

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

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Three europium-doped pyrochlores including $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$, $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$, and $\text{Nd}_2\text{Zr}_2\text{O}_7:\text{Eu}$ were tested to determine their lifetimes as a function of temperature. These pyrochlores were examined to determine their suitability as thermographic phosphors, in systems that use these materials for thermal barrier coatings. Results show that $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$ and $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$ can be used to measure surface temperatures up to approximately 600°C and 800°C , respectively. However, $\text{Nd}_2\text{Zr}_2\text{O}_7:\text{Eu}$ showed little propensity for use as a thermographic phosphor.

I. Introduction

Phosphor thermometry has become an increasingly significant method of making surface temperature measurements. The primary benefits of this type of thermometry are that no surface contact is required and temperature measurements can be done remotely. This method requires the use of a phosphor that has exhibits one or more of the following changes with variations in temperature: change in lifetime, change in relative intensities of emission peaks, or shifts in the emission peak wavelengths¹. Phosphors that maintain thermographic properties at very high temperatures ($>1200^\circ\text{C}$) are particularly interesting because these phosphors can also be used as thermal barrier coatings.

Thermal barrier coatings have been used as applications to metallic components in order to insulate the components from extremely high temperatures and the effects of thermal fatigue, prolonging the lifetimes of the protected components. In addition, deposition of these coatings on the components in a gas turbine allows the turbine to operate at higher temperatures increasing its efficiency². Ytria stabilized zirconia (YSZ) is the most commonly used thermal barrier coating primarily because of its durability and thermal performance at currently used turbine operating temperatures. However, long-term use of YSZ is limited to operating temperatures below approximately 1200°C at which point phase transformations occur in the material that lead to the formation of cracks in the coating³. The development of new gas turbines operating at higher temperatures than 1200°C poses the need for the development of accompanying thermal barrier coatings that can withstand those increased temperatures.

Pyrochlores are one type of material of interest for thermal barrier coating applications at higher temperatures than those sustainable by YSZ. Pyrochlores are a class of materials that follow the chemical structure $\text{A}_2\text{B}_2\text{O}_7$ in which A and B can be a wide range of rare-earth elements and transition metals, respectively. Pyrochlores have shown potential as thermal barrier coating materials primarily because testing of zirconate pyrochlores has shown them to have lower thermal conductivities than YSZ². In addition, pyrochlores have high coefficients of thermal

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expansion which can help prevent cracking and deformation in coatings made from such compounds. In fact, many of these materials are refractory at temperatures above 1500° C². Doping of these materials on both the A and B sites can alter the properties of the materials. Furthermore, there a large number of compounds adhering to the pyrochlore structure that have widely different properties without any doping⁴. An additional benefit is that often rare-earth doped pyrochlores can act as thermographic phosphors in which emission is temperature-dependent, allowing for remote, non-contact temperature measurements along with insulation capabilities.

II. Experimental

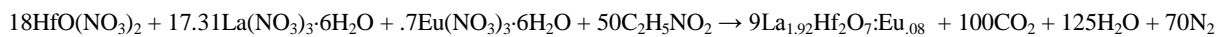
A. Sample Selection

The pyrochlores chosen for this research included La₂Zr₂O₇, La₂Hf₂O₇, and Nd₂Zr₂O₇. La₂Zr₂O₇ has been shown to have many properties that make it an excellent choice for thermal barrier coatings: low thermal conductivity, high melting point, and moderate thermal expansion coefficient⁵. The thermal conductivity of La₂Zr₂O₇ is approximately 20% lower than that of YSZ and it exhibits thermal stability at temperatures over 1200° C for long periods of time⁵.

In addition, the temperature-dependent lifetimes of these particular compounds have not been thoroughly studied. They all have potential as materials in thermal barrier coatings, and consideration of these materials as thermographic phosphors is warranted. The samples needed to be doped with a rare earth element so they will luminesce when excited. The rare earth dopant substitutes into the A³⁺ site of the pyrochlores because of the similar size in atomic radius. Europium, Eu³⁺, was used as the dopant in this research because it has been shown to allow for temperature measurements of over 1200° C when used in other pyrochlores⁶.

