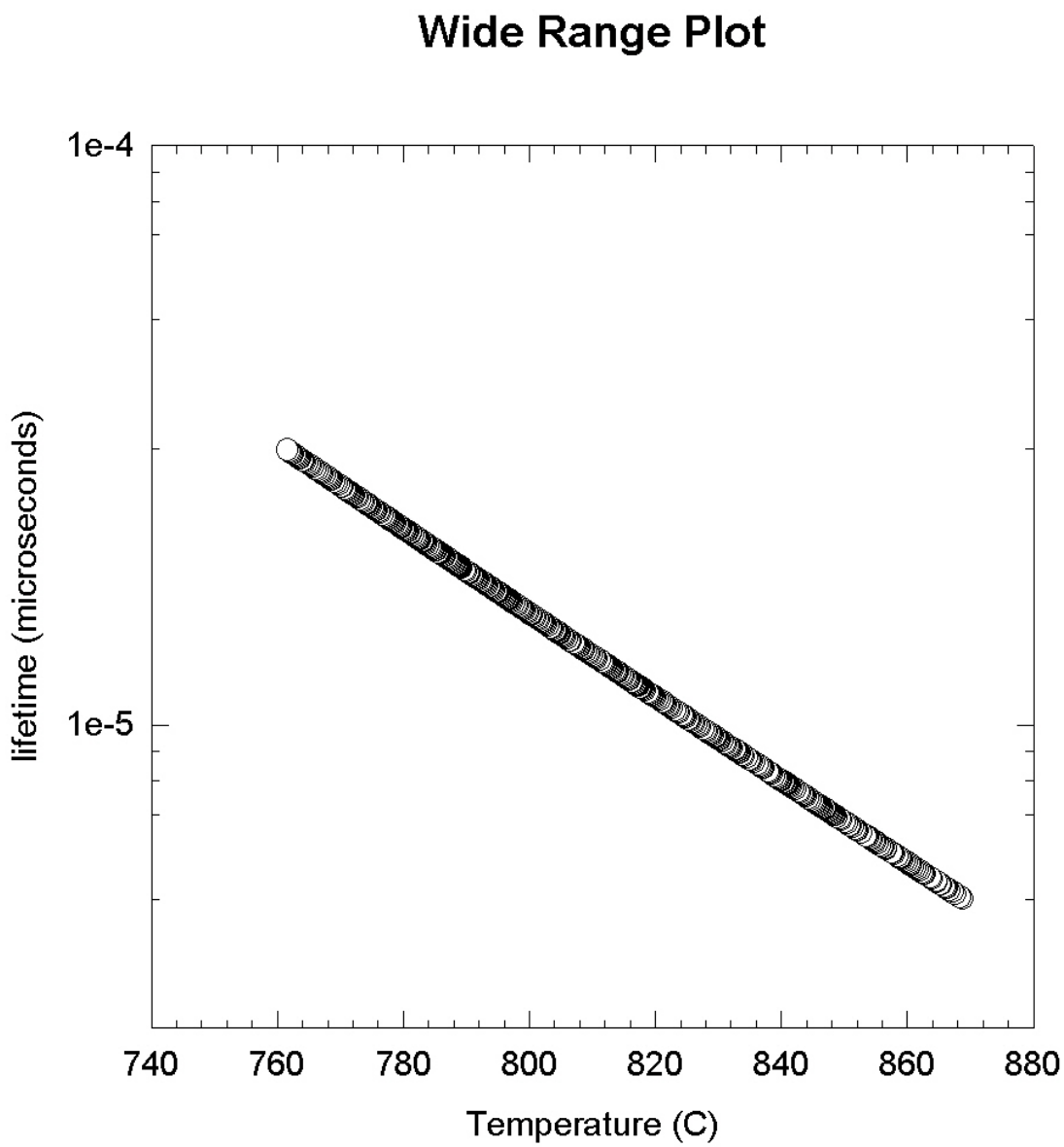

Cates, M.R., et al "Ultra High Precision Phosphor Thermometry Near 1100 K," *Proceedings of The 8th Symposium on Temperature, Chicago, IL USA, NIST, American Institute of Physics (AIP), College Park, MD USA, 10/21/2002-10/24/2002.*

# High Resolution View of Calibration



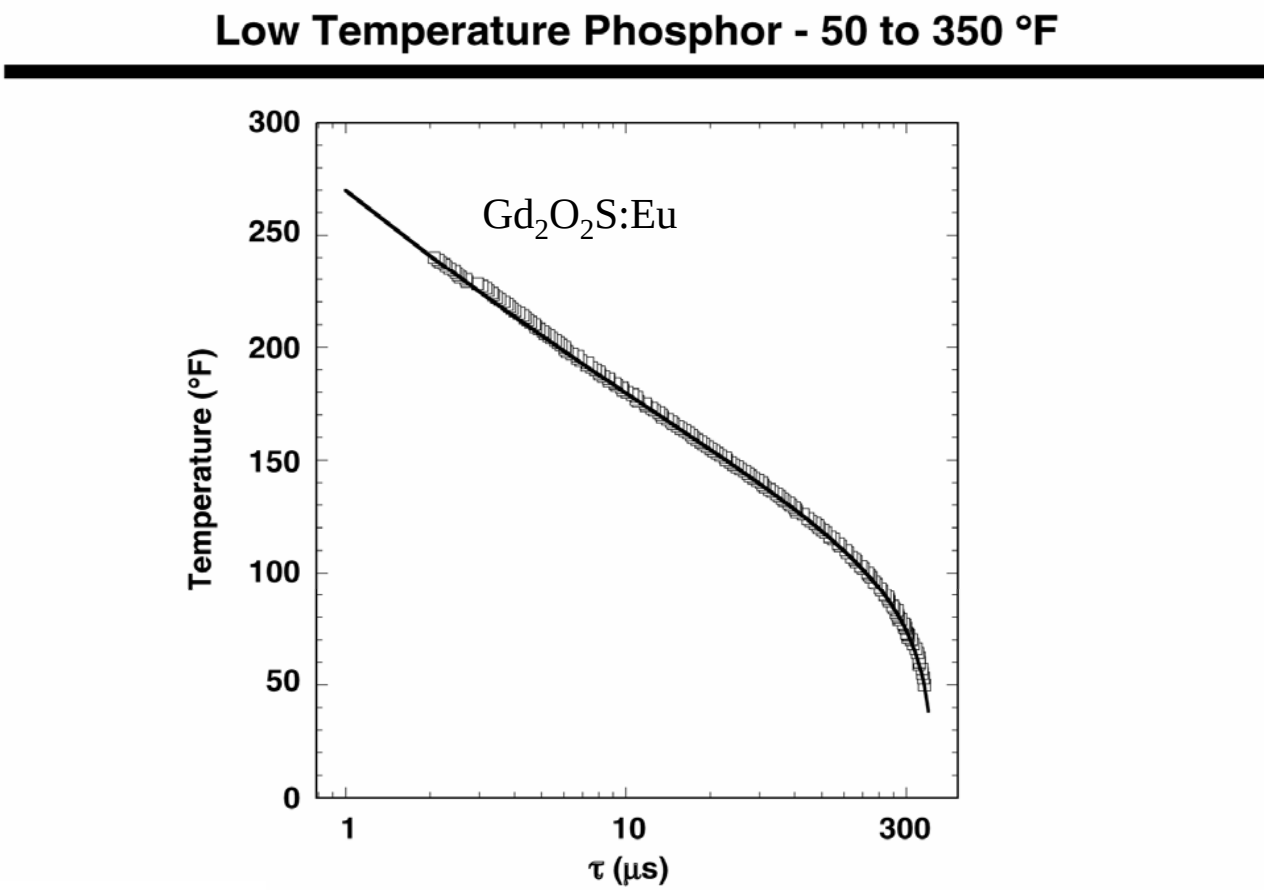

Cates, M.R., et al "Ultra High Precision Phosphor Thermometry Near 1100 K," *Proceedings of The 8th Symposium on Temperature, Chicago, IL USA, NIST, American Institute of Physics (AIP), College Park, MD USA, 10/21/2002-10/24/2002.* Re-plot of Figure 1

# Temperature vs Lifetime

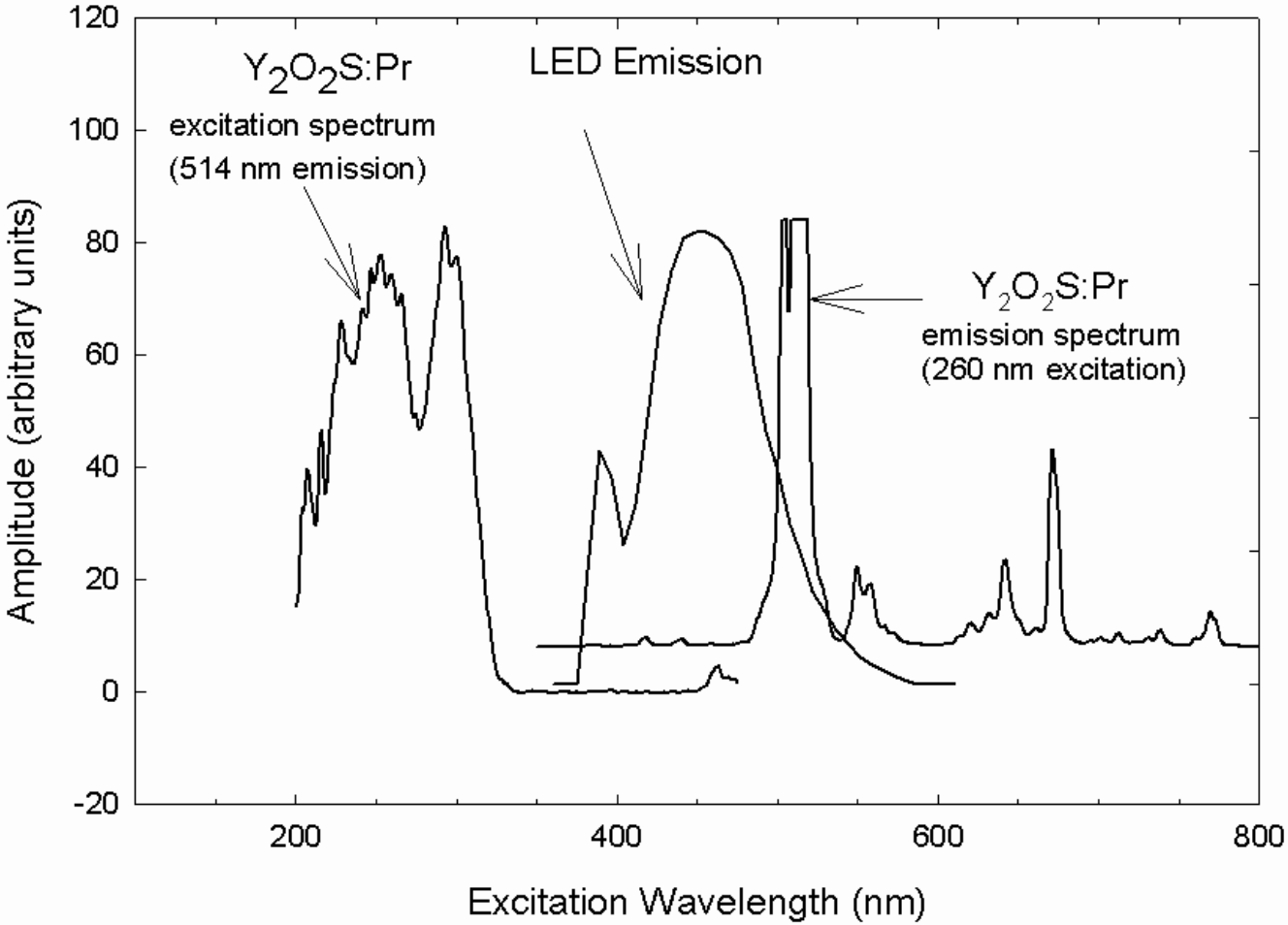



Cates, M.R., et al "Ultra High Precision Phosphor Thermometry Near 1100 K," *Proceedings of The 8th Symposium on Temperature, Chicago, IL USA, NIST, American Institute of Physics (AIP), College Park, MD USA, 10/21/2002-10/24/2002*. Re-plot of same data as Figure 1

