Europium-doped Pyrochlores for Use as Thermographic Phosphors in Thermal Barrier Coatings

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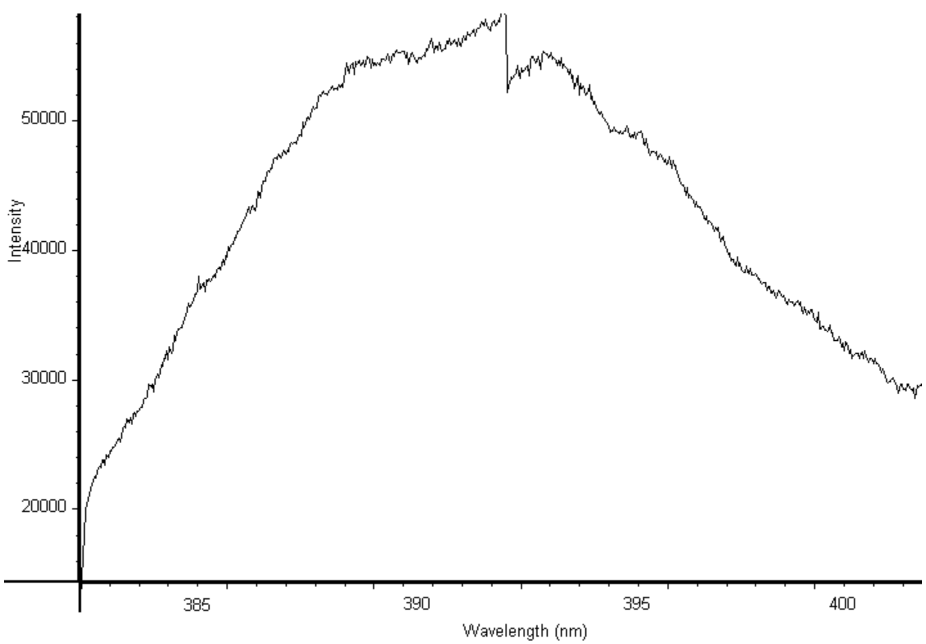
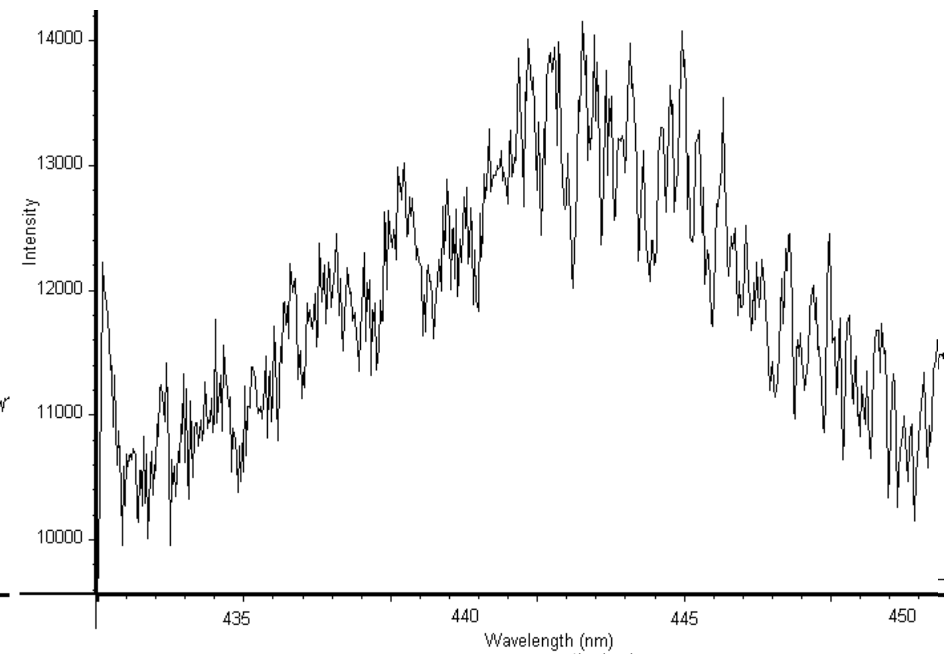
Phosphor Thermometry

- Use of thermographic phosphors – emission properties change with varying temperature (decay time, peak wavelengths, relative intensities of peaks)
- i.e. ZnO:Ga shows shifting peaks as temperature increases
- Remote, non-contact temperature measurements