B. Sample Synthesis

The samples were created using a simple method of combustion synthesis. Aqueous solutions were prepared using the stoichiometric molar ratios of metal nitrates (lanthanum nitrate, neodymium nitrate, europium nitrate), oxynitrates (hafnium oxynitrate, zirconium oxynitrate), and glycine. The samples were doped at 4 mol % with europium. The stoichiometric equation for the aqueous solution used to synthesize the La₂Hf₂O₇ is shown below:



The aqueous solutions were placed in crucibles and combusted on a hot plate at 540° C. After approximately 10 minutes, the water in the solution finished boiling off and a flame erupted from the crucible. A large volume of light, porous white powder formed in the crucible when the La₂Zr₂O₇ and La₂Hf₂O₇ samples were combusted. In the case of the Nd₂Zr₂O₇ sample, the powder was light, porous, and had the same texture but was a faint blue color. All three samples were calcined at 1200° C in air to remove carbon impurities that entered the samples during the combustion process.

III. Results and Discussion

A. X-ray Diffraction Characterization

After synthesis the samples were characterized by X-ray diffraction (XRD). The results for each sample were compared to their respective references published by the Joint Committee on Powder Diffraction Standards (JCPDS). For La₂Zr₂O₇, the reference is 17-450; for La₂Hf₂O₇, the reference is 37-1040; for Nd₂Zr₂O₇, the reference is 78-1618. The XRD scan results shown below in Figs. 1, 2, and 3 have been standardized to the highest peak using the JCDPS references. The red lines represent the JCPDS reference peaks and the blue peaks represent the scan data.

There are slight differences in the locations of the peaks when comparing the reference data to the experimental data. The difference in the locations of the peaks is explained by the doping process for all the samples. The JCDPS reference data include pure samples that do not have any europium dopant. Doping with europium replaces atoms from the A³⁺ site (La and Nd in this case) with europium atoms, altering the crystalline structure of the samples. The shifting effect is more pronounced in the lanthanum samples (La₂Zr₂O₇ and La₂Hf₂O₇) than in the Nd₂Zr₂O₇ because of the difference in atomic radius. Europium's atomic radius is closer to that of neodymium than that of lanthanum meaning the europium dopant has less of an effect on the crystalline structure of the Nd₂Zr₂O₇ than on the crystalline structures of the lanthanum compounds.

The more noticeable difference between the reference data and experimental data involves the relative intensities of the peaks. Although the location of the peaks matches that of the reference, the relative magnitude of the intensities of the secondary peaks did not match the reference. This discrepancy can most likely be attributed to the chaotic nature of combustion synthesis process. The process is quick but tends to introduce impurities and does not guarantee stoichiometry.

B. Spectroscopic Characterization

The room-temperature spectroscopic characterization of these compounds was done using a Quantmaster 500 spectrofluorometer. The device uses a xenon lamp excitation source. Emission spectra for each of the compounds were taken using an excitation wavelength of 532 nm. Although the spectra for $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$ and $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$ showed highly visible peaks, the spectrum for $\text{Nd}_2\text{Zr}_2\text{O}_7:\text{Eu}$ did not. The $\text{Nd}_2\text{Zr}_2\text{O}_7:\text{Eu}$ did not show any luminescence with an excitation wavelength of 532 nm nor with any other excitation wavelengths tried (470nm, 390 nm, 337 nm). The emission spectrum for $\text{Nd}_2\text{Zr}_2\text{O}_7:\text{Eu}$ showed no luminescence. The emission spectra for the two lanthanum compounds showed emission peaks at 611 nm and 627 nm. Past 630 nm, the emissions for both were significantly less intense compared to the emissions in the 560 to 620 nm range.

The excitation spectra for both lanthanum compounds were taken using an emission wavelength of 611 nm which was the largest emission peak found from the emission spectra. The excitation spectra for both lanthanum compounds shows that effective excitation wavelengths include: 300 nm, 390 nm, 470 nm, 490 nm, and 530 nm.

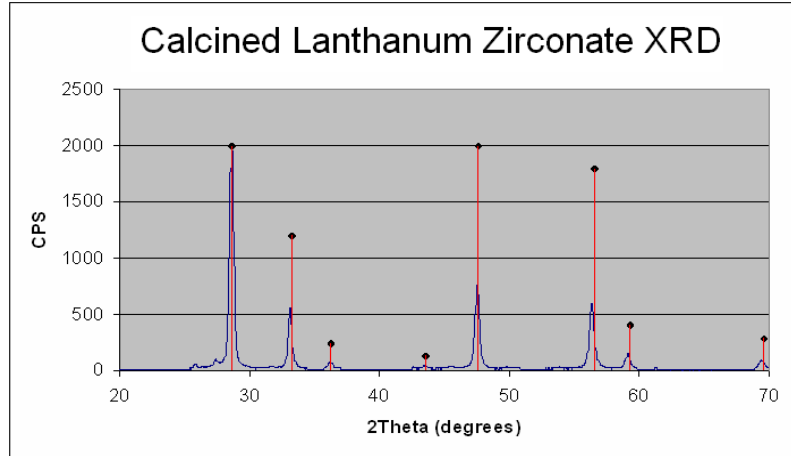


Figure 1. XRD Results for Calcined $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$

