National Aeronautics and Space Administration

Temperature Sensing Above 1000°C Using Cr-Doped $GdAlO_3$ Spin-Allowed Broadband Luminescence

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9th International Temperature Symposium
Anaheim, CA
March 20, 2012

Background

- Thermographic phosphor temperature measurements use luminescence from transition metal or rare earth dopants.

Transition metal (e.g., Cr^{3+}) 3d transitions	Rare earth (e.g., Dy^{3+}) 4f transitions
Unshielded	Shielding by 5s & 5p electrons
Strongly phonon & bonding coupled	Weakly phonon & bonding coupled
Very strong spin-allowed absorption oscillator strength✓	Very weak spin-forbidden oscillator strength (by ~4 orders of magnitude)
Strong thermal quenching $Cr:Al_2O_3$ performs up to 600°C	Weak thermal quenching✓ Dy:YAG performs up to 1700°C
Short λ emission not available (R lines @~700 nm)	Short λ emission available✓ (Dy^{3+} @456 nm)

- No high luminescence intensity phosphors for T>1000°C where high intensity is needed in presence of strong thermal radiation background.

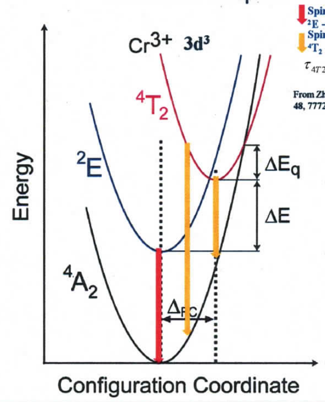
Objective

- Obtain best-of-both-worlds performance of high intensity emission that persists above 1000°C.

Approach

- Select Cr-doped phosphor with strong crystal field at dopant site to delay thermal quenching of luminescence.
    - Cr-doped $GdAlO_3$ (Cr:GAP)
- Utilize shorter-wavelength spin-allowed broadband emission for reduced interference from thermal radiation background.
- Demonstrate extended high temperature performance above 1000°C.
- Demonstrate optical thermometer using luminescence decay of Cr:GAP.

Basis for Phosphor Matrix Selection



Spin-forbidden R-line emission $^2E \rightarrow {}^4A_2$

Spin-allowed broadband emission $^4T_2 \rightarrow {}^4A_2$

$$\tau_{4T2} = \tau_{2E} = \tau_{2E}^{R} \frac{1 + 3e^{-\Delta E/kT}}{1 + \alpha e^{-\Delta E/kT} + \beta e^{-(\Delta Eq + \Delta E)/kT}}$$

From Zhang, Z., Grattan, K.T.V., and Palmer, A.W., *Phys. Rev. B* 48, 7772 (1993).

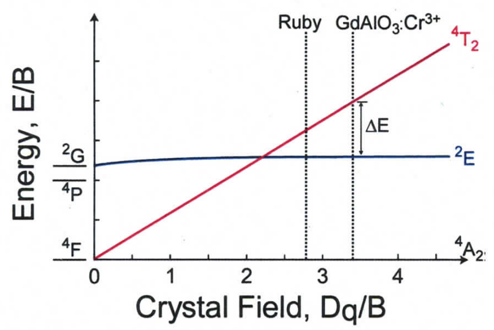
For α,β » 1, increase ΔE, ΔEq for longer τ.

$^4T_2$ (short-lived but population stabilized by thermal equilibrium with ^2E reservoir level)

^2E (long-lived reservoir level)

$^4A_2$

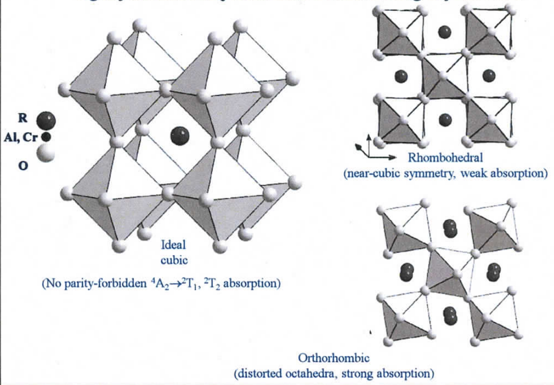
Tanabe-Sugano Diagram



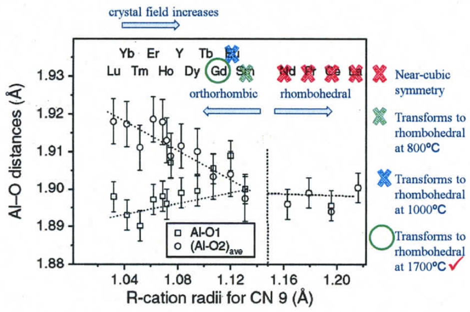
Increase ΔE by selecting matrix with stronger crystal field at dopant site.