294 K, Peak at about 392.5 nm



450 K, Peak at about 441.3 nm

Thermal Barrier Coatings

- Protect metallic components from extremely high temperatures and effects of heat fatigue
- Insulation for components in gas turbines allows for higher operating temperatures and better efficiency
- Two primary characteristics for coating: low thermal conductivity and high thermal expansion coefficient
- Yttria stabilized zirconia (YSZ) is currently the most commonly used thermal barrier coating material
- YSZ can not be used reliably for temperatures > 1200° C
- New materials for thermal barrier coatings must be developed to provide insulation for gas turbines operating above 1200° C

Pyrochlores

- Class of materials that follow the chemical structure $A_2^{3+}B_2^{4+}O_7$

  A = rare-earth element (Y, La, Nd, Sm, Eu, Gd)

  B = transition metal (Ti, Zr, Hf, Sn)
- Generally have low thermal conductivities and high thermal expansion coefficients making them attractive as materials in thermal barrier coatings
- Rare-earth doped pyrochlores have been shown to have temperature-dependent lifetimes up to very high temperatures by Gentleman and Clarke (2005)

Goal

- Determine the suitability of three different europium-doped pyrochlores as thermographic phosphors –

  $La_2Zr_2O_7$:Eu, $La_2Hf_2O_7$:Eu, $Nd_2Zr_2O_7$:Eu
- Create calibration curve of luminescent lifetime as a function of temperature for these three compounds
- Selected compounds have low thermal conductivity, high melting points, and adequate thermal expansion coefficients
- Temperature-dependent emission lifetimes have not been thoroughly studied for these compounds
- Very convenient to have insulation material that doubles as a way to measure surface temperatures

Sample Synthesis

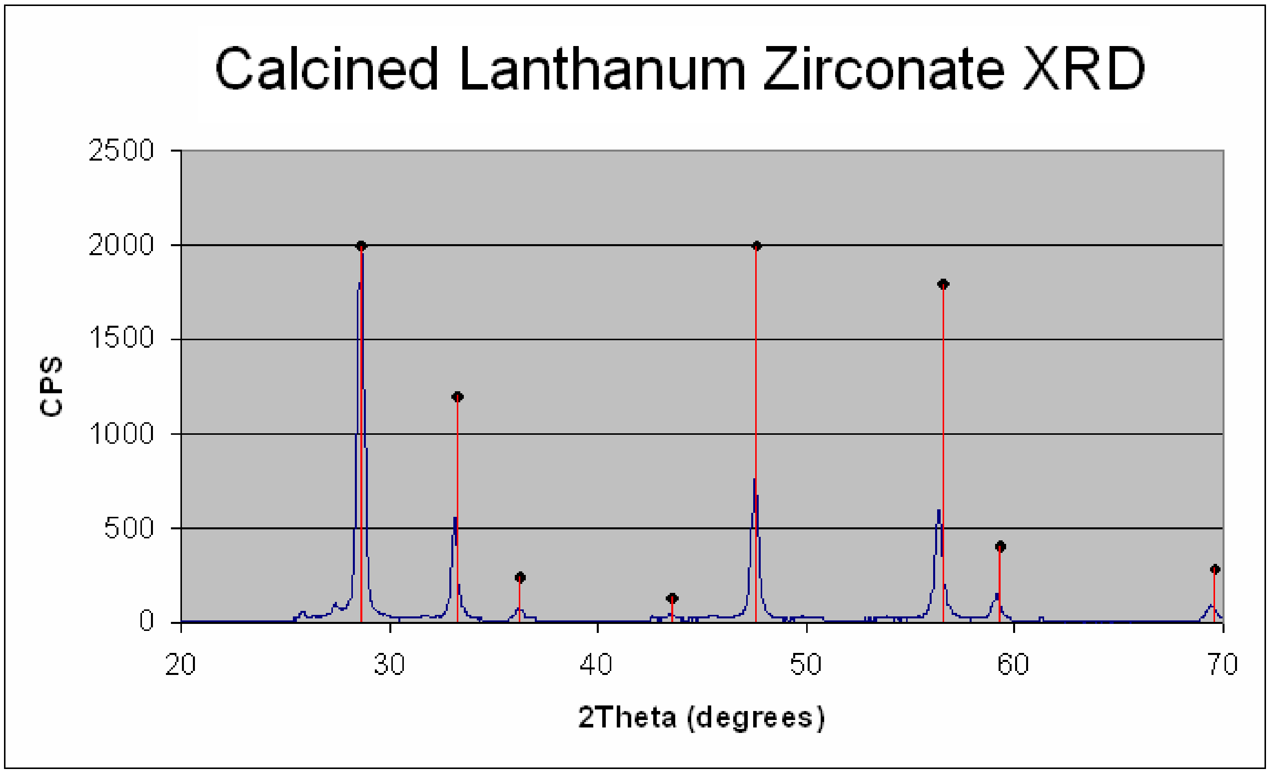
- Aqueous solutions formed using stoichiometric molar ratios of metal nitrates, oxynitrates, and glycine
- Samples doped at 4 mol % with europium which substitutes into the A^{3+} site of the pyrochlore
- Example stoichiometric equation used to synthesize $La_2Hf_2O_7$:Eu

