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X-ray Excitation of Thermographic Phosphors

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Abstract: A compelling diagnostic approach for characterizing reacting solids would be simultaneous X-ray probing combined with surface temperature measurements of the sample. Phosphor thermometry shows promise at providing this type of measurement through characterization of the induced emission of phosphor particles coated on the surface of a sample. Typical thermographic phosphors are excited using UV/visible radiation in the form of a laser, and several thermographic phosphors exist which are also known X-ray scintillators. One such X-ray scintillator, Gd_2O_2S:Tb, is explored here to determine if its induced emission remains thermographic during X-ray excitation. Measured spectra show a temperature sensitivity between 22-80 °C. These measured spectra and two intensity ratio calibrations are compared to those found in literature for this phosphor during UV excitation. These results serve as an important first step towards simultaneous X-ray probing and surface temperature measurements of a sample and show for the first time that the induced emission of a thermographic phosphor can remain thermographic during X-ray excitation.

Keywords: X-ray, thermographic phosphors, reacting solids, propellants

1. Introduction

Temperature is arguably the most important thermodynamic property to monitor of any given system. As such, there exist several methods for temperature measurement, which include more conventional methods such as thermocouples and pyrometry, along with more advanced diagnostic techniques developed over the past few decades. Selection of an appropriate thermography technique is dependent upon the application being considered. For reacting solids, high spatial and temporal resolutions are typically required due to the highly transient behavior intrinsic to these materials. These constraints rule out the use of thermocouples, since these can suffer from thermal lag and by their nature are point measurements. Pyrometry is also best ruled out since precise temperature measurements would require knowing the emissivity of the reacting material's surface, which can change with time [1]. Emission from the reacting surface and flames while taking the measurement can also interfere with pyrometry measurements. Inherent emission is also an issue with phosphors but exhibits a greater range of methods to isolate the signal than for pyrometry.

A method of thermography which has been shown to address the issues plaguing the other techniques described above is phosphor thermometry [2,3]. In this technique, thermographic phosphor particles are excited by a light source (typically a laser) which causes these particles to enter a higher energy level. Phosphorescence in the UV/visible range is then emitted as these

phosphors relax back down to their ground level. These thermographic phosphor particles consist of a ceramic matrix doped with either a transition or rare-earth metal. The dopants (also called activators) typically absorb and emit the radiation in this process, whereas the host ceramic remains mostly transparent to the excitation radiation [3]. The competing effects of radiative and non-radiative transfer processes as the thermographic phosphors return back to the ground level are the reason for their temperature sensitivity [1]. The non-radiative processes depend only upon internal energy modes, which are temperature dependent. Two different characteristics of the emitted light from the phosphors can be temperature dependent: the lifetime and the spectral response of the emission. Therefore, two different methods of phosphor thermometry arise. The so-called lifetime method involves measuring the lifetime decay of the light intensity of the emission coming from the phosphor particles. The lifetimes measured with each pulse of radiation can then be matched to a calibration to obtain temperature measurements of a sample. The second method, known as the intensity ratio method, involves taking the ratio of the light intensity of two different spectral bands of the induced phosphorescence. This ratio can again be matched to a calibration curve to determine temperature. The bands selected to be used in this ratio depend on the thermographic phosphor and are strategically selected to provide the most temperature sensitivity over the largest temperature range possible. Previous studies have found that these methods of phosphor thermometry can be used in challenging environments, such as flame spread scenarios [4], turbulent jets [5], and gas turbine combustors [6].

Typically, excitation energy of the incident radiation directed at the thermographic phosphors ranges from the near IR to UV. For example, many thermographic phosphors are excited using the third or fourth harmonics of an Nd:YAG laser, which corresponds to laser light with wavelengths of 355 nm and 266 nm, respectively [3]. However, the focus of this study is to yield thermographic phosphorescence via excitation with X-ray radiation. In general, there are two approaches that can be taken to produce this type of emission from phosphors. The first is to excite thermographic phosphors in a manner described previously except replacing the laser source with an X-ray source. Any induced phosphorescence could then be captured and analyzed to determine if the selected thermographic phosphor remains temperature sensitive during X-ray excitation. The second approach would be to excite other phosphors which are not necessarily thermographic but are known to be sensitive to X-ray radiation. These are commonly called X-ray phosphors or X-ray scintillators and are often used in the medical field for X-ray imaging [7]. These phosphors serve to intensify the image produced by medical imaging devices by producing many photons (hundreds or thousands) within the UV/visible range from a single X-ray photon. The UV/visible photons are responsible for creating the image on a film coated with a silver-halide emulsion. Since these X-ray phosphors produce emission within this range, it is therefore worthwhile to explore whether their emission is temperature dependent in a similar manner to known thermographic phosphors.