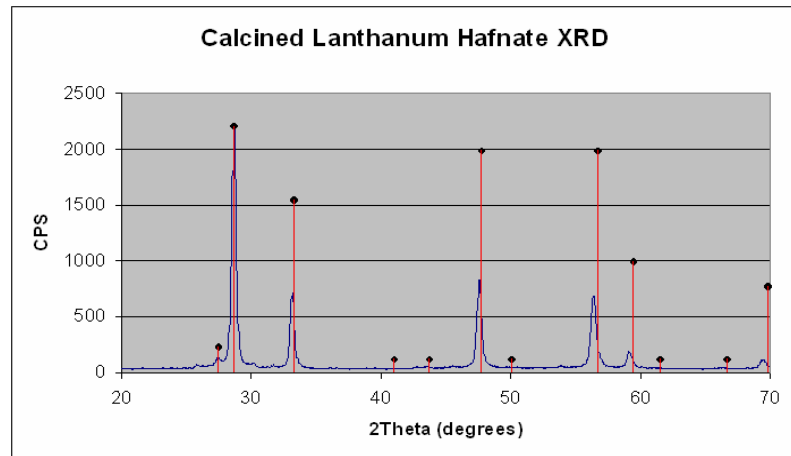


Figure 2. XRD Results for Calcined $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$

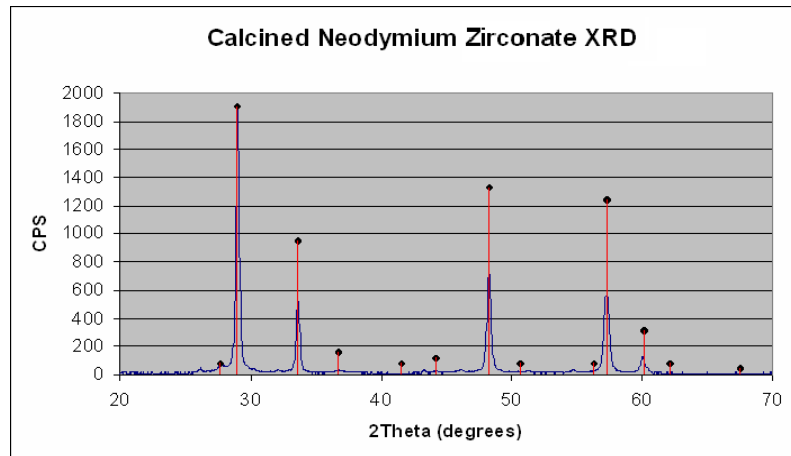
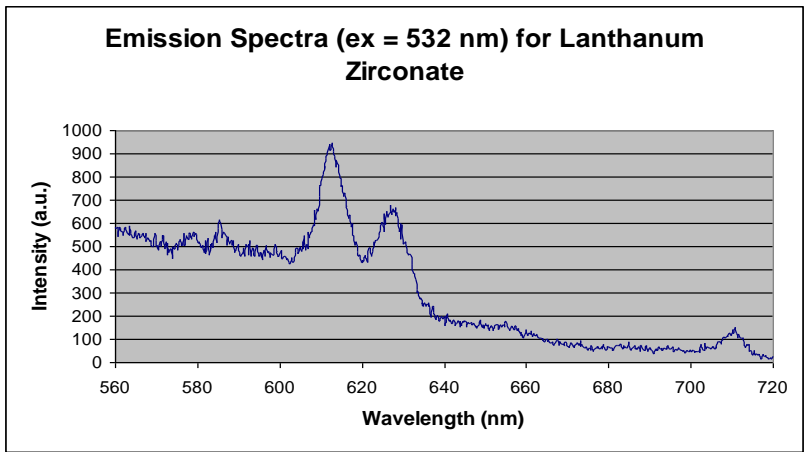
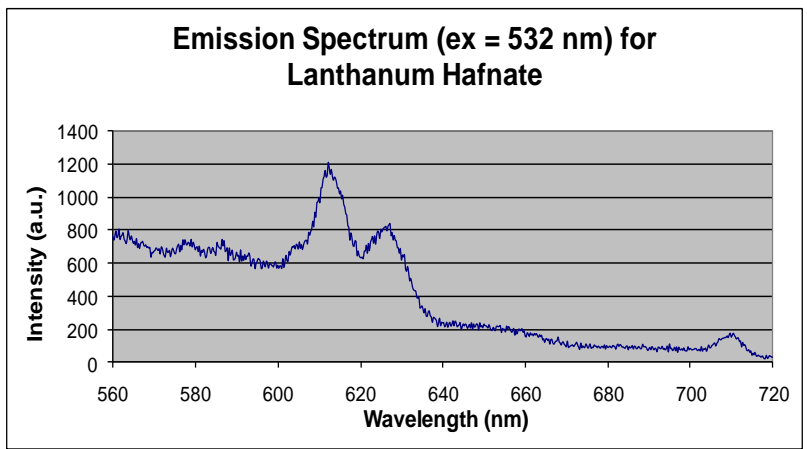


