Decay time characteristics of La_2O_2S: Eu and La_2O_2S: Tb for use within an optical sensor for human skin temperature measurement.

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Abstract

This study is focused on the development of a remote temperature sensing technology, i.e. optical laser-based sensor, using thermographic phosphors for medical applications particularly within an electromagnetically hostile MRI (magnetic resonance imaging) environment. A MRI scanner uses a strong magnetic field and radio waves to generate images of the inside of the body. The quality of the image improves with increasing magnetic resonance, however, the drawback of applying a greater magnetic strength is the inducement of heat into the body tissue. Therefore, monitoring the patient's temperature inside MRI is vital but until now, a practical solution for temperature measurement did not exist.This paper shows Europium doped Lanthanum Oxysulphide (La_2O_2S: Eu) and Terbium doped Lanthanum Oxysulphide (La_2O_2S: Tb) are both temperature sensitive to low temperature range of 10-50^oC when under ultraviolet (UV) excitation. The emission spectra and decay time characteristics of these phosphors were demonstrated. The results indicate that La_2O_2S: Eu has a quenching rate of 13.7m$^oC^{-1}$ and 4m $^oC^{-1}$ at 512nm and 538nm, respectively. In addition, La_2O_2S: Tb has a lower quenching rate of 4.19m $^oC^{-1}$ at 548nm due to its faster decay time.

Keywords: phosphors, photoluminescent, decay time, temperature dependence

OCIS codes: 120.0120, 160.5690, 280.6780, 250.5230, 170.3650, 300.2530

Introduction

The growing interest in the field of optical sensors, has highlighted the need for research to develop remote sensor technology with adequate sensing capabilities to meet specific needs. The increased use of this remote temperature sensing technology is mainly due to the immunity of optical signals to electromagnetic interference [1]. Numerous applications take advantage of this attribute within the field of engineering, aerospace and security, as well as medicine. Medical examples include monitoring a patient's body temperature when within a MRI system or when suffering from hyperthermia [2, 3].

In the past few years, a research programme carried out at Nottingham Trent University (NTU, UK) concentrated on the development of a surface thermometry technique for high temperature sensing within a gas turbine[4-6]. The work utilised the most commonly investigated thermographic phosphor, Europium doped Yttrium Oxide (Y_2O_3: Eu) via a technique referred to as Phosphor Thermography (PT) [4, 7].

The concept of phosphor-based optical sensors is to utilise an UV pulsed laser to excite the phosphor on the end of the probe and the resulting fluorescence is monitored. The temperature is subsequently determined by measuring the decrease of fluorescence intensity with time after the laser pulse has ceased, an example of this is illustrated in Figure 1. The initial sharp rise in the emission is due to the dominating excitation pulse. Consequently, the decay time of the phosphorescence can be deduced according to the

single exponential decay relation:

$$I(t) = I_O \exp(-\frac{t}{\tau}) \qquad (1)$$

(where I(t) = intensity at time t, I_0 = initial intensity at time 0 and τ = decay time)[8].

It should be noted that a double exponential decay relationship was also fitted but resulted in a less accurate fit (<90% r^2 factor- the coefficient of determination) with both decay constants being within 5% of each other; a clear indication that the single exponential was accurate (r^2> 99.5%).

This work is aimed at investigating the sensing capabilities of various phosphor materials for use within an optical sensor to detect temperature changes associated with the human body when in electromagnetically harsh environments such as the MRI environment. Hence, the preliminary stage of this research has concentrated on the temperature sensing range around that of the human skin, namely 27-37^{o}C [9, 10]. In this paper, the resulting photoluminescent (PL) properties and decay time measurements of the potential candidate phosphor powders, i.e. La_2O_2S: Eu and La_2O_2S: Tb within the temperature range of 10-50^{o}C are presented.

Experimental Procedures

Two commercially available phosphors La_2O_2S: Eu at the standard dopant concentration of 8 atomic % and La_2O_2S: Tb at 1 atomic % were investigated in this work. Both

phosphors exist in the form of powders. These phosphor powders have been pressed to form a pellet (5mm in diameter and 2mm±1mm in thickness) which can then be held on a test coupon. Five pellets of each phosphor sample were tested. These samples can be placed within a cooled incubator (IPP 200) for conducting PL and decay time measurements at various temperatures. A calibrated T-type thermocouple was attached at the back of the sample and the temperatures over time were displayed and recorded using the Picolog software. The difference of the controlled and measured temperatures was approximately +- 0.1^{o}C throughout the working temperature range.The PL and decay time systems are aligned on an optical table as illustrated in Figure 2.