$$18HfO(NO_3)_2 + 17.31La(NO_3)_3 \cdot 6H_2O + .7Eu(NO_3)_3 \cdot 6H_2O + 50C_2H_5NO_2 \rightarrow 9La_{1.92}Hf_2O_7{:}Eu_{.08} + 100CO_2 + 125H_2O + 70N_2$$

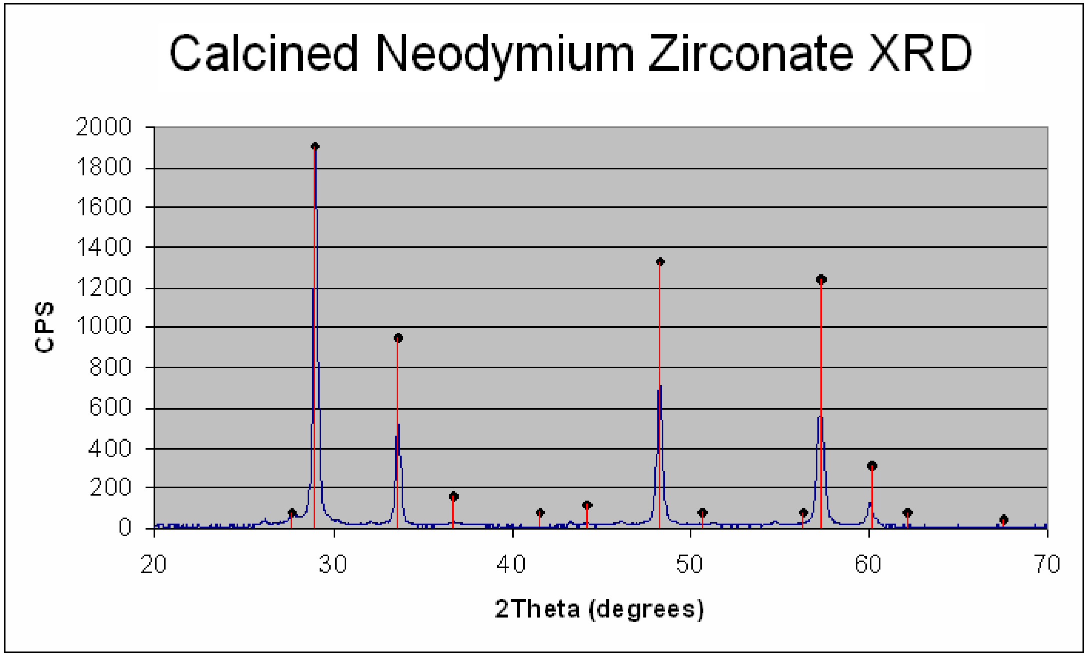
- Samples combusted on a hot plate at about 540° C