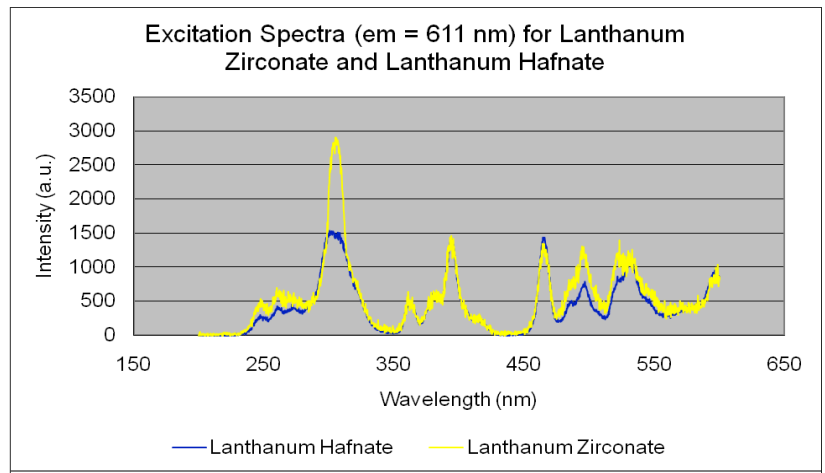
Figure 3. XRD Results for Calcined $\text{Nd}_2\text{Zr}_2\text{O}_7:\text{Eu}$



**Figure 4. Emission Spectrum for $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$
Excitation Wavelength = 532 nm**



**Figure 5. Emission Spectrum for $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$
Excitation Wavelength = 532 nm**



**Figure 6. Excitation Spectra for $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$ and $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$
Emission Wavelength = 611 nm**

C. Lifetime as a Function of Temperature

The ultimate goal of this research was to determine the luminescent lifetime of each of these compounds as a function of temperature. A modified Thermolyne 47900 furnace was used to heat the samples. The furnace was outfitted with a small hole at the top to allow a laser to excite the samples inside the furnace. In this research, an SRS NL 100 Nitrogen Laser was used to excite the samples with a wavelength of 337 nm. The emissions of the samples were captured using a fiber optic cable connected to a Hamamatsu 5783 photomultiplier tube (PMT) using a 10 k Ω resistor to acquire a better signal. The PMT was connected to a Tektronix TDS5034B Digital Phosphor Oscilloscope which displayed the signal that was captured.

The samples were tested one at a time in the furnace. Results were taken starting at room temperature; then the temperature of the furnace was set to 100°C and a measurement was taken. A measurement was then taken at every increment of 50°C after that (150°C, 200°C, etc). The temperature was incremented until the emissions became too weak to properly measure indicating the compounds had fully quenched. The lifetime was determined by measuring the logarithmic decay from 15% to 35% of the entire signal captured.

Lifetime data was retrieved for both lanthanum compounds but not the neodymium zirconate which did not show any luminescence even at room temperature. The results that show for both $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$ and $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$, the quenching temperature is about 400°C. Prior to the quenching temperature, both compounds have relatively constant lifetimes regardless of temperature. The $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$ fully quenches at about 800°C at which point the lifetime becomes constant. The $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$ fully quenches at about 600°C.