For decay time measurements, a nitrogen (N_2) pulsed laser (VSL-337ND, $\lambda_{excitation}$ =337nm, <4ns pulse width and a repetition rate of 20Hz at the average excitation power of 6mW) was utilised to excite the phosphor within the incubator. The emitted luminescence was collected by a quartz rod. This is positioned perpendicular to the emitting surface in order to maximise the collection of emitted light, which is subsequently passed through a cut-on filter (wavelength > 380nm) attached to the monochromator (DMC1-03, Optometrics LLC.). Consequently, the monochromator transmitted the fluorescence to a photomultiplier tube (Electrons Tube, 9558QB) that served as a detector. A waveform processing oscilloscope (Gould DSO 4072) displayed,

digitised and stored the data for subsequent analysis. The oscilloscope was set up to average the signals received over a period of about 1 minute in order to enhance the signal-to-noise ratio and this equates to 1200 decay rate signals. For comparison purposes, the decay constant was always calculated from the same time domain (3-5 μs after the 4ns laser excitation pulse) with the standard form of the single exponential equation.

For PL emission spectra, the quartz rod is replaced with an optical fibre which transmits the optical signal to a spectrometer (S2000, Ocean Optics Inc (OOI)) and conveyed to the computer by OOI software.

Results and Discussion

Europium doped Lanthanum Oxysulphide (La_2O_2S: Eu)

Previous work[11] has reported the temperature dependent peaks of La_2O_2S: Eu occur only at 512nm and 538nm. However, over the temperature range of 10-50^{o}C, measurement of the PL spectra of La_2O_2S: Eu acquired at NTU indicate that no spectral shift occurs within this temperature range. Figure 3 shows a typical emission spectrum for La_2O_2S: Eu when excited at 337nm with a nitrogen laser. The results of decay time measurement show temperature dependencies of 512nm and 538nm when excited by a nitrogen laser at 337nm, while the other emission wavelengths are temperature

independent. Temperature dependencies of emission intensity for 512nm (corresponding to the energy levels of $^5D_2$ to $^7F_3$) in La_2O_2S: Eu and also decay times for 538nm (the emission of $^5D_1$ to $^7F_1$ transition) [12] are illustrated in Figure 4. The decay time of a phosphor is observed to decrease with increasing temperature. These transitions that occur between the ^5D levels and charge transfer states (CTS) of La_2O_2S: Eu can be described with the model developed by Fonger and Struck[12]. Their analysis suggested the Eu ^5D_J states quench sequentially (J= 3, 2, 1, 0) with increasing temperature. This is because each ^5D state empties thermally via charge transfer. Hence, an empirical correlation of decay time with temperature can provide the basis for a temperature measurement. A simple model proposed by Simons et al. [13] is used to deduce the fluorescence decay time of a phosphor with varying temperature. The relevant expression is:

$$\tau_d = \tau_q \exp\left(-Q(T - T_Q\right) \qquad (2)$$

By definition, the decay time (τ_d) is related to the component temperature (T) above the quenching point (T_Q), where τ_q is the decay time at the quenching point. The quenching rate Q is defined as the temperature change required for the decay time to decrease exponentially and is therefore a measure of the temperature sensitivity of the phosphor – the measurement sensitivity improves with increasing quenching rate. Each pellet

sample showed consistency of decay constant measurement. The decay time characteristics of 512nm from 10-50^{o}C as illustrated in Figure 4, indicating a quenching rate of 13.7m $^{o}C^{-1}$ with its fast decay time of 4.97-1.91μs. Hence demonstrating that La_2O_2S: Eu is a highly temperature-sensitive phosphor to be used within the desired optical sensor. In addition, the decay time of La_2O_2S: Eu at 538nm peak decreases consistently with a decay time of 38.8-29μs and has a quenching rate of 4m $^{o}C^{-1}$.

Terbium doped Lanthanum Oxysulphide (La_2O_2S: Tb)

The PL spectra of La_2O_2S: Tb excited by a nitrogen laser (337nm) are shown in

Figure 5, which exhibit multiple peaks. La_2O_2S: Tb appears as a green emitting phosphor since the host is doped with Terbium and its dominant peak is centred at 544nm. Again, no spectral line shifts occur with varying temperatures for this PL measurement.