# Low-temperature response

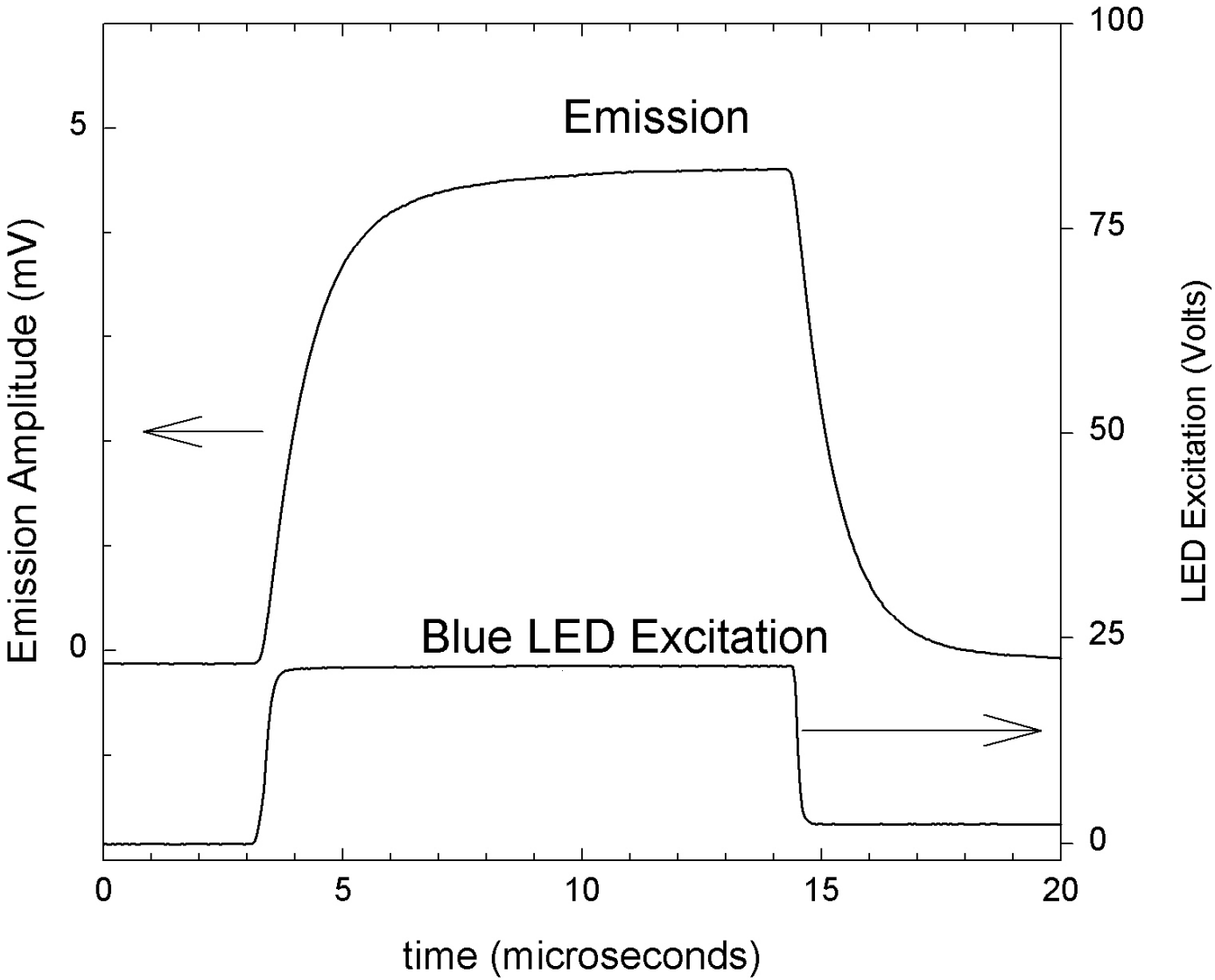


# This LED not a good match but produces fluorescence




S. W. Allison, M. R. Cates, and G. T. Gillies, "Excitation of thermographic phosphors using a blue light emitting diode: Spectral characteristics and instrumentation applications," Rev. Of Scientific Instruments 73(4) April 2002.