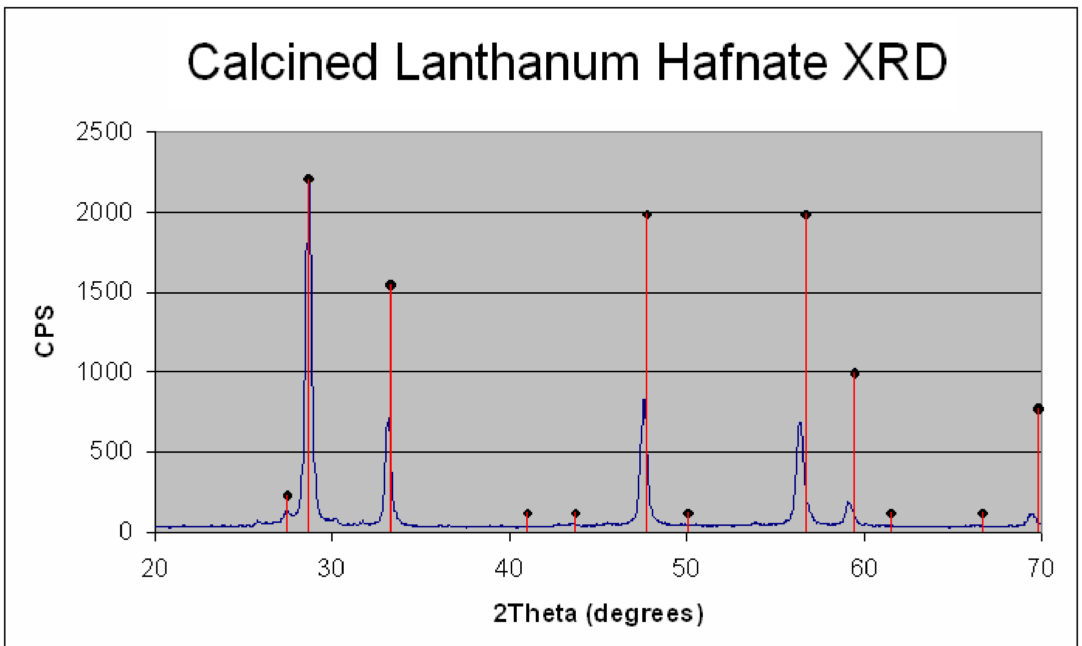
X-Ray Diffraction Characterization

- Compare results to JCPDS references to determine if samples had been synthesized correctly



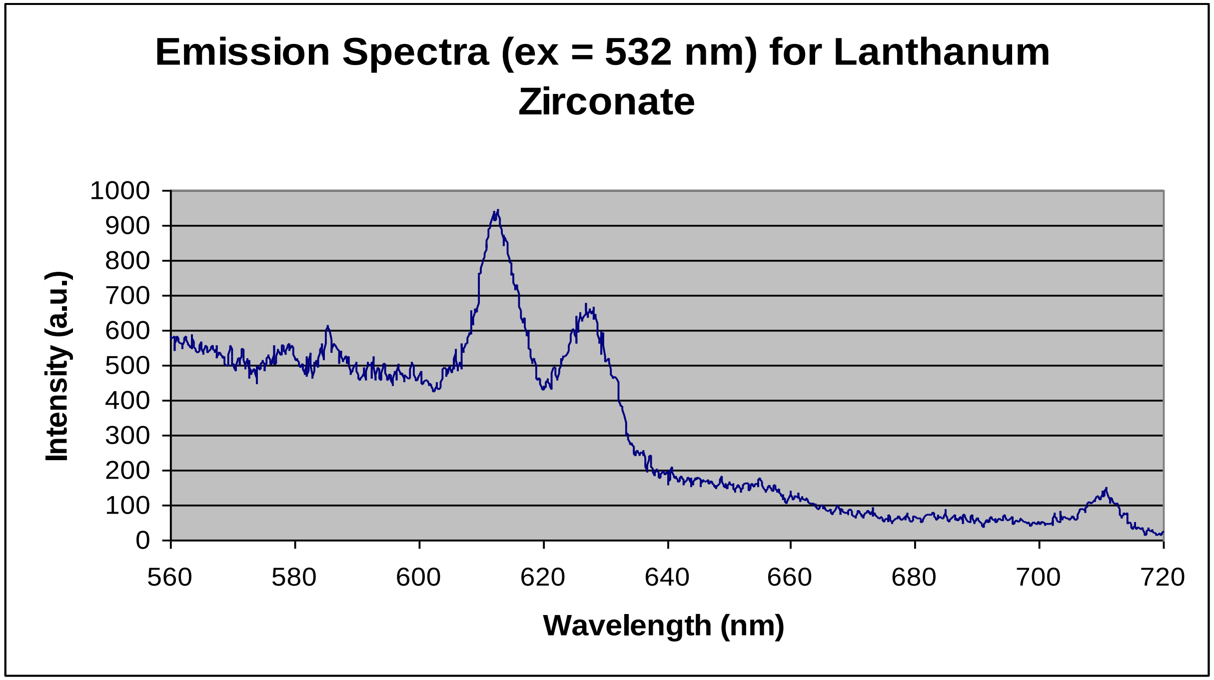
- Trend of peaks match up well with reference data
- Abnormalities caused by volatile nature of combustion synthesis and europium dopant