Although very little work has been reported to determine the temperature sensing capabilities of La_2O_2S: Tb, the results obtained in this work have suggested that the decay times of this phosphor are strongly dependent upon its temperature, as indicated in Figure 6. Of more importance, the temperature dependent characteristics occur at most of the emission intensities in La_2O_2S: Tb, i.e. $^{5}D_4$ to $^{7}F_J$ transitions [14] compared to only two emission lines of La_2O_2S: Eu. According to Struck and Fonger, again similar

to La_2O_2S: Eu, the thermal quenchings of Tb in La_2O_2S are attributed to the CTS crossover relaxation to Frank-Condon shifted states.

The decay times and the quenching rates of La_2O_2S: Tb are tabulated in Table1, the results clearly show that 548nm peak is more sensitive to temperature variation due to its higher quenching rate, relating this to equation (2), the measurement sensitivity improves with increasing quenching rate.

Conclusions

The results presented in this work indicate that both of the proposed thermographic phosphors, La_2O_2S: Eu and La_2O_2S: Tb could be ideal candidates to meet the requirements of a desired optical sensor subject to their sensing capabilities within the narrow temperature range of interest, 10 – 50^oC. However, it is essential to adopt a robust temperature sensing technique, i.e. decay time characterisation which is independent of excitation source and ambient light allowing a greater accuracy and a better repeatability to be achieved.

This research is particularly interested in the temperature dependent peak 512nm of La_2O_2S: Eu due to its impressive quenching rate of 13.7m$^oC^{-1}$ suggesting this phosphor is highly sensitive to temperature variations. The results obtained at NTU agree with those derived from illustrated data within the publication by L.M. Coyle et al.[15]: the 514nm emission line of La_2O_2S: Eu has the quenching rate of 13.7m$^oC^{-1}$ under 337nm excitation. Alaa Omrane et al.[16] demonstrated the decay times of La_2O_2S: Eu over 30-150^oC, the quenching rate measured from the graph is 15.9m$^oC^{-1}$ at 512nm line with 355nm excitation. Their results have shown a slight improvement in the quenching rate and this may due to the fine-tuned excitation wavelength. Nonetheless, the fast decay times of La_2O_2S: Tb with relatively low quenching rates of 2.28 - 4.19m$^oC^{-1}$ at various emission wavelengths are evidently indicating it could be suitable for used in

temperature measurements. To date, no relevant data for La_2O_2S: Tb has yet been reported in the public domain. We are presently analysing various dopant concentrations of La_2O_2S: Eu and La_2O_2S: Tb attributed to their temperature dependencies. These results plus more in depth studies of the dopant concentration quenchings and temperature dependencies cited above will be subsequently reported. In addition, the design of an optical sensor will be followed and further investigations will be carried out within an MRI scanner in order to overcome the complexities of non-invasive temperature measurement such as determining the thermal conductivity between the bonding of the phosphor and human skin as well as an investigation into the potential problem associated with the Zeeman splitting. The average MRI scanner utilises a magnetic field strength of $\leq$1.5 Tesla, and hence should not be problematic for such a sensor.

Acknowledgement

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Figure Captions

Figure 1: Example of single exponential decay profiles of La_2O_2S: Eu at various temperatures under 337nm excitation. The inset graph indicates a single exponential decay fitting with an accuracy of >99.9%.

Figure 2: Set up for photoluminescent and decay time experiment.

Figure 3: A typical emission spectrum for La_2O_2S: Eu excited by a nitrogen laser at room temperature.