There exist several phosphors which bridge both paths described above, being both X-ray scintillators and producing a thermographic response when excited via laser. These include Gd_2O_2S:Tb and $CdWO_4$, which have both been used as X-ray phosphors in the past [7] and have shown thermographic properties during laser excitation. Gd_2O_2S:Tb has been shown to have temporal temperature sensitivity between 593-673 °C [8] and a spectral temperature sensitivity between 573-613 °C [9] when excited via laser. $CdWO_4$ has been shown to have a temporal temperature sensitivity between 573-843 °C when excited by 266 nm laser light [10]. Gd_2O_2S:Tb was selected for study in this paper as it was available on-hand to the authors. Results presented

here show the spectral shift of the induced phosphorescence of this phosphor in a certain temperature range when excited by an X-ray source. Intensity ratio calibrations for this phosphor are also obtained from the spectra. These results are compared to previously published results during excitation of Gd_2O_2S:Tb using UV radiation. Utilizing the temperature-sensitive phosphorescence of these phosphors under X-ray excitation is hoped to allow simultaneous surface temperature measurements and X-ray probing of reacting samples in the future.

2. Methods / Experimental

Gd_2O_2S:Tb phosphors were obtained in the form of premade X-ray scintillator screens. A portion of the screen was cut to size and adhered to a stainless-steel L-bracket using epoxy. A hot plate (Talboys) was used to vary the temperature of this substrate during experiments. The hot plate and substrate were placed in the path of a Comet MXR-451HP/11 X-ray source, operated at maximum output, for excitation. In addition, two plano-convex lenses (Lattice Electro Optics) were placed adjacent to the hot plate to collect the induced emission from the phosphors. Light was collected from a single point on the phosphor sample, collimated between the two plano-convex lenses, and then focused into one end of an optical fiber. This fiber then sent the light to a spectrometer (Ocean Optics). This spectrometer and the corresponding software provided by the manufacturer were used to measure the spectra of the phosphorescence at various temperatures. The temperature of the phosphor sample was monitored by a thermocouple attached to the L-bracket (on the opposite face of the phosphor screen) along with a handheld thermocouple reader (Omega Engineering). Figure 1 shows a schematic of this experimental setup. Note that the spectrometer is not shown here, as it was placed further away from the rest of the setup and shielded with lead to reduce interferences from the X-ray source.