Matrix Candidate: $RAlO_3$ Perovskite

Tightly bonded AlO_6 Octahedra Exhibit Strong Crystal Field

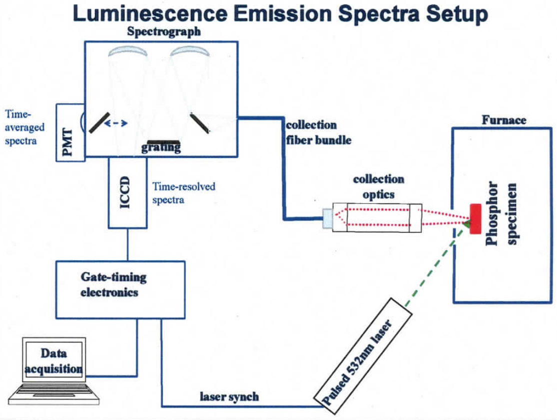


$RAlO_3$ Perovskite
Selection of Rare Earth

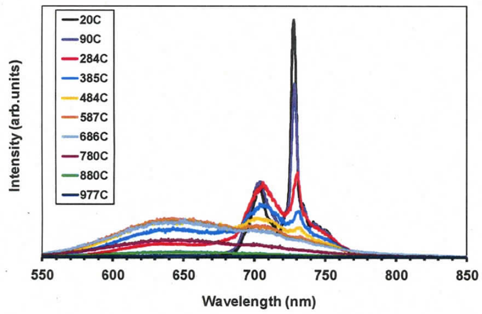


From Vasylechko, L., Sensyshyn, A., and Bismayer, U., "Perovskite-Type Aluminates and Gallates," in *Handbook on the Physics and Chemistry of Rare Earths, Vol. 39*, edited by K.A. Gschneidner, Jr., J.-C.G. Bünzil, and V.K. Pecharsky, Netherlands:North-Holland, 2009, p. 201.

Luminescence Emission Spectra Setup

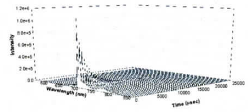


Time-Averaged Luminescence Emission
Cr(0.2%):GAP

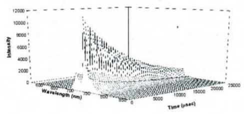


Time-Resolved Luminescence Emission
15°C

Cr(0.1%):Al_2O_3



Cr(0.2%):GAP



$\tau = 3.0\,\text{msec}$

$I_{\max} = 1081148$

$\tau = 13.1\,\text{msec}$

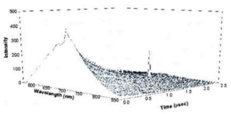
$I_{\max} = 11736$

$$\frac{\tau_{\text{Cr:GAP}}}{\tau_{\text{Cr:Al}_2\text{O}_3}} = 4.4$$

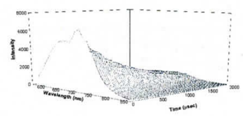
$$\frac{I_{\max\ \text{Cr:GAP}}}{I_{\max\ \text{Cr:Al}_2\text{O}_3}} = 0.011$$

Time-Resolved Luminescence Emission
584°C

Cr(0.1%):Al_2O_3



Cr(0.2%):GAP



$\tau = 0.97\,\mu\text{sec}$

$I_{\max} = 407$

$\tau = 1.03\,\text{msec}$

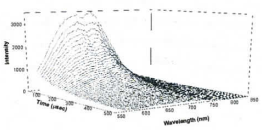
$I_{\max} = 6646$

$$\frac{\tau_{\text{Cr:GAP}}}{\tau_{\text{Cr:Al}_2\text{O}_3}} = 1062$$

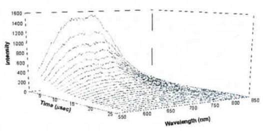
$$\frac{I_{\max\ \text{Cr:GAP}}}{I_{\max\ \text{Cr:Al}_2\text{O}_3}} = 16.3$$