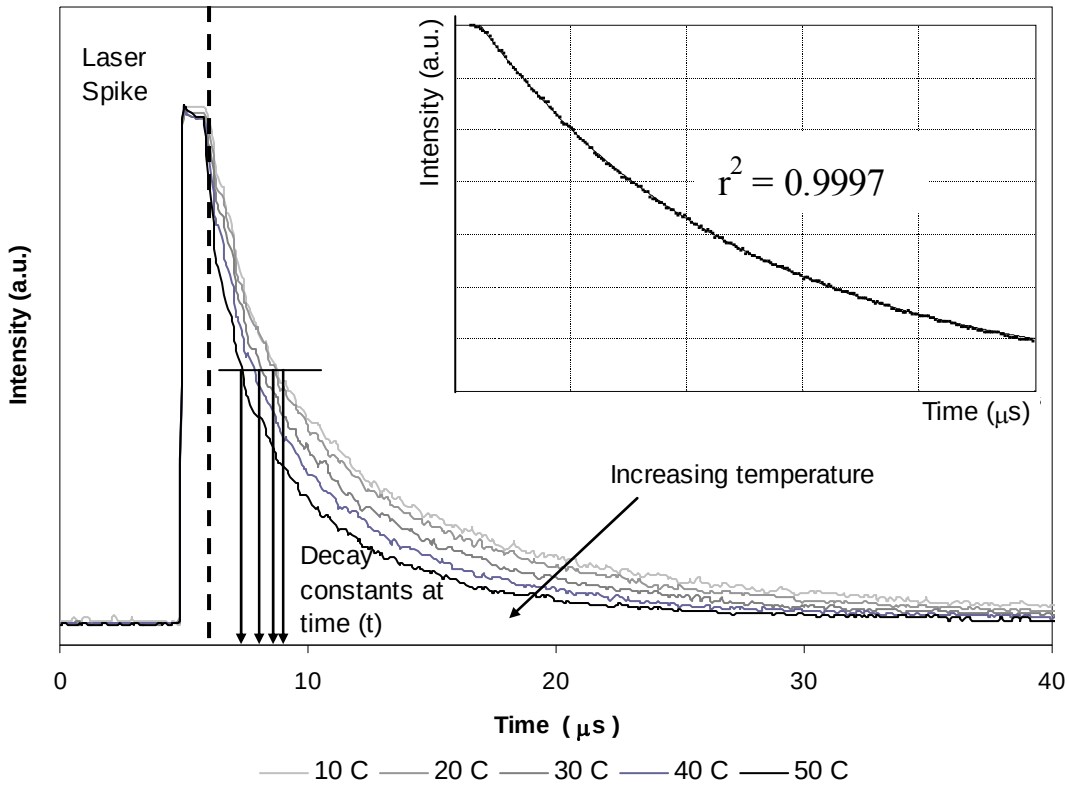
Figure 4: Decay time characteristics of La_2O_2S: Eu at 512nm and 538nm under 337nm excitation.

Figure 5: A typical emission spectrum for La_2O_2S: Tb excited by a nitrogen laser (337nm) at room temperatures.

Figure 6: Decay constant against temperature for different emission wavelengths of La_2O_2S: Tb.

Table Caption

Table 1: Decay time of La_2O_2S: Tb under 337nm excitation.



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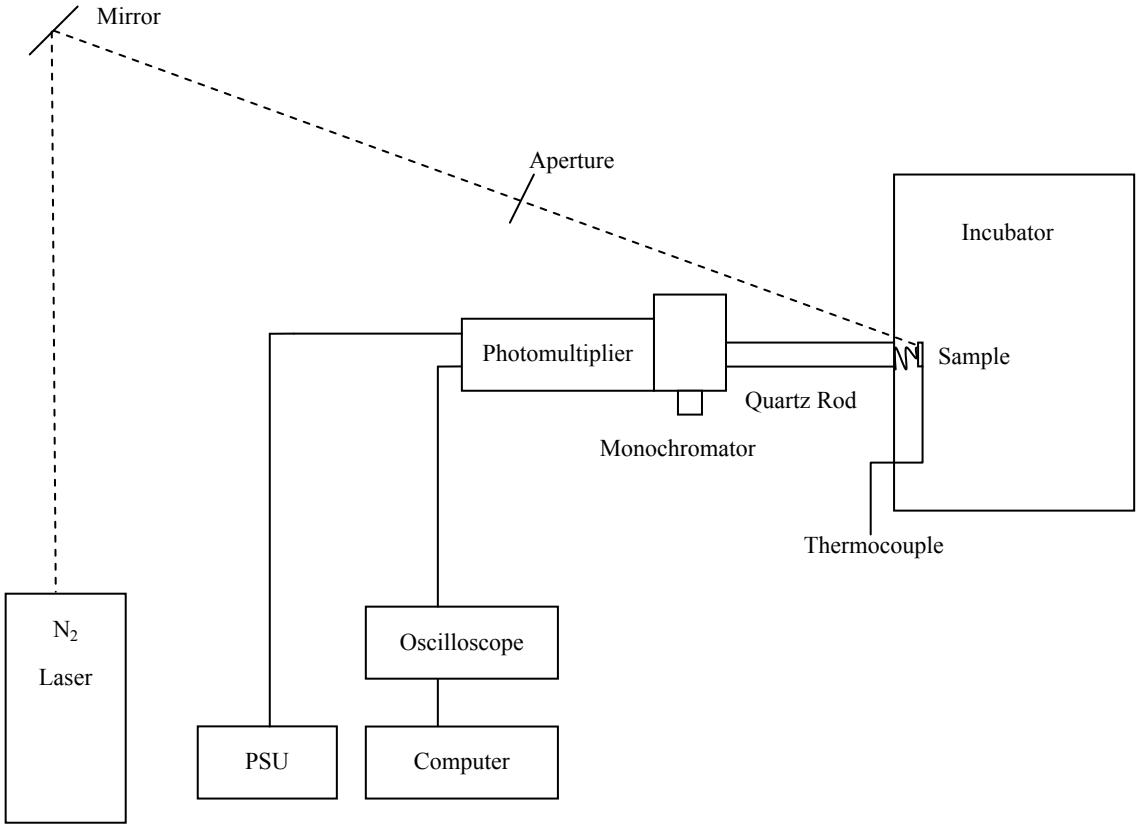