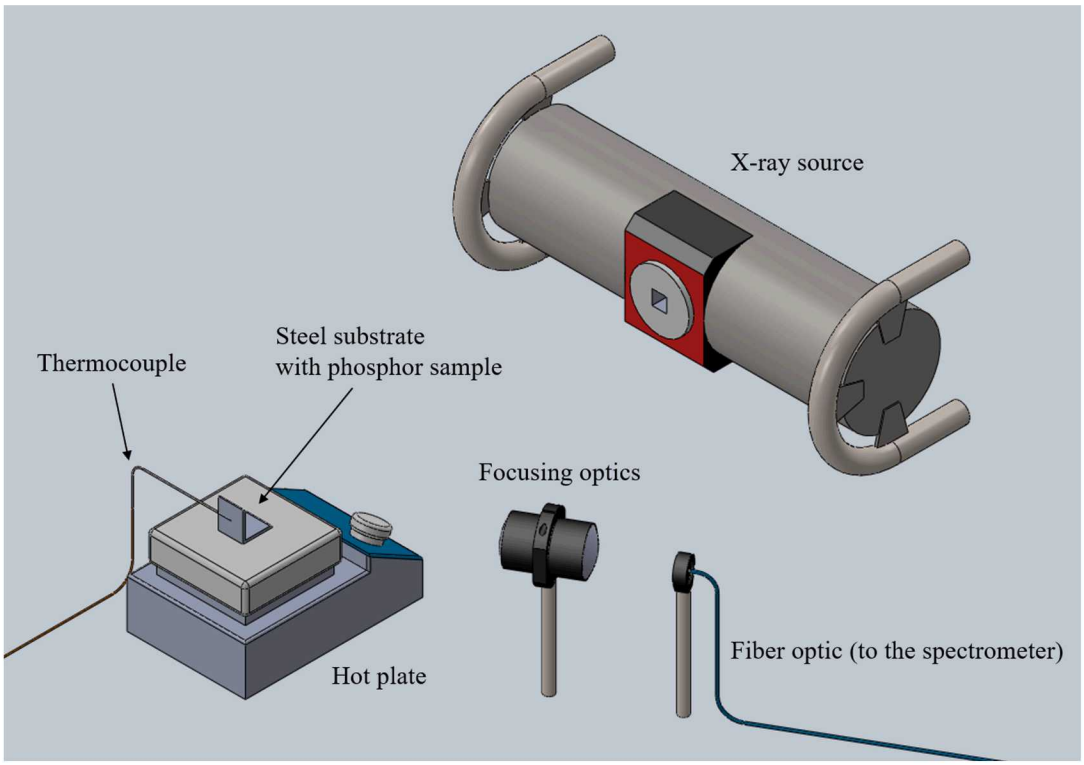

Figure 1. Experimental setup used for X-ray excitation of Gd_2O_2S:Tb phosphors.

The spectrometer used during these experiments needed to be calibrated. The shift in the spectra was corrected using a Hg-Ne pencil style calibration lamp (Newport, model 6034). This lamp was placed in the experimental setup and illuminated the spectrometer. A total of 9 spectra of the lamp's output were captured and averaged in Matlab. The lines observed in this averaged spectrum were then correlated to known spectral lines provided by the lamp's manufacturer. Several of these lines were correlated to the measured spectra. The differences between these correlated lines were calculated. The differences calculated were all very close to one another (within 1 nm), therefore it was assumed that the shift in the spectrum was adequately linear with wavelength. The average was taken between the differences of each correlated line. This linear shift was applied to all measured spectra presented in this paper.

3. Results and Discussion

Gd_2O_2S:Tb Spectral Response with Varying Temperature

Output data files from the Ocean Optics software containing spectral data were analyzed using Matlab. Several spectra were captured at temperatures of 22 °C, 40 °C, 60 °C, and 80 °C. The spectra at each temperature were averaged and plotted together, shown in Figures 2 and 3 below. 15 spectra were averaged for the data at 22 °C; all others are the average of 5 spectra. The background emission was captured at each temperature prior to any excitation of the phosphor sample. These background spectra were used to background subtract the average spectra at each temperature. It is clear from both figures that a shift in the spectral response of the Gd_2O_2S:Tb sample is present as temperature is varied (though this is more clear in Figure 3 which shows some of the peaks in more detail). Curiously, it is apparent that the trend in intensity shift between temperatures is the opposite for some spectral bands. For example, all bands seen in Figure 3 decrease in intensity as temperature increases except for the band between 485 nm and 500 nm, which has the opposite trend. Bands with opposite trends can be exploited for intensity ratio calibrations, as the ratio of bands with opposite trends should produce the most temperature-sensitive ratios.

The results presented here are best compared to those presented by Cates et al. in which they explored the induced emission of Gd_2O_2S:Tb when excited using a UV lamp [9]. The authors of this study show the spectrum of the emission from this phosphor when excited using UV radiation in Figure 9 of their paper (they do not note the temperature at which this spectrum was measured). Similarities can be seen in the UV induced spectrum and the X-ray induced spectra. Peaks are seen at similar spectral bands in each set of results, though the intensities vary between UV excitation and X-ray excitation. For example, the spectral band between 540 nm and 560 nm has a much higher relative intensity compared to peaks at other spectral bands in the X-ray excited spectra when compared to the UV excited spectrum. In general, the trends seen in the relative intensities of the peaks in the X-ray excited spectra do not precisely match the trends seen in the UV excited spectrum. However, the induced emission of the phosphor under X-ray excitation is clearly thermographic such that an intensity ratio calibration can be made using these spectra between the temperatures measured in this study.