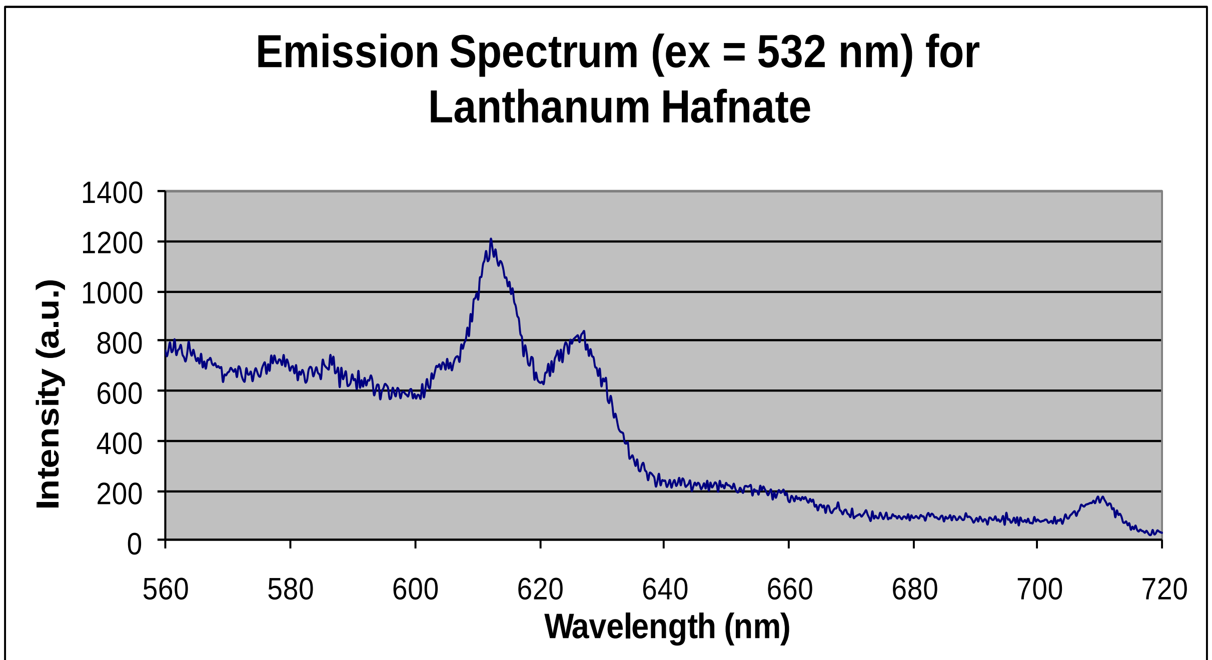

Calcined Neodymium Zirconate XRD
CPS
2000
1800
1600
1400
1200
1000
800
600
400
200
0
20
30
40
50
60
70
2Theta (degrees)


Calcined Lanthanum Hafnate XRD
CPS
2500
2000
1500
1000
500
0
20
30
40
50
60
70
2Theta (degrees)