Figure 2: Set up for photoluminescent and decay time experiment.

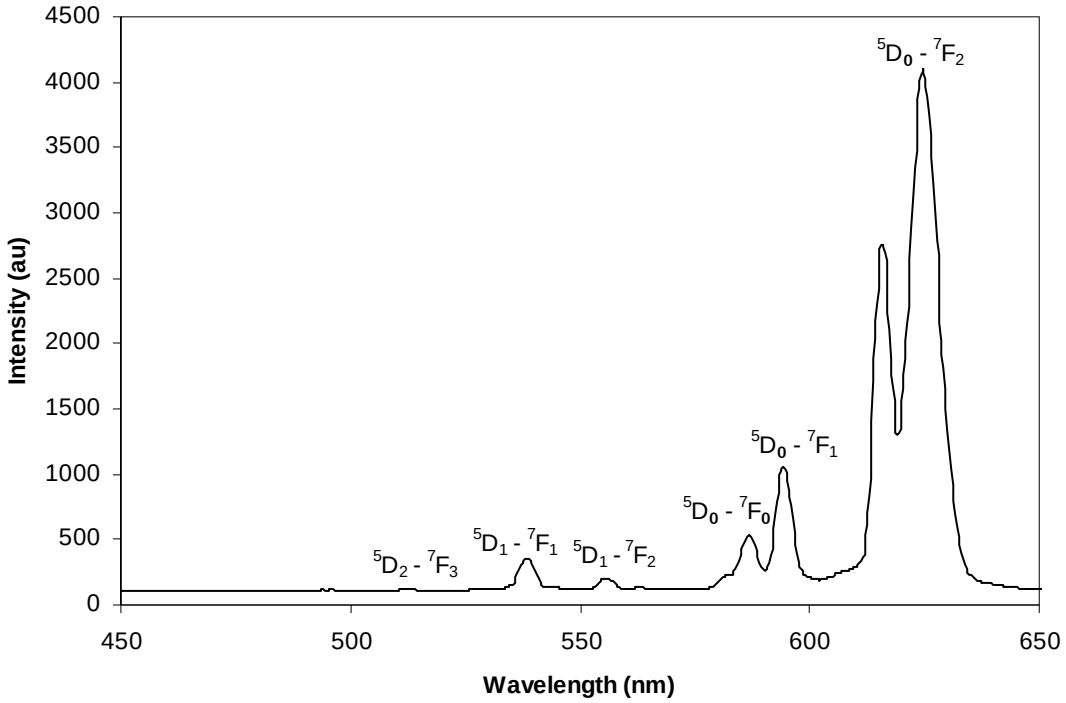

Figure 3: A typical emission spectrum for La_2O_2S: Eu excited by a nitrogen laser at room temperature.