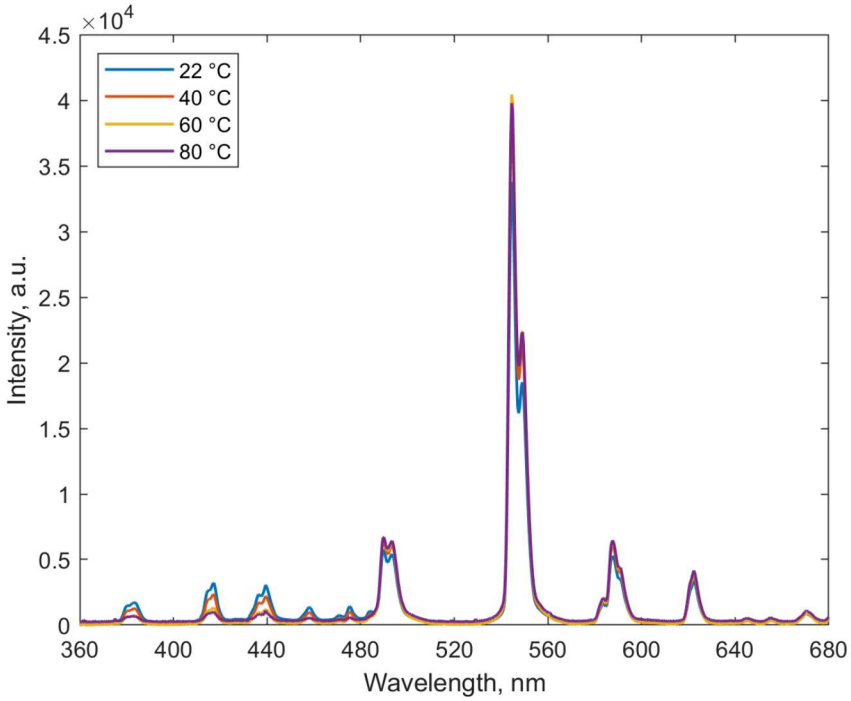

Figure 2. Average spectra of the phosphorescence from the Gd_2O_2S:Tb sample excited by the X-ray source at various temperatures.

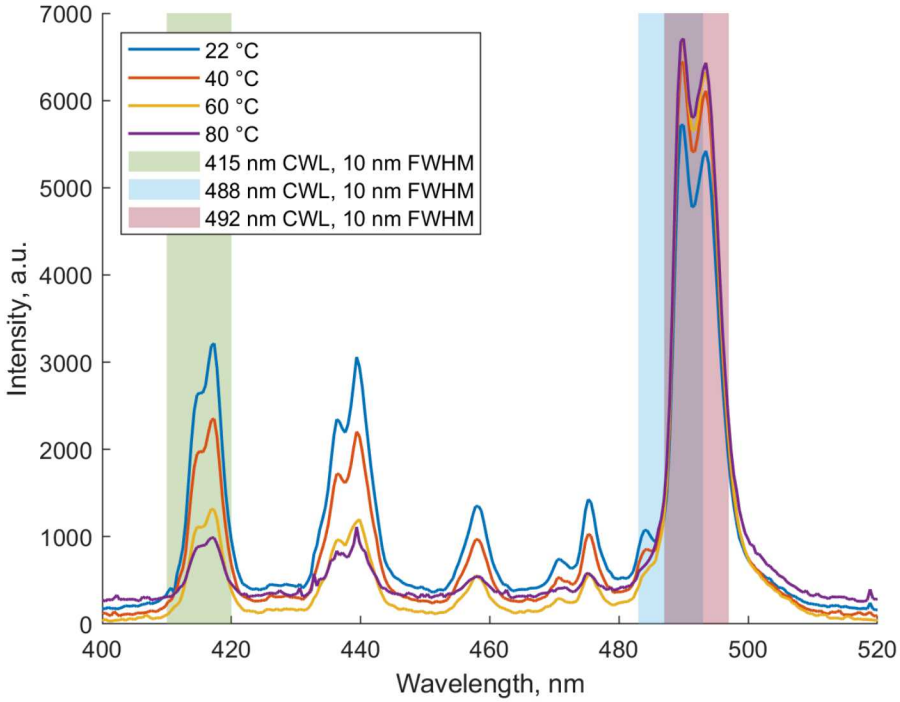

Figure 3. A closer view of some of the peaks seen in the average spectra of the phosphorescence from the Gd_2O_2S:Tb sample excited by the X-ray source at various temperatures. The shaded areas represent the location and width of the bandpass filters simulated to create the intensity ratio calibrations below.