# $Y_2O_2S$:Pr

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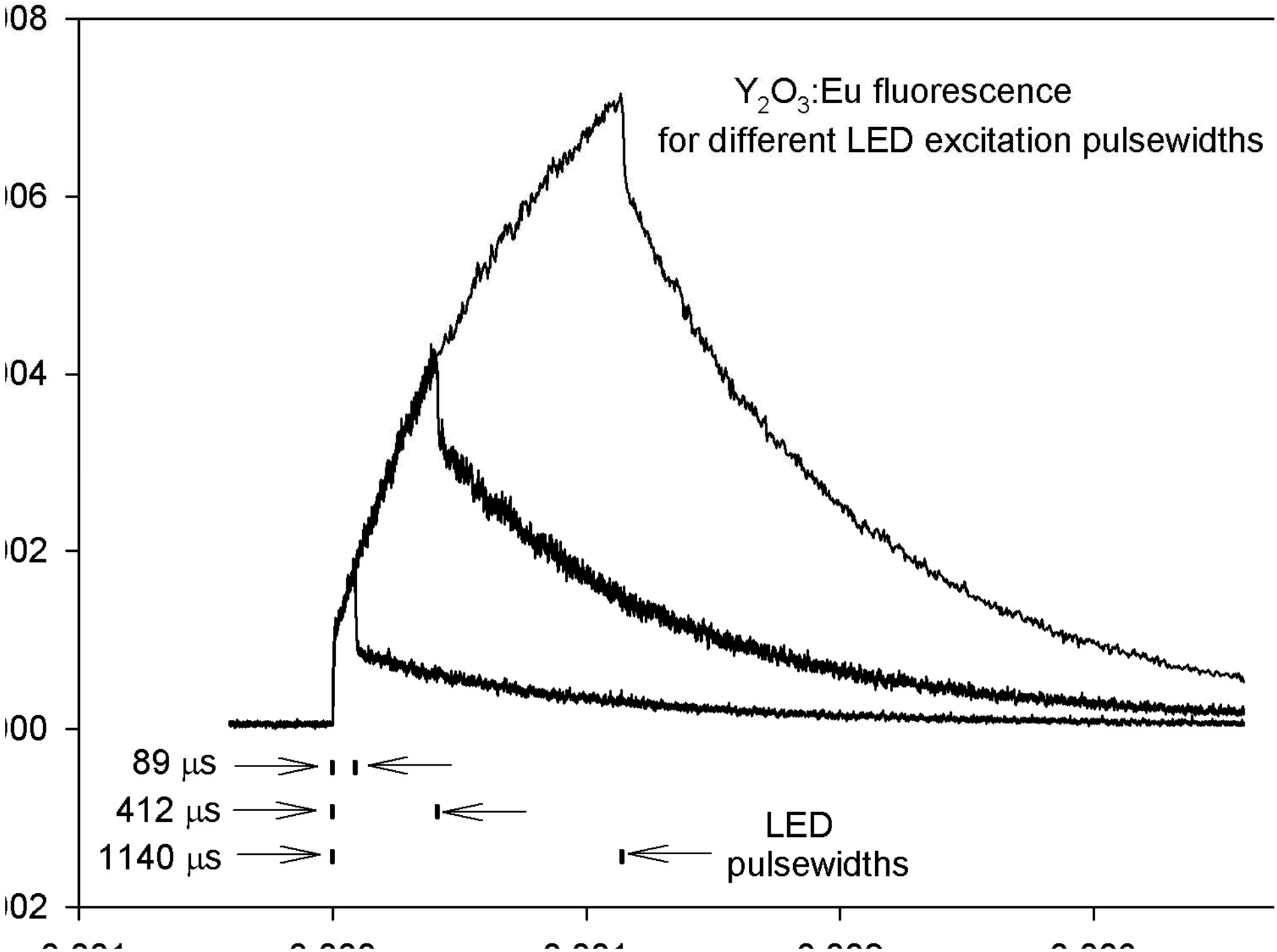
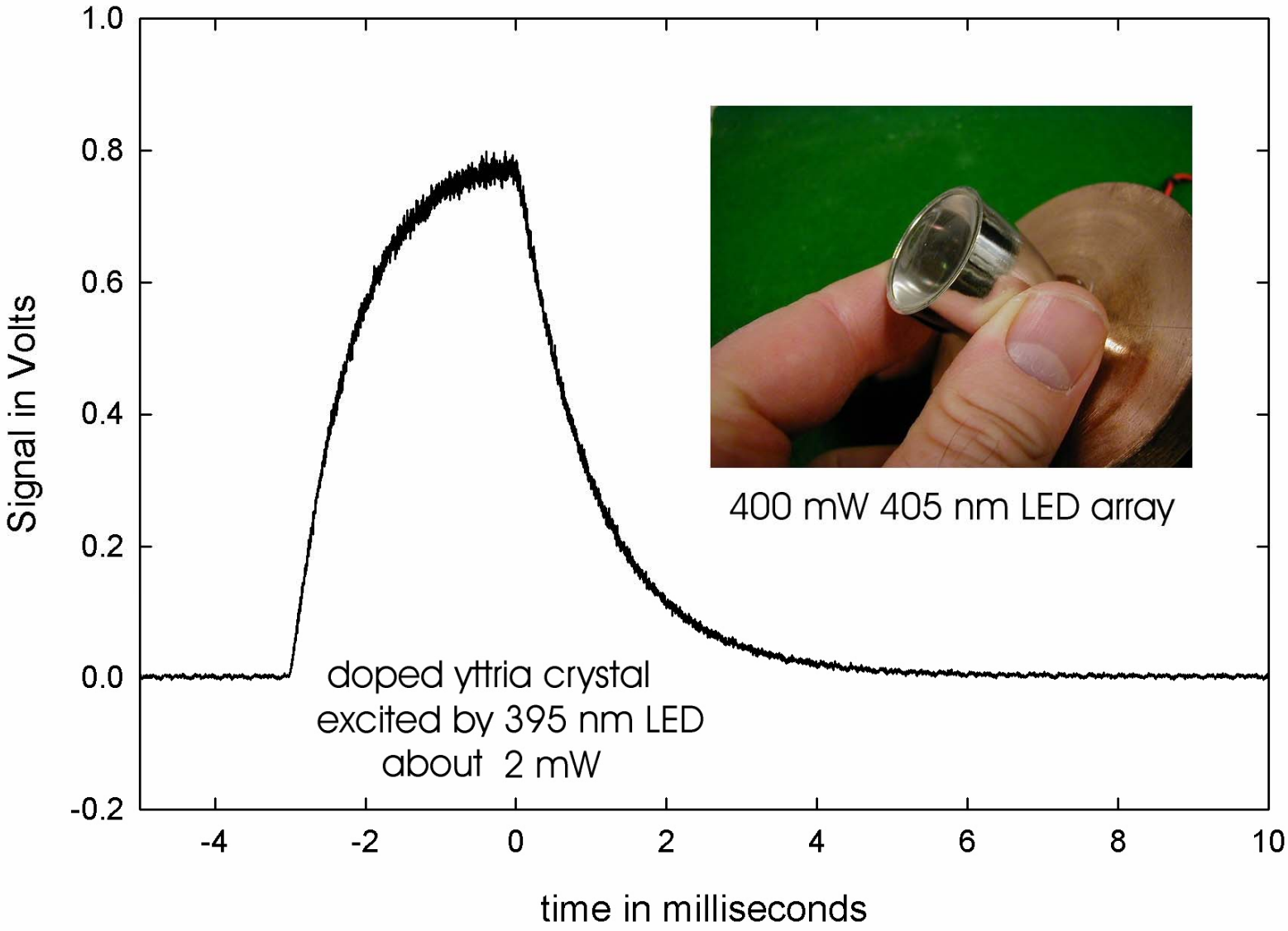
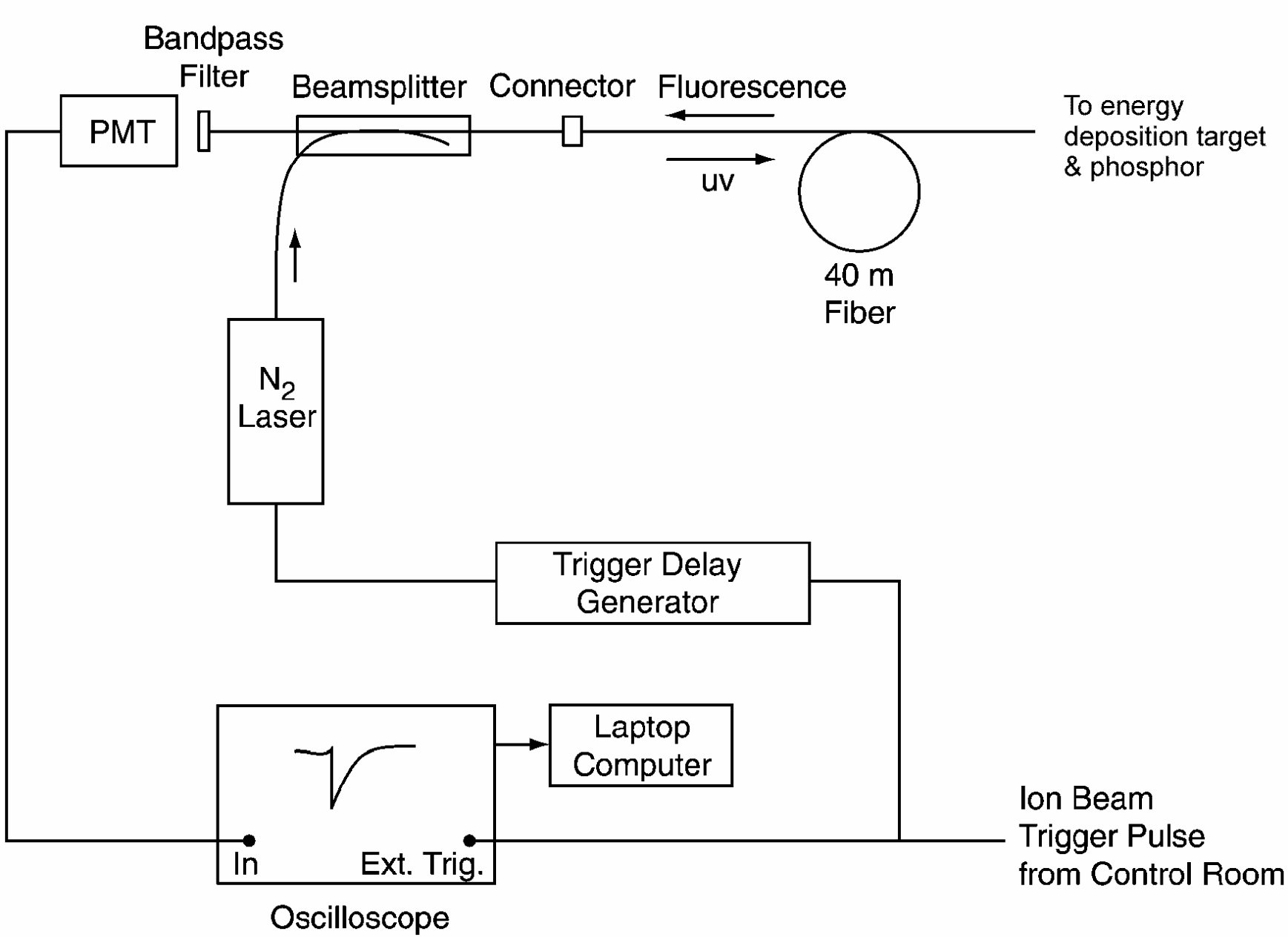

$Y_2O_3$:Eu fluorescence
for different LED excitation pulsewidths
89 μs
412 μs
1140 μs
LED
pulsewidths

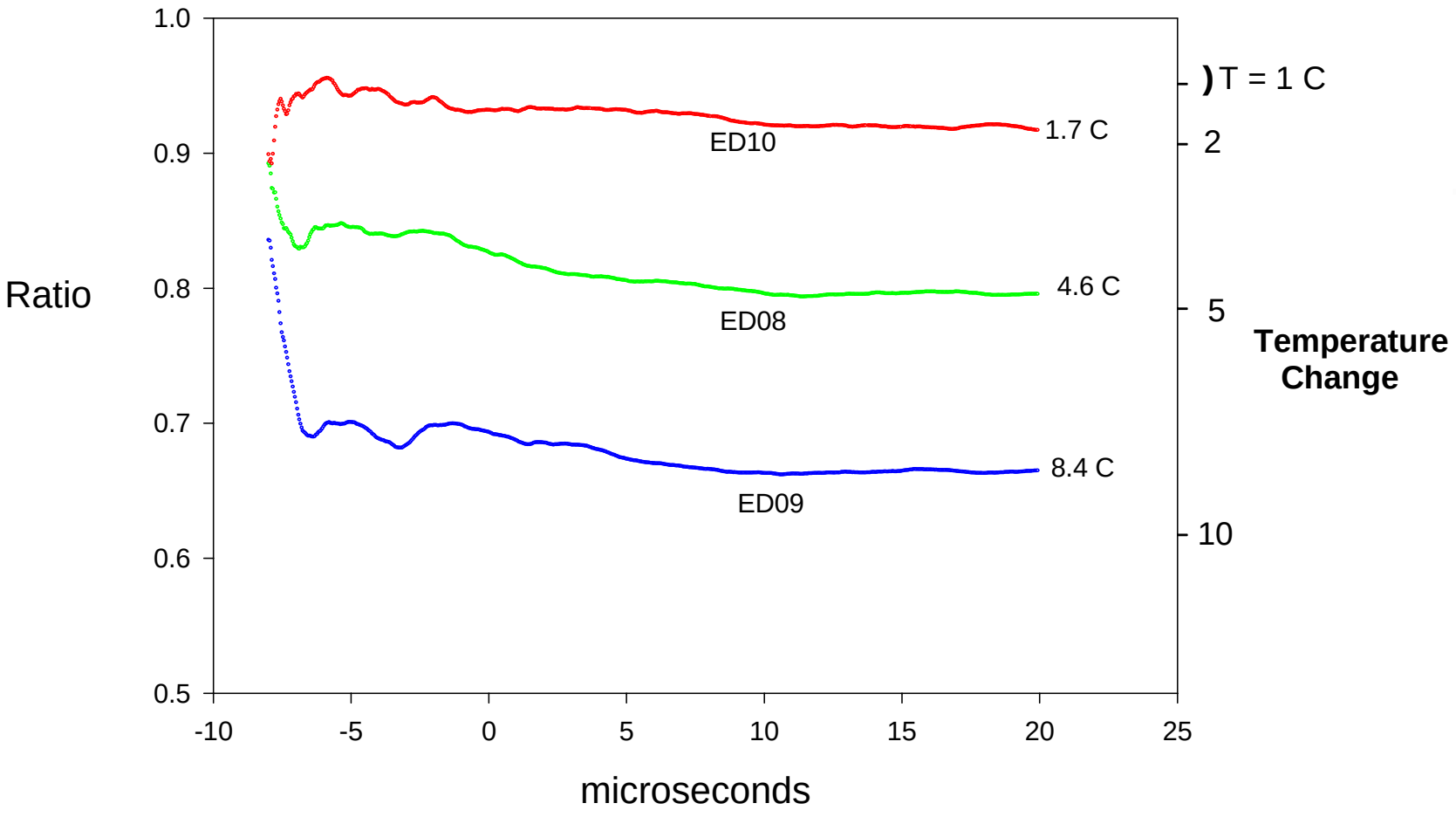
## New LED Light Sources Available




S. W. Allison, S. M. Goedeke, M. R. Cates, and G. T. Gillies,"Progress toward an atomic temperature standard" published in the proceedings of the 49th International Instrumentation Symposium of the ISA, Orlando, FL., May 2003.