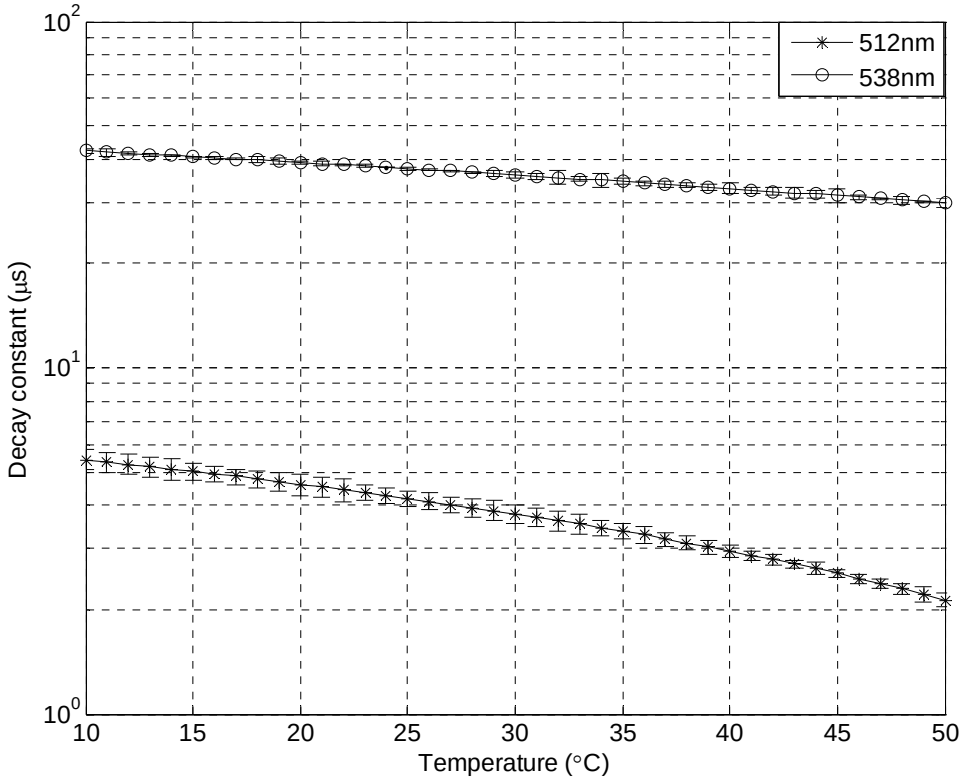

Figure 4: Decay time characteristics of La_2O_2S: Eu at 512nm and 538nm under 337nm excitation.