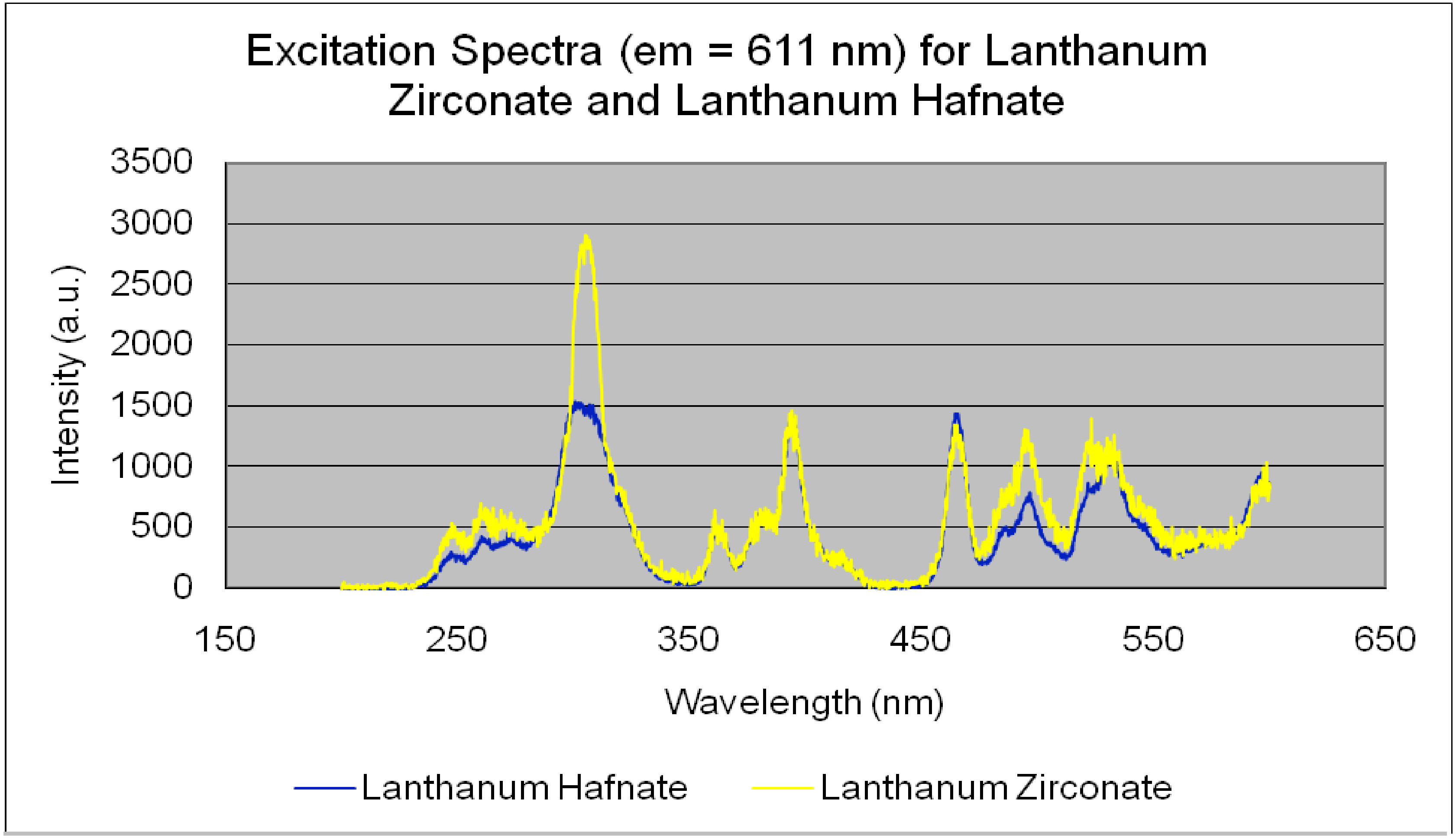
Spectroscopic Characterization

- Determine what peak we should look at when conducting the lifetime testing
- Emission spectra using excitation wavelength of 532 nm taken for all three compounds
- $Nd_2Zr_2O_7$:Eu showed no luminescence even when other excitation wavelengths were used