S. W. Allison, M.R. Cates and D.L. Beshears 2002. "Recent Developments Involving Thermographic Phosphors," Proceedings of The Ninth Annual Pressure Sensitive Paint Workshop, Washington, DC USA , Leatech, Leatech, Baltimore, MD USA, 04/08/2002-04/11/2002.

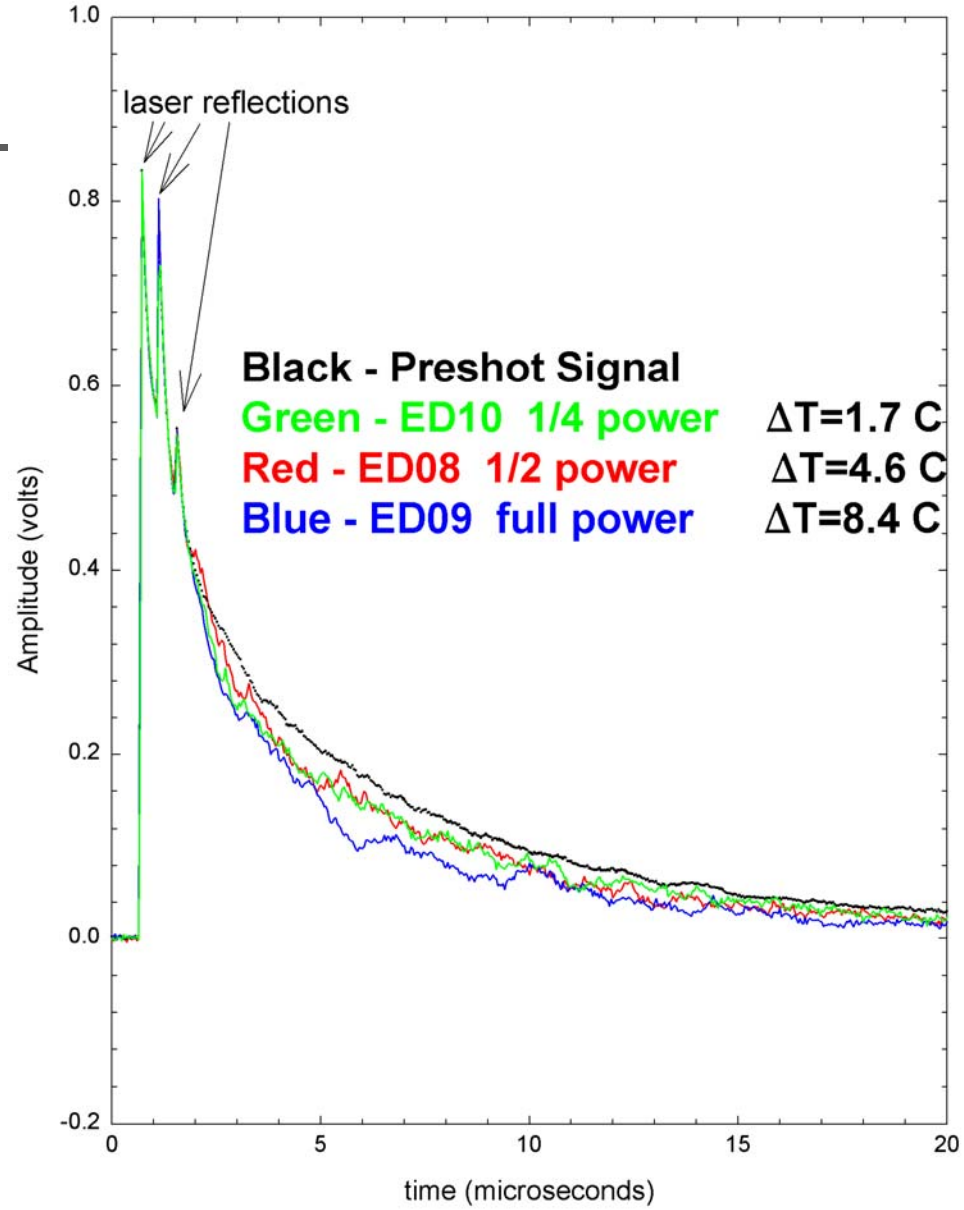



Ratio of integrated signal 1.1 ms after shot
to integrated preshot signal

Beshears, D.L., et al. 2001. *Temperature Rise Measurements for a Simple Mercury Target Exposed to the WNR Proton Beam*, SNS101050200-TR007-R00 .

# Phosphor Thermometry
## temperature sampled 1.1 ms after shot

S. W. Allison, M.R. Cates and D.L. Beshears 2002. "Recent Developments Involving Thermographic Phosphors," Proceedings of The Ninth Annual Pressure Sensitive Paint Workshop, Washington, DC USA, Leatech, Leatech, Baltimore, MD USA, 04/08/2002-04/11/2002.

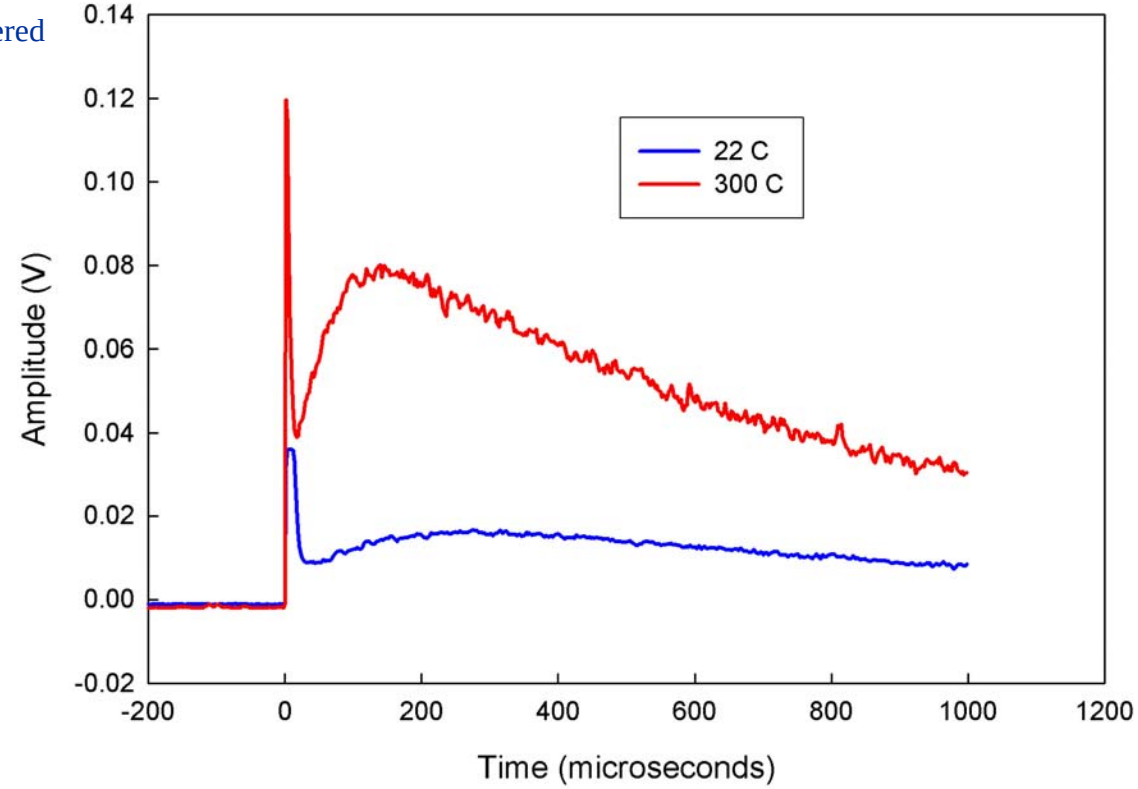


# Another consideration:  Rise Time

The rise time decreases with temperature

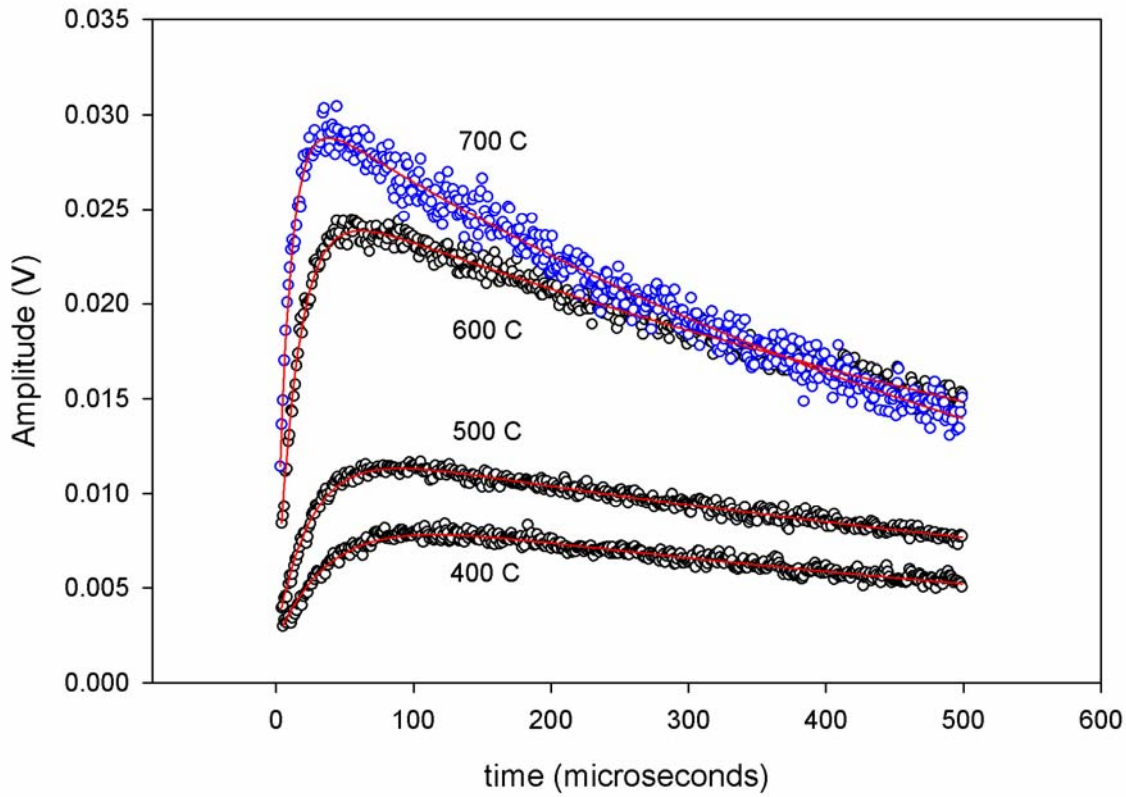
It also increases as dopant concentration is lowered

The traces above are for a 0.5 Eu sample




Allison et al. Fluorescence Rise time Measurements for High Temperature Fluorescence-Based Thermometry, ORNL Report.