Intensity Ratio Calibration

Two intensity ratio calibrations were found using two different combinations of three narrow wavelength bands found within the spectral data. These bands can be seen in Figure 3 above and are represented by the shaded areas in this plot. They have their center wavelengths (CWL) at 415 nm, 488 nm, and 492 nm, and they all have a full width half maximum (FWHM) of 10 nm. When finding the intensity ratio at each temperature, the average intensity of the 415 nm band was used in the numerator and either of 488 nm band or 492 nm band was used in the denominator. These bands were selected since, as mentioned previously, opposite trends in the intensity at these wavelengths were seen in the spectra as temperature was varied and should therefore provide the highest sensitivity to temperature. These bands also correspond to the 415 nm and 490 nm spectral lines selected by Cates et al. for their intensity ratio calibration, allowing for a more direct comparison to their results [9]. Note that the authors of this study do not specify the exact optical filters used to obtain the signal at these two lines. Therefore, the spectral bands selected here were based on the CWL and FWHM of optical filters readily available from Edmund Optics (stock numbers 65-620, 86-626, and 65-633, which correspond to the bands centered at 415 nm, 488 nm, and 492 nm, respectively). To obtain the calibration curves, the average intensity was calculated in Matlab at each temperature for each of the spectral bands. The ratio was then taken between the average intensities of each spectral band (in the manner described previously) for each temperature. The results found in this study for X-ray excitation of Gd_2O_2S:Tb are plotted along with those for UV excitation from Cates et al. [9] in Figure 4 below. The curve fits between the data points for each data set were found using cubic spline data interpolation in Matlab. Overall, the trends between all the calibrations appear similar, as the ratios all decrease with increasing temperature. The X-ray excitation curves show a higher sensitivity in the intensity ratio to temperature compared to UV excitation, though they all appear to approach a constant intensity ratio as temperature increases past 70 °C. The calibrations between UV and X-ray excitation do appear to be quite different, however, this difference is mostly caused by the differences in the experimental setup used in this study and that used by Cates et al. [9]. Brübach et al. mention that the spectra of the phosphorescence is dependent upon factors such as excitation energy and optical alignment [1]. Therefore, the obvious difference in these boundary conditions between the present study and that performed by Cates et al. [9] produces differing calibration curves. It is important that similar trends are seen here between UV and X-ray excitation.

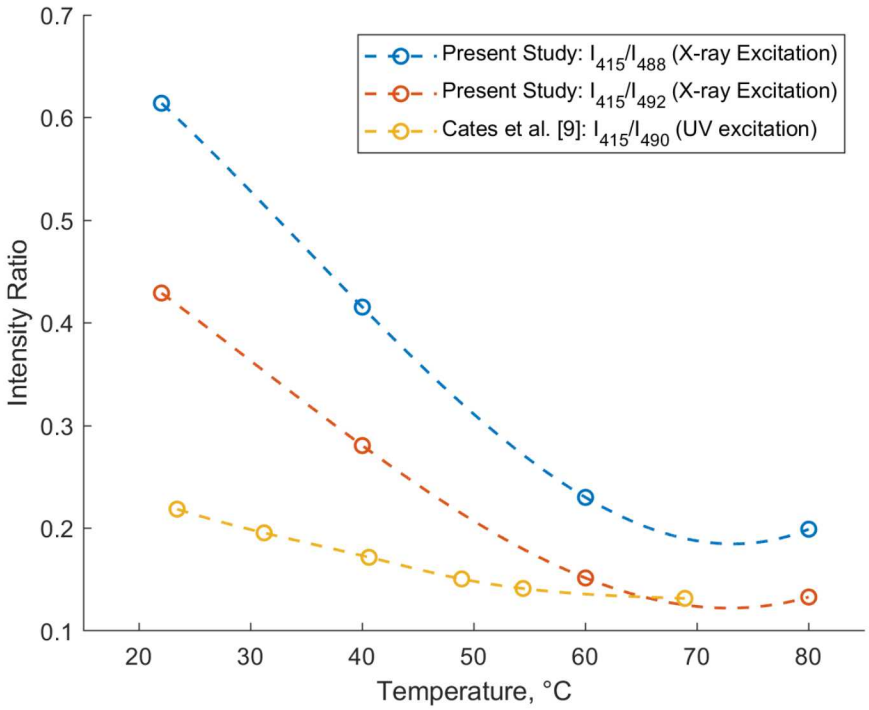

Figure 4. Intensity ratio calibrations for Gd_2O_2S:Tb phosphors using X-ray and UV radiation as the excitation source. UV excitation results are from Cates et al. [9].

4. Conclusions

It has been shown that a known X-ray scintillator with thermographic properties when excited via laser radiation remains thermographic when excited with X-ray radiation. The spectra of the induced emission from Gd_2O_2S:Tb phosphors was measured at various temperatures and was shown to be remain temperature dependent when excited with X-rays. The spectral bands observed in these spectra match the locations of those seen from the induced emission from this phosphor when excited with UV radiation, though the intensities of these bands do not match. Two intensity ratio calibrations were then able to be formed from these measured spectra and show a similar trend to a reported intensity ratio calibration for this phosphor under UV excitation. These results serve as an important first step towards simultaneous X-ray probing and surface temperature measurements using only X-ray radiation for both diagnostic methods and not relying on additional lasers for phosphor thermometry measurements. Future work should explore other thermographic phosphors sensitive at high temperatures to determine if they can provide temperature sensitivity in ranges more applicable to combustion applications during X-ray excitation.

6. References

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