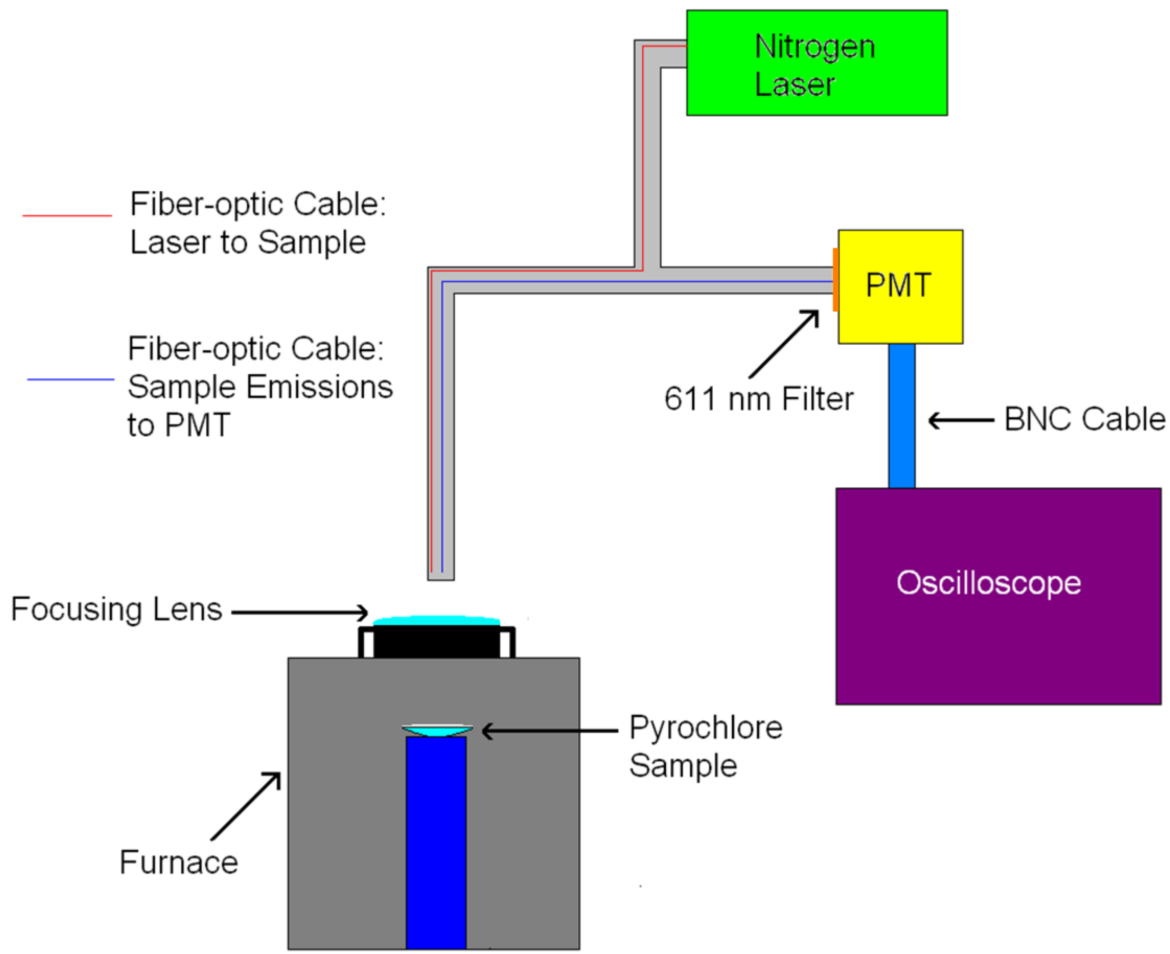


- Dominant peak at 611 nm with another smaller peak at 627 nm
- Emissions are much less intense past about 640 nm
- Excitation spectra for both lanthanum compounds were taken using a 611 nm emission wavelength



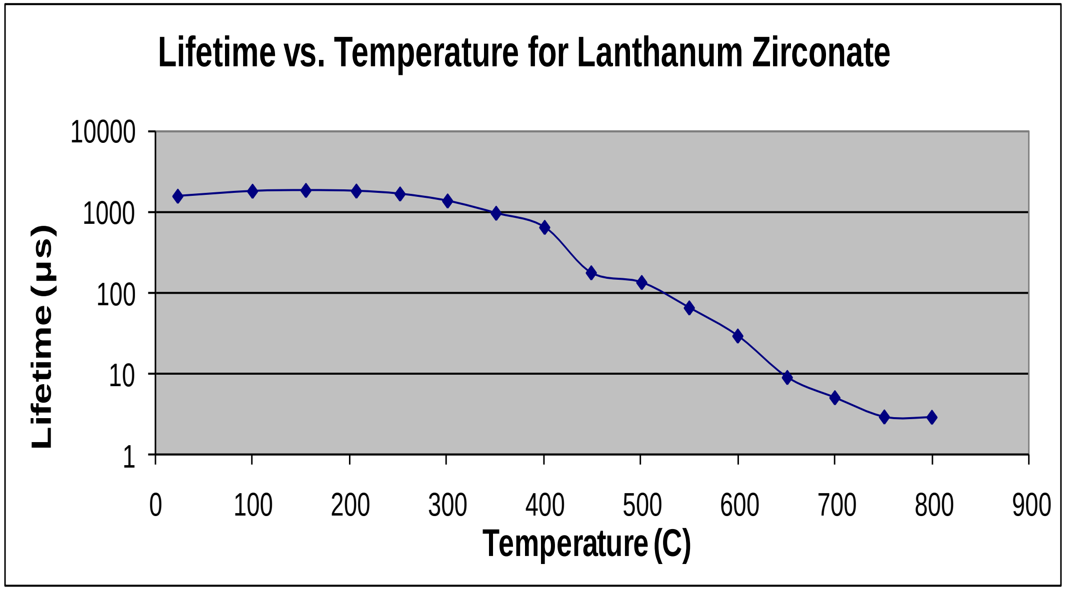
Excitation Spectra (em = 611 nm) for Lanthanum Zirconate and Lanthanum Hafnate
Intensity (a.u.)
3500
3000
2500
2000
1500
1000
500
0
150
250
350
450
550
650
Wavelength (nm)
Lanthanum Hafnate
Lanthanum Zirconate