# Signals for 0.5% crystal



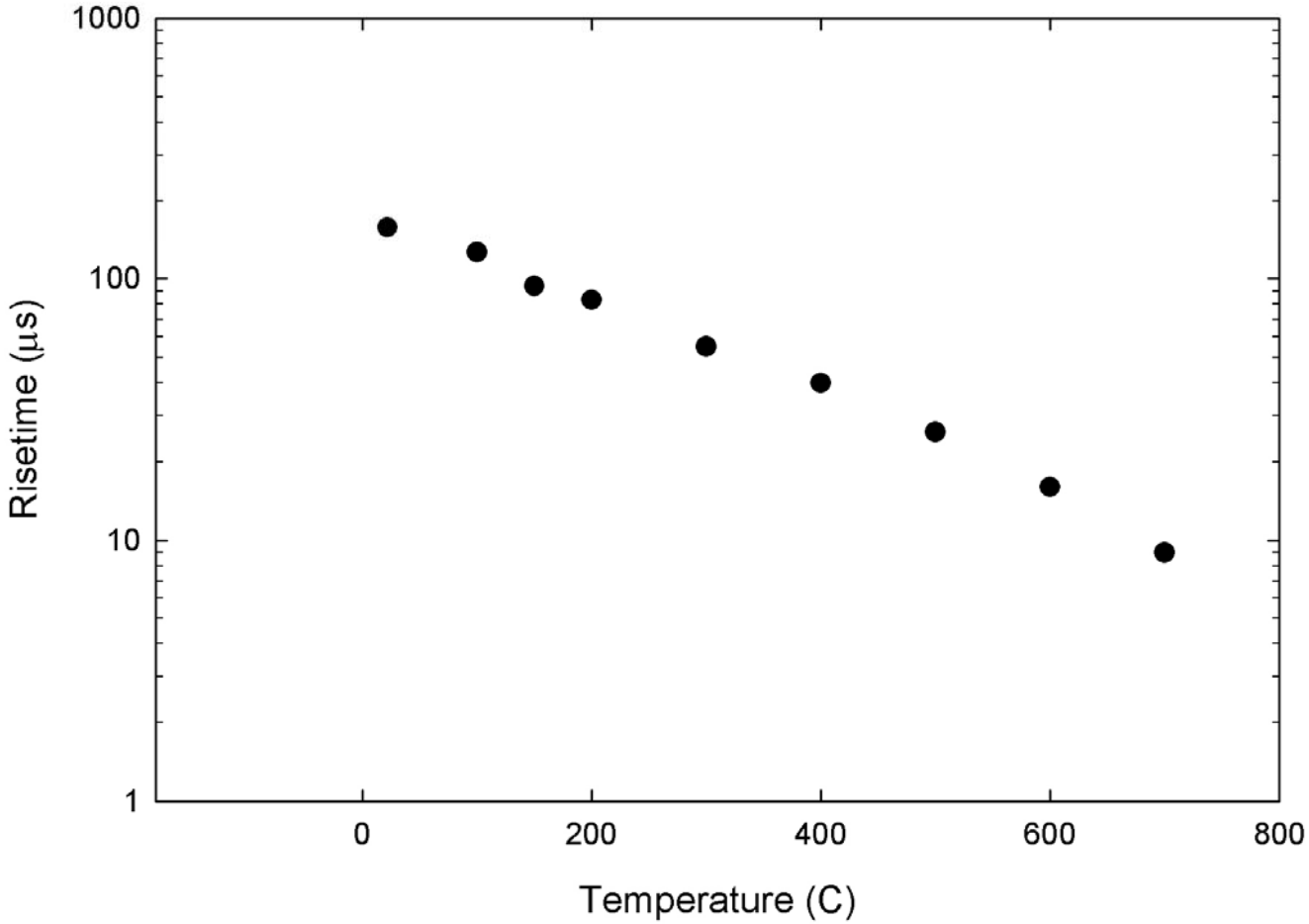

Allison et al. Fluorescence Rise time Measurements for High Temperature Fluorescence-Based Thermometry, ORNL Report.

# Model for rise and decay times

$$n_{total} = \left[ n_1 + n_2 \left( 1 - \exp\left\{ \frac{-t}{\tau_{Rise}} \right\} \right) \right] \exp\left\{ \frac{-t}{\tau_{Decay}} \right\}$$

**Model according to R. M. Ranson, E. Evangelou, and C. B. Thomas, "Modeling the fluorescent lifetime of Y2O3:Eu" Applied Physics Letters, Vol 72(21), pp. 2663-4, 1998.**

# Rise times versus Temperature 0.5% sample




Allison et al. Fluorescence Rise time Measurements for High Temperature Fluorescence-Based Thermometry, ORNL Report.

# Coatings tests

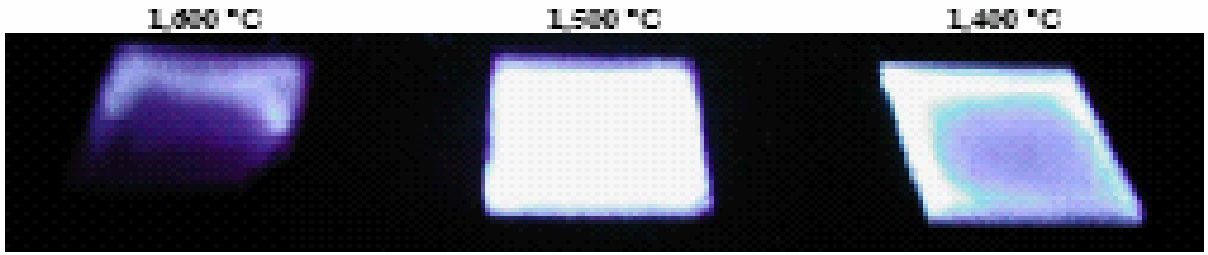



Figure 3. Ultraviolet stimulated fluorescence from a 100% ZAP and 30% YAG:Dy paint (by volume) at 1,600, 1,500, and 1,400 °C

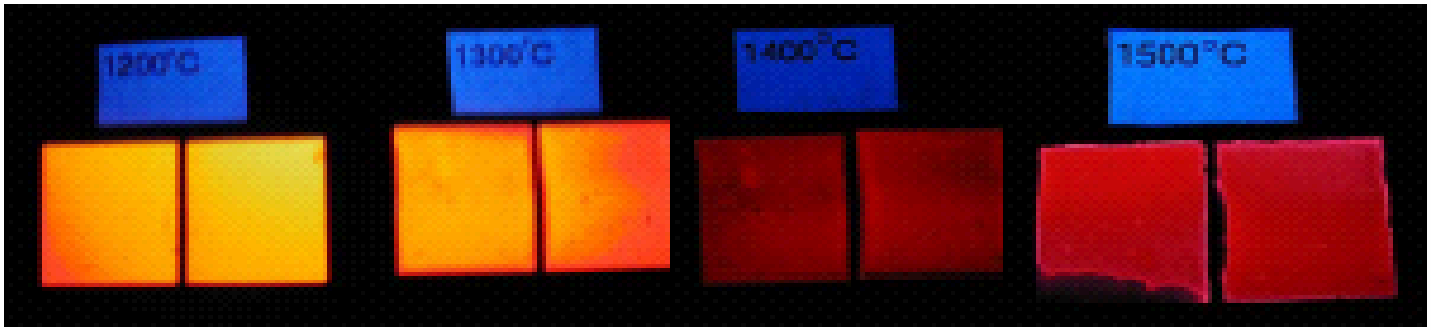
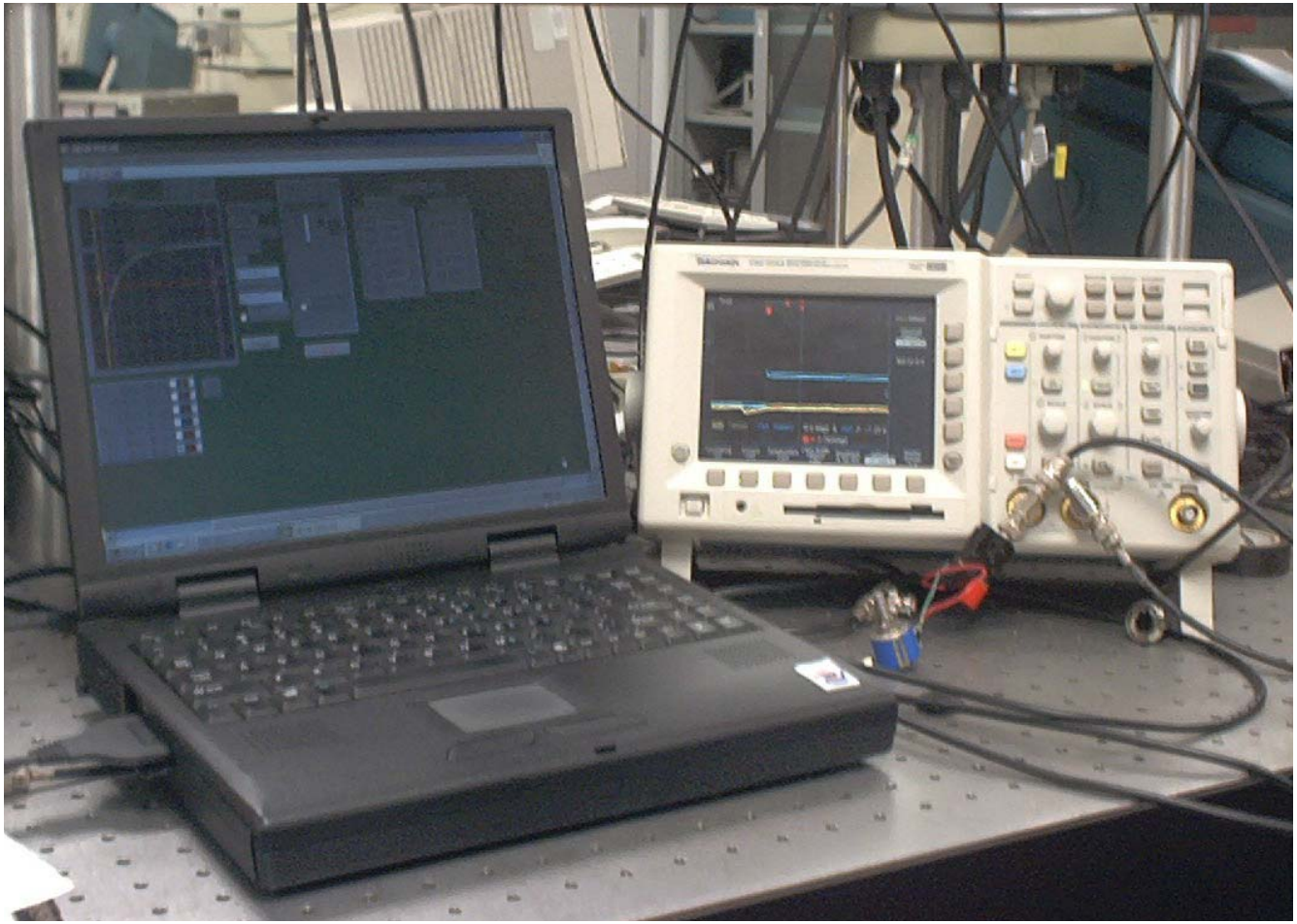