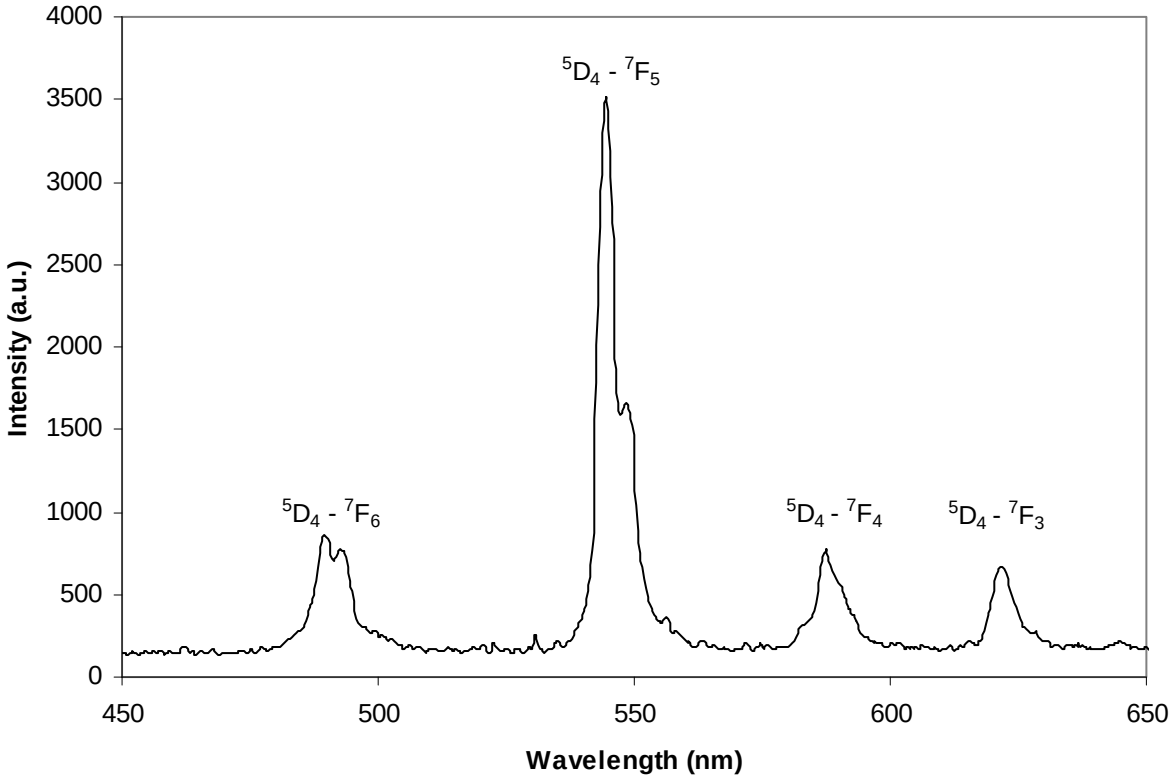

Figure 5: A typical emission spectrum for La_2O_2S: Tb excited by a nitrogen laser (337nm) at room temperatures.

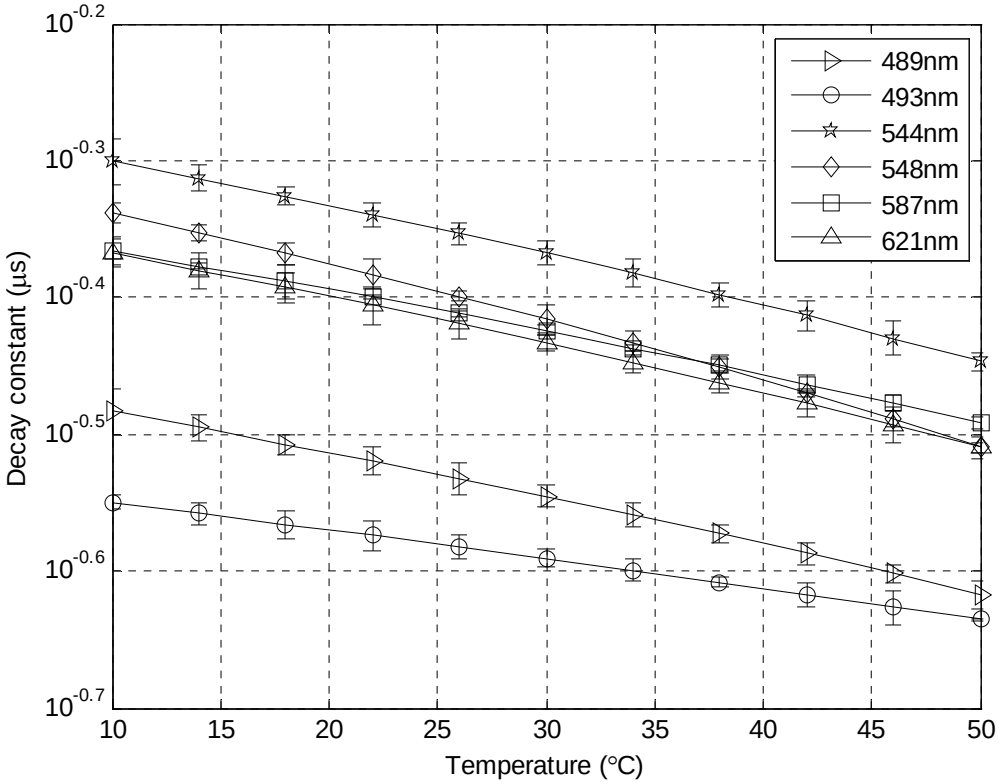

Figure 6: Decay constant against temperature for different emission wavelengths of La_2O_2S: Tb.

Table 1: Decay time of La_2O_2S: Tb under 337nm excitation.

Emission Wavelength (nm)	Decay times (μs) (10- 50°C)	Quenching rate (m^oC^{-1})
489	0.39 - 0.25	3.40
493	0.39 - 0.23	2.28
544	0.48 - 0.37	2.94
548	0.47 - 0.32	4.19
587	0.36 - 0.28	2.61
621	0.42 - 0.37	3.33