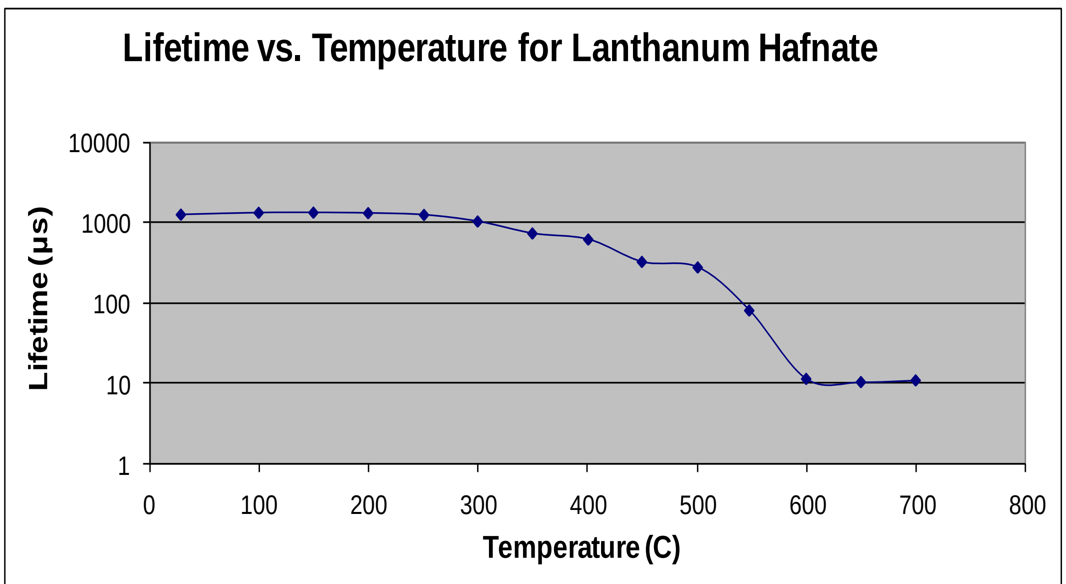
Lifetime Testing Setup



- Modified Thermolyne 47900 furnace allows for temperature-dependent measurements
- SRS NL 100 Nitrogen Laser used as 337 nm excitation source
- Hamamatsu 5783 PMT with a 10 kΩ resistor to acquire a better signal
- Measurements taken at room temperatures, 100° C, then 50° C increments until signal became too weak to measure
- LabView software calculated lifetime based on logarithmic decay from 15% to 35% of total signal

Lifetime as a Function of Temperature





- No lifetime results for $Nd_2Zr_2O_7$:Eu because no luminescence found
- Both lanthanum compounds have fairly constant lifetimes with increasing temperature until about 400° C, the quenching temperature
- $La_2Zr_2O_7$:Eu fully quenches at about 800° C
- $La_2Hf_2O_7$:Eu fully quenches at about 600° C
- Quenching temperature to fully quenched temperature is range through which these compounds can be used as thermographic phosphors

Conclusions

- Combustion synthesis was successfully used to create the europium-doped pyrochlores for testing
- $Nd_2Zr_2O_7$:Eu showed no luminescence using multiple excitation sources and thus can not be used as a thermographic phosphor
- $La_2Zr_2O_7$:Eu and $La_2Hf_2O_7$:Eu show temperature-dependent variation in emission lifetime but only for relatively low temperatures – no use for gas turbines
- $La_2Zr_2O_7$:Eu suitable from 400° C to 800° C and $La_2Hf_2O_7$:Eu suitable from 400° C to 600° C
- Future Work: better excitation wavelength, different dopant percentages

Acknowledgments

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- Thanks particularly to Dr. Steve Allison who allowed the use of his lab and equipment and helped with the experimental setup