Figure 4. Ultraviolet stimulated fluorescence from a 100% ZAP and 50% $Y_2O_3$:Eu paint (by volume) at 1,200, 1,300, 1,400, and , 1,500 °C

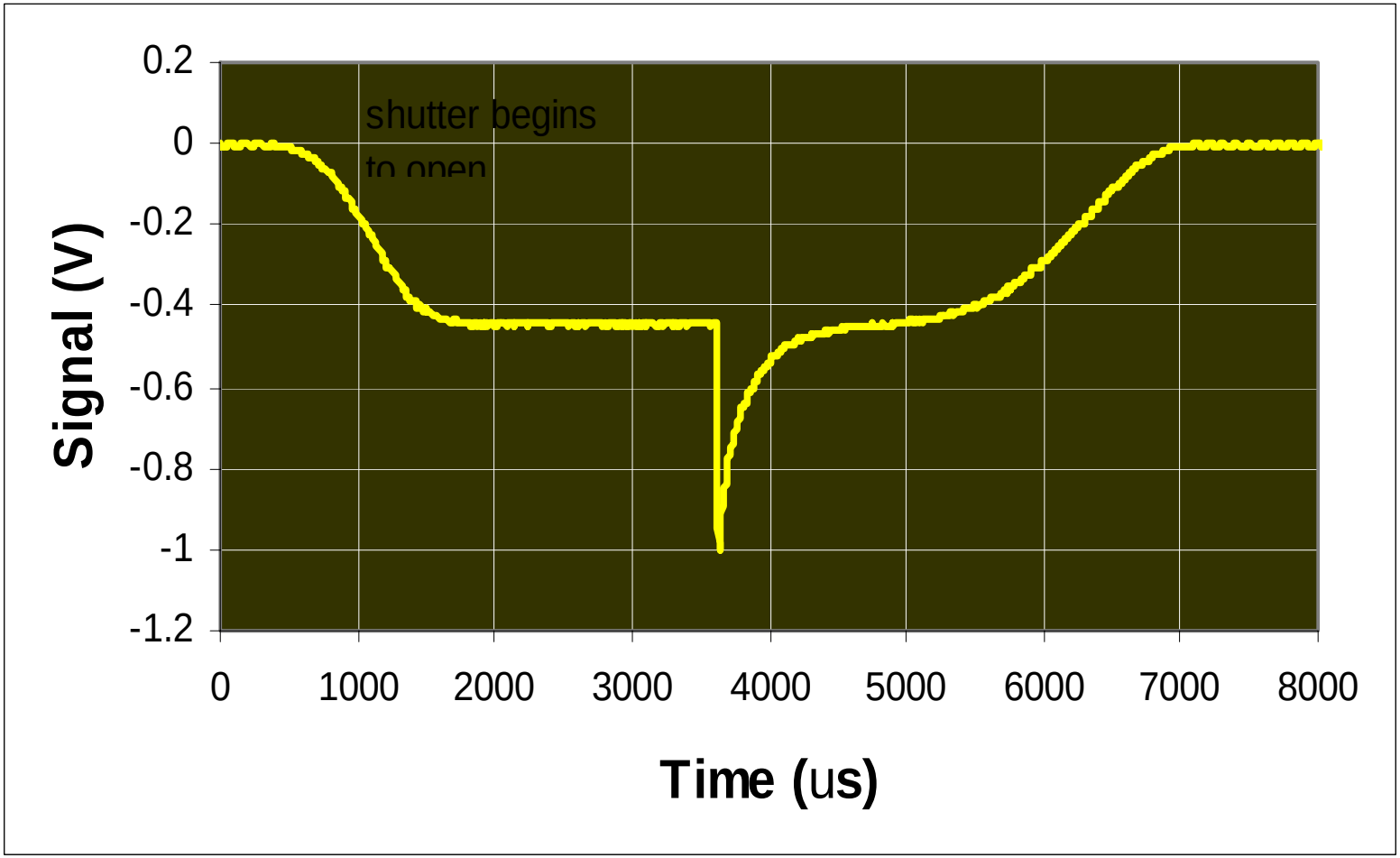
Hollerman, WA, et al. 2003. "Use of Phosphor Coatings for High Temperature Aerospace Applications,"

*AIAA Jounal, Cleveland, Oh USA, NASA Glenn Research Center, AIAA, , USA, 07/20/2003-07/23/2003.*