Time-Resolved Luminescence Emission
Cr(0.2%):GAP

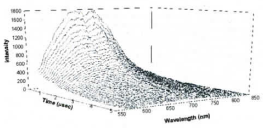
778°C



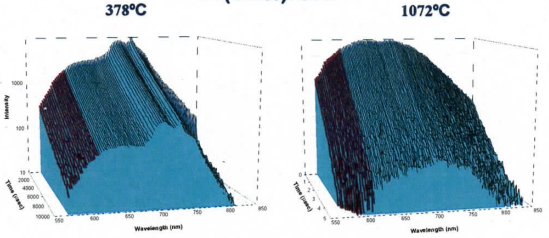
973°C



1072°C

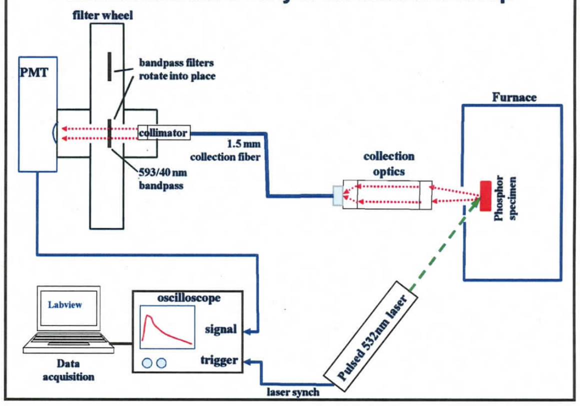


Time-Resolved Luminescence Emission
Logarithmic Intensity Scale
Cr(0.2%):GAP

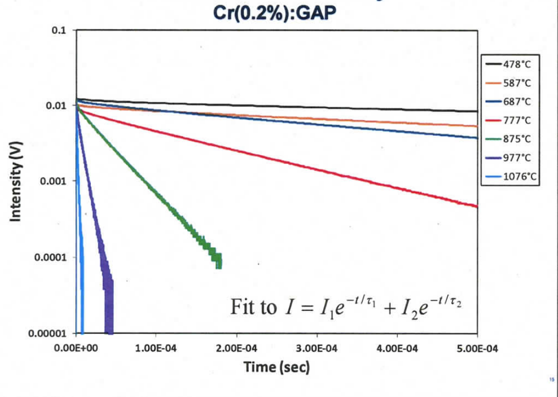


- Nearly single exponential.
- Uniform decay rate over wavelength range.
- Adequate signal for decay time determination at wavelengths as short as 570 nm.
- Collect luminescence decay measurements with bandpass filter @593 nm, FWHM = 40 nm to minimize interference from thermal radiation background.

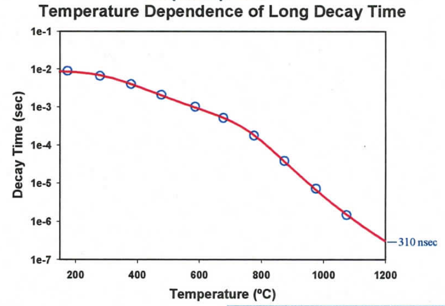
Luminescence Decay Measurement Setup



Luminescence Decay
Cr(0.2%):GAP



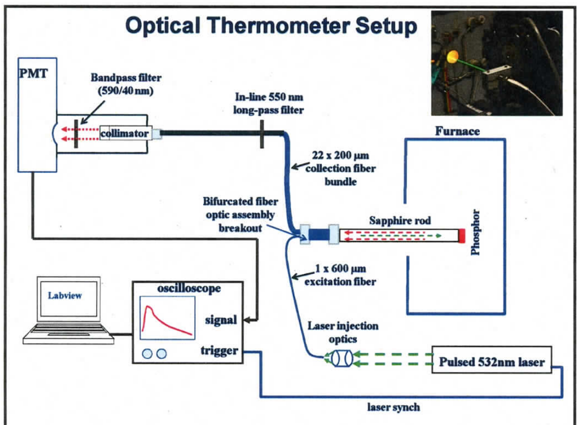
Luminescence Decay Temperature Dependence
Cr(0.2%):GAP



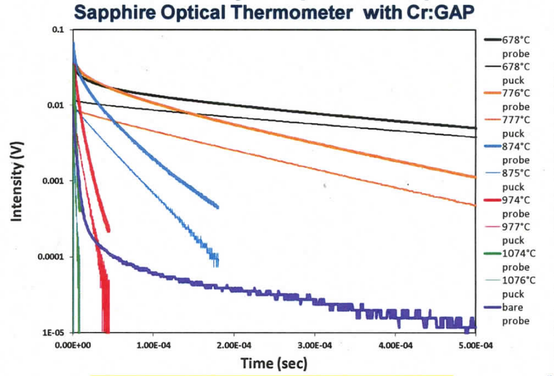
Fit to $\tau = \tau_{2E}^{R} \dfrac{1 + 3e^{-\Delta E/kT}}{1 + \alpha e^{-\Delta E/kT} + \beta e^{-(\Delta E_q + \Delta E)/kT}}$

	Cr:GAP	Cr:Al_2O_3
τ^R ($^2E \rightarrow {}^4T_2$)	8.9 msec	4.20 msec
ΔE	3600 cm^{-1}	2350 cm^{-1}

Optical Thermometer Setup



Luminescence Decay Temperature Dependence
Sapphire Optical Thermometer with Cr:GAP



Bare probe response will limit usefulness to T<1100°C.

Summary

- Spin-allowed broadband luminescence from Cr:GAP exhibits exceptional persistence to high temperature for thermographic phosphor temperature measurements up to 1200°C.
  - Strong crystal field.
  - Spin-allowed broadband emission from $^4T_2$ level "stabilized" by underlying long-lived ^2E reservoir level.
  - Growth of spin-allowed broadband emission shifts emission to more useful shorter wavelengths (730→570 nm).
- Optical thermometer based on Cr:GAP decay at tip of sapphire lightguide demonstrated to 1075°C.
  - Sapphire fluorescence limits usefulness to T<1100°C.

Acknowledgments

- Funding by the NASA Fundamental Aeronautics Mission Directorate Seedling Fund.