D. Discussion

Of the three europium-doped pyrochlores tested, only $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$ and $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$ showed suitability as thermographic phosphors. The lifetimes of the emissions for both of these pyrochlores vary from 400°C until they reach a certain higher temperature, 800°C for $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$ and 600°C for $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$. Thus, $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$ is suitable as a thermographic phosphor throughout a temperature range of 400°C to 800°C and $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$ is suitable as a thermographic phosphor throughout a temperature range of 400°C to 600°C.

The $\text{Nd}_2\text{Zr}_2\text{O}_7:\text{Eu}$ did not luminesce at all when excited by a range of sources, even at room temperature. Although $\text{Nd}_2\text{Zr}_2\text{O}_7:\text{Eu}$ may still have some use as an insulation material, it can not be used as a thermographic phosphor since it gives off no measurable emissions when excited.

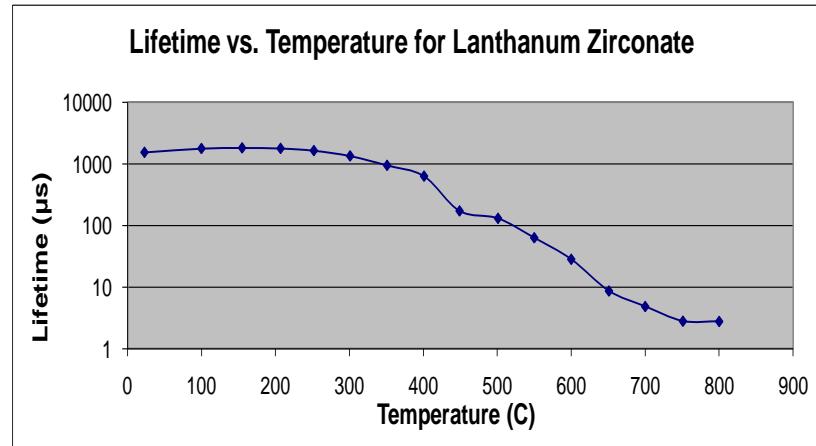


Figure 7. Lifetime for $\text{La}_2\text{Zr}_2\text{O}_7:\text{Eu}$ with Increasing Temperature

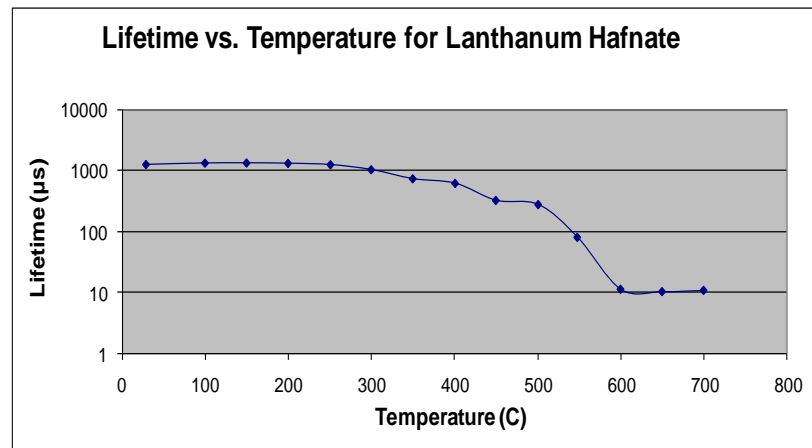


Figure 8. Lifetime for $\text{La}_2\text{Hf}_2\text{O}_7:\text{Eu}$ with Increasing Temperature

IV. Conclusion

$\text{La}_2\text{Zr}_2\text{O}_7\text{:Eu}$ is suitable as a thermographic phosphor up to 800°C and $\text{La}_2\text{Hf}_2\text{O}_7\text{:Eu}$ is suitable as a thermographic phosphor only up to 600°C. These temperatures are not high enough for them to be used as thermographic phosphors in thermal barrier coatings. They can be used in applications that operate under their respective maximum temperatures as an insulation material and thermographic phosphor. However, these temperatures are too low for use in gas turbines.

Future work includes the testing these compounds with a different excitation source and testing additional pyrochlores. A 337 nm excitation source was used in this research based on availability, but as seen in Fig. 6, this is a poor excitation wavelength to produce intense emissions. It is possible that using an excitation wavelength that produces more intense emissions such as 532 nm would allow the lifetime of these compounds to be measured up to higher temperatures. As mentioned before, there are a large number of compounds that adhere to the pyrochlore structure. Additional testing of such materials with different rare earth dopants could yield a compound that provides excellent insulation and is suitable as a thermographic phosphor up to temperatures higher than 1200°C.

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