# Data Collection

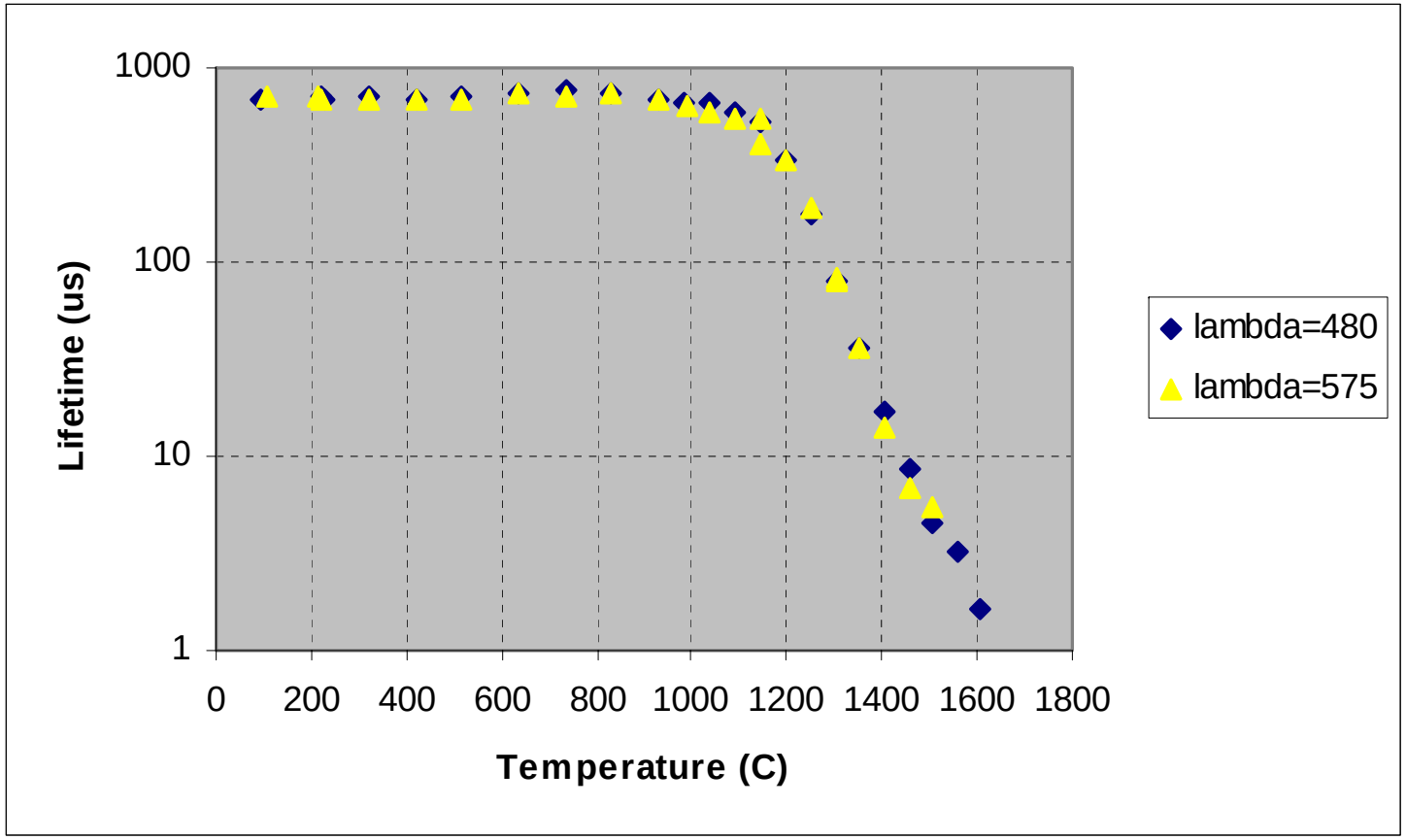


# YAG:Dy 453-nm emission on blackbody background at 1306 C



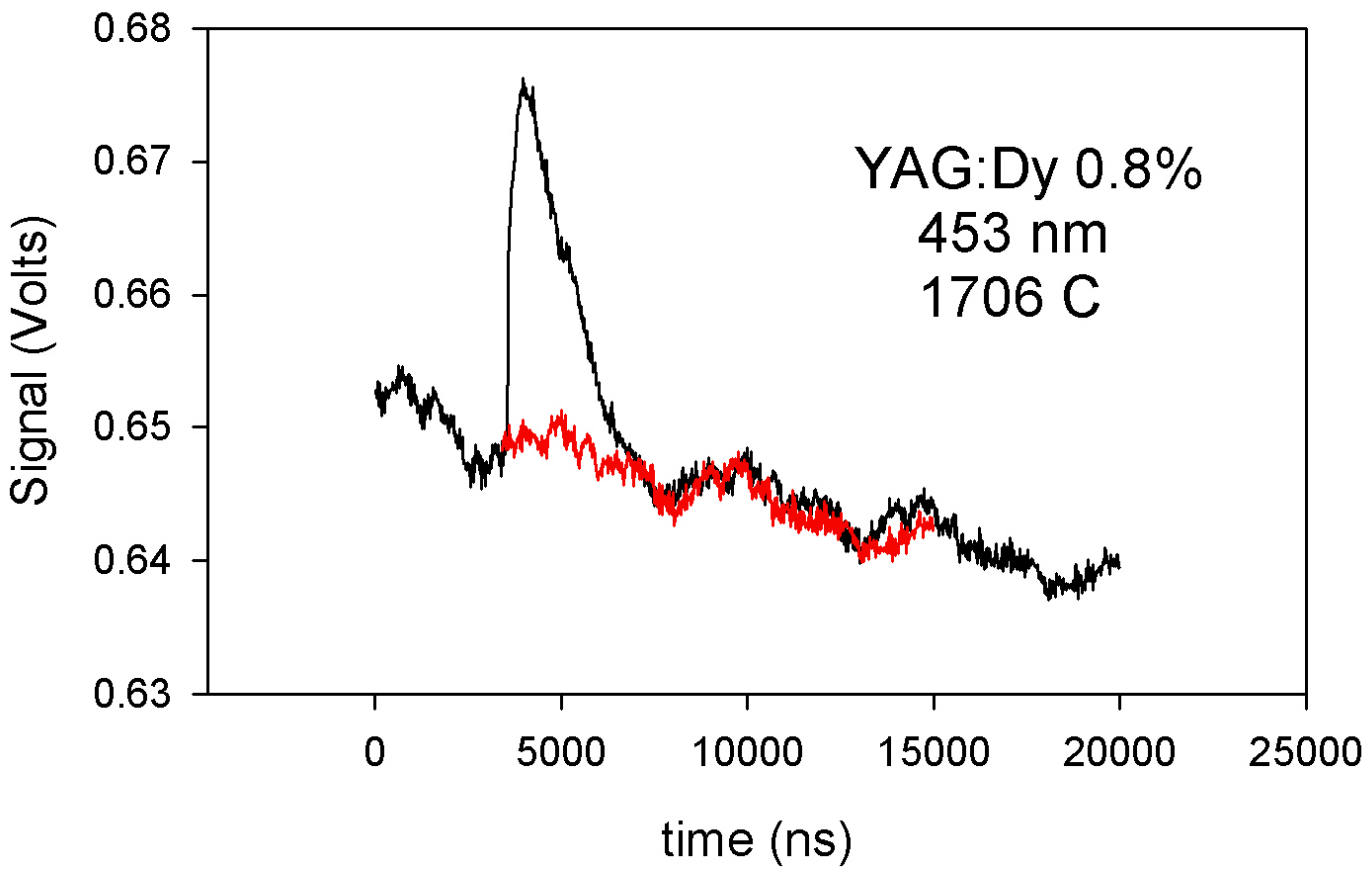

M. R. Cates, S. W. Allison, S. L. Jaiswal, and D. L. Beshears, "YAG:Dy and YAG:Tm Fluorescence to 1700 C" Proceedings of the 49th International Instrumentation Symposium of the ISA, Orlando, FL., May 2003.

# YAG:Dy temperature response




M. R. Cates, S. W. Allison, S. L. Jaiswal, and D. L. Beshears, "YAG:Dy and YAG:Tm Fluorescence to 1700 C" Proceedings of the 49th International Instrumentation Symposium of the ISA, Orlando, FL., May 2003.

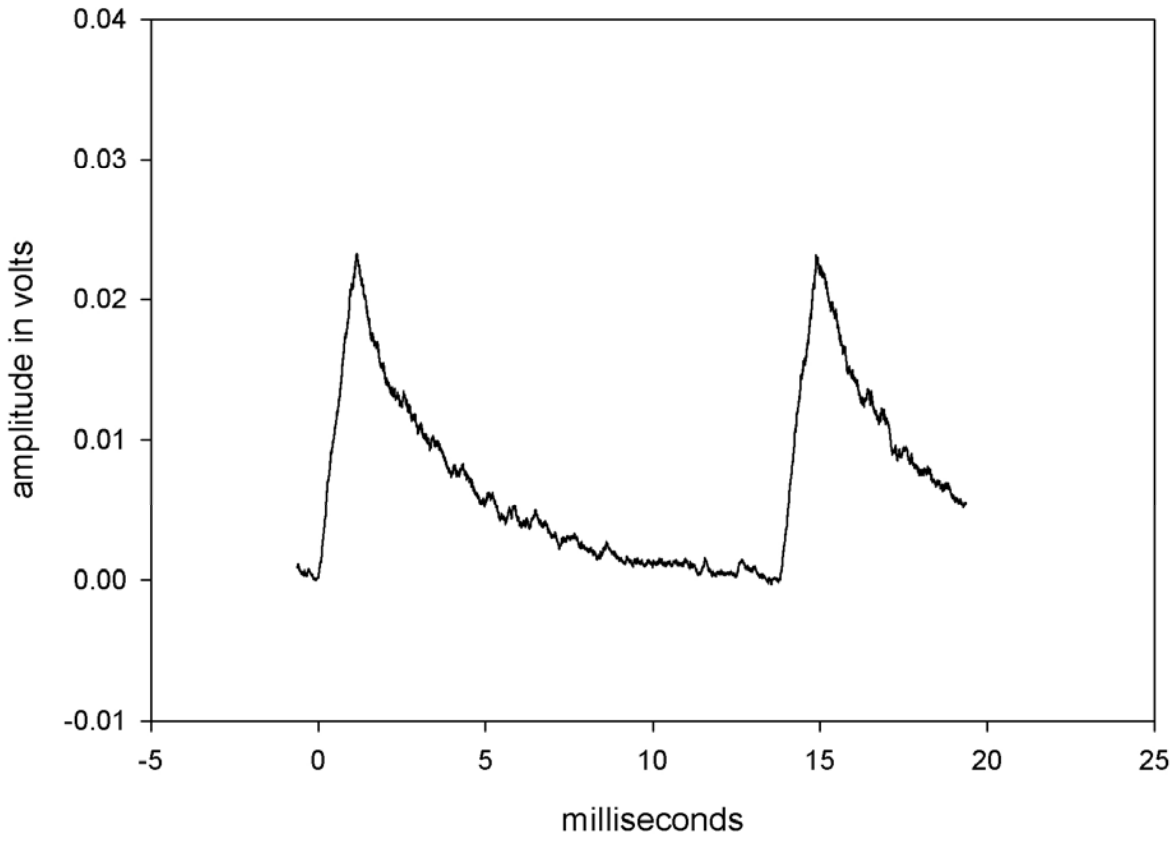
# Signal & background at 1706 C




M. R. Cates, S. W. Allison, S. L. Jaiswal, and D. L. Beshears, "YAG:Dy and YAG:Tm Fluorescence to 1700 C" Proceedings of the 49th International Instrumentation Symposium of the ISA, Orlando, FL., May 2003.

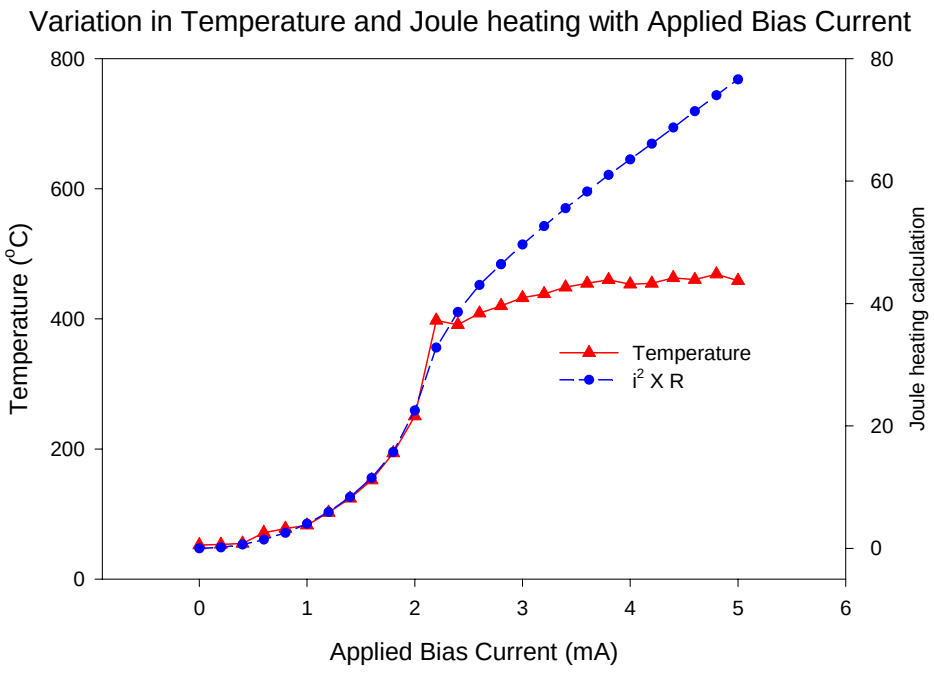
# LED-induced fluorescence from a micro-cantilever

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




Allison, S.W., et al. 2003. "Phosphor Thermometry at ORNL," *Proceedings of The 8th Symposium on Temperature: Its Measurement and Control In Science and Industry, Chicago, IL USA, NIST/ISA, American Institute of Physics (AIP), College Park, MD USA, 10/21/2002-10/24/2002.*

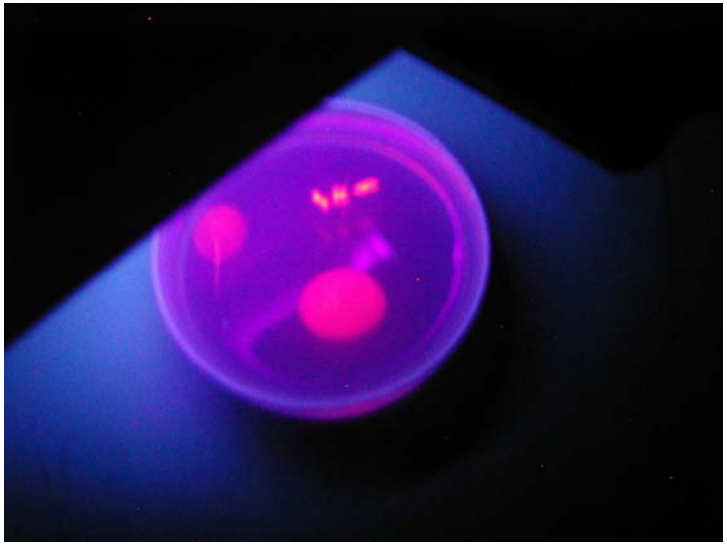
# Temperature of Microcantilever



Allison, S.W., M.R. Cates and D.L. Beshears 2002. "Recent Developments Involving Thermographic Phosphors," *Proceedings of The Ninth Annual Pressure Sensitive Paint Workshop, Washington, DC USA, Leatech, Leatech, Baltimore, MD USA, 04/08/2002-04/11/2002*.

# Nanoparticles for Novel Infusion Therapies for Brain Tumors

- Promise for new therapeutic modality
- For circumventing “blood brain barrier”
- May serve as potential drug carrier to kill infiltrative brain tumor cells.

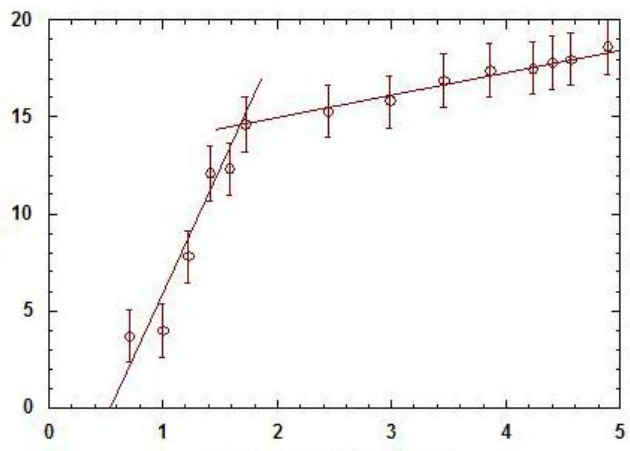


Red fluorescence due to $Y_2O_3$:Eu nanoparticles in brain phantom gell.

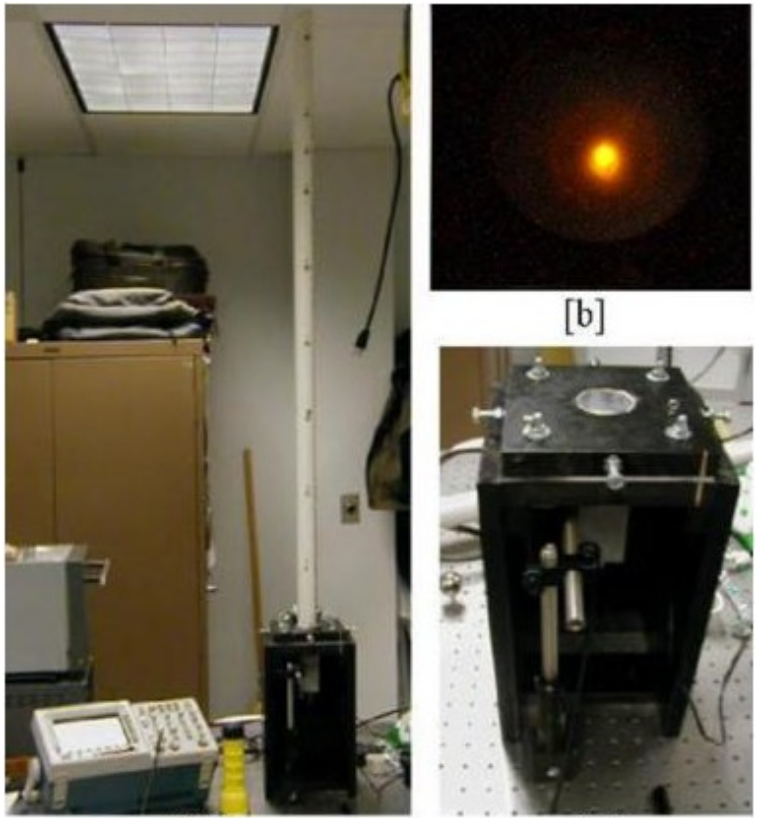
G. T. Gillies, S. W. Allison, and B. M. Tissue “Positive pressure infusion of fluorescent nanoparticles as a probe of the structure of brain phantom gelatins,” Nanotechnology 13, 484-486, 2002.

Allison, SW, et al. 2004. "On the Use of Phosphors for Flow Measurements," *Proceedings of the 11th Internation Symposium On Flow Visualization Conference, Notre Dame, IN USA, DOE, 11th International Conference, Notre Dame, IN USA, 08/09/2004-08/2/2004.*

# Triboluminescence for Impact Sensing




**Plot of the relative light as a function of impact velocity for ZnS:Mn powder.**

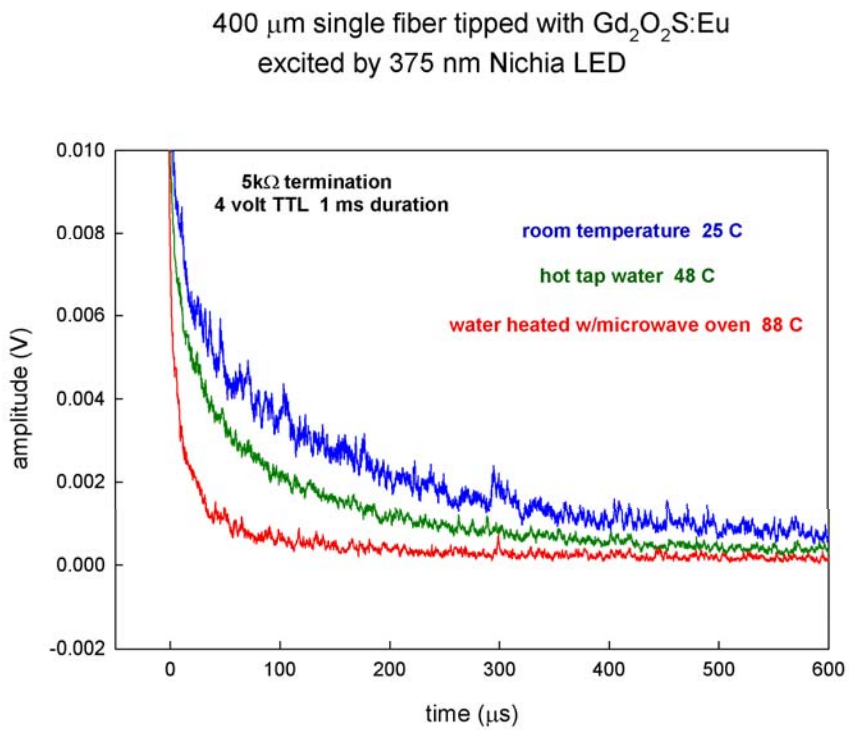



**ORNL's experimental arrangement for the first generation drop tower.**


Goedeke, S.M., et al. 2003. "Triboluminiescence and its Application to Space-Based Damage Sensors," *CD-ROM, Huntsville, AL USA, Advanced Sensor Development Consortium, NASA MSFC, Huntsville, AL USA, 05/13/2003-05/15/2003*.

Hollerman, WA, et al. 2003. "Use of Phosphor Coatings for High Temperature Aerospace Applications," *AIAA Jounal, Cleveland, Oh USA, NASA Glenn Research Center, AIAA, , USA, 07/20/2003-07/23/2003*.

# Fuel Cell Related Measurement




Early investigation of this phosphor showed weak signal to noise.

Automotive sensors are required to meet performance and cost targets for measuring physical conditions and chemical species in fuel cell systems.

Current sensors do not perform within the required ambient and process conditions, do not possess the required accuracy and range, and/or are too costly

Targets - Automotive Fuel Cell Systems, Temperature

Sensors must conform to size, weight, and cost constraints of automotive applications

Operating range: -40 to 150°C

Response time: -40 to 100°C range <0.5 seconds with 1.5% accuracy; 100 to

150°C range <1.0 seconds with 2% accuracy

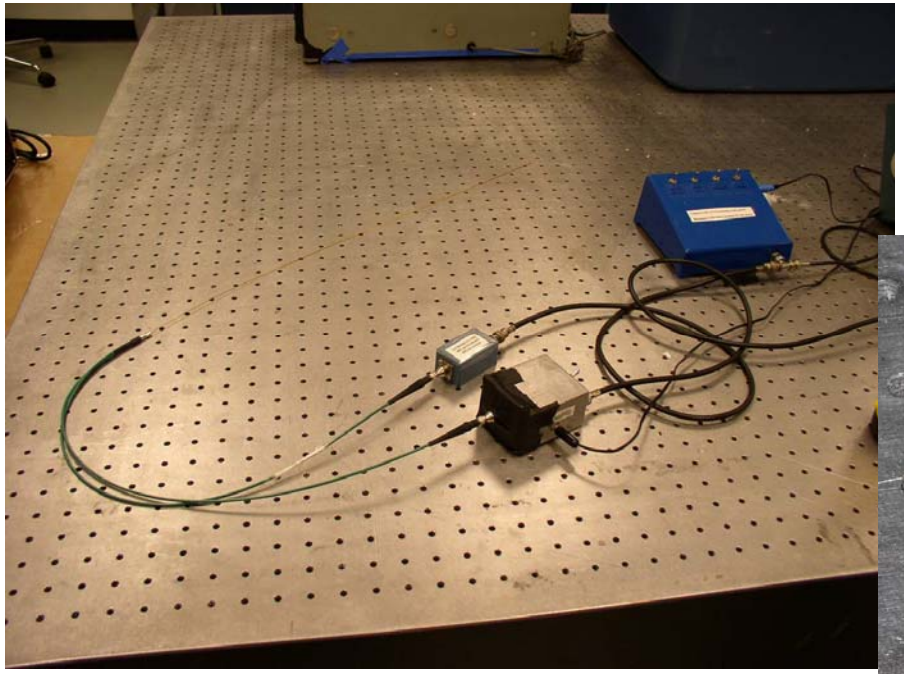
Gas environment: high humidity reformer/partial oxidation: H2 30% - 75%,

CO2, N2, H2O, CO at 1 - 3 atm total pressure.

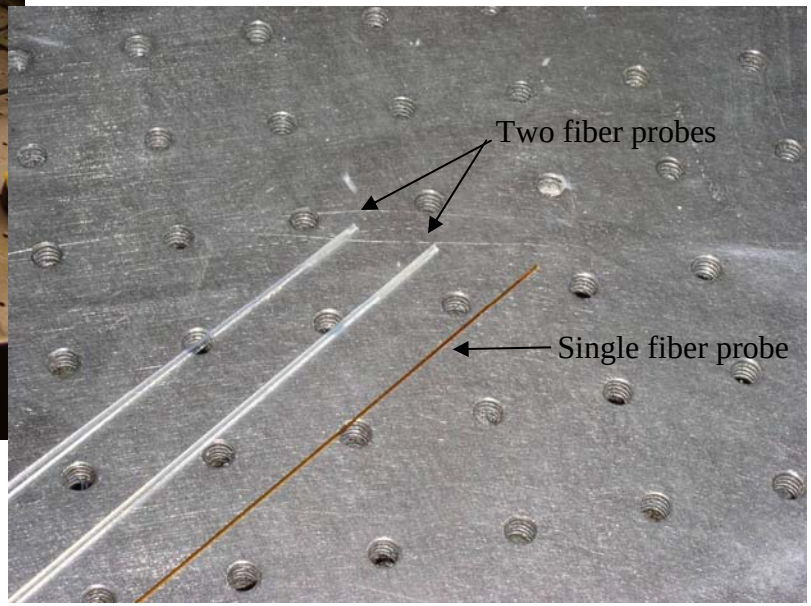
Insensitive to flow velocity.

From 2003 DOE progress report – available on the web

# Basic components for demo



Close-up of probe tips →




Measurements in PEM fuel cell recently accomplished.

From 2004 Annual Review

## What we hope to work on in the near future

- PEM fuel cells
- SOFC fuel cells
- Rail gun diagnostics
- Combustion engines
- Transient applications
- Triboluminescence for impact sensing
- Heating and Air Conditioning Heat Exchangers
- Neuroscience related

# A Useful 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).
- 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.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