An advanced lifetime measurement method by square wave excitation and lock-in amplifier

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Abstract. Achieving the radiation decay rate with high accuracy is crucial for all light emitters and absorbers. Therefore, a wide variety of measurement approaches have been developed for the measurement of radiation decay rate. Herein, we introduce a method to measure the decay rate with a common photoluminescence intensity setup without any modification. The square wave created by simply turning the output of the laser on and off is used as the excitation waveform, and a lock-in amplifier is used to gather the detected signal, making it a cost-effective way. Moreover, the constructed method can be used in a wide range of frequencies, detection voltages, and lifetimes. Finally, we applied the derived method to measure the photoluminescence lifetime of the first excited state of erbium ions in upconverting erbium-ytterbium silicate samples.

1. Introduction

An excited sample emits photons with a decay time, which is called photoluminescence lifetime. A precise knowledge of the lifetime is crucial for all light emitters (i.e., lasers, LEDs) and absorbers (i.e., solar cells, photodetectors) to investigate photophysical or photochemical processes occurred in the material. Therefore, numerous lifetime measurement techniques are developed, and these techniques can be divided into two main groups: time domain methods and frequency domain methods. In time domain methods, the sample is illuminated with a train of light pulses, and emission is detected with a time-resolved spectrometer. The decay time is determined from the slope of the natural logarithm of the intensity (Figure 1.a). On the other hand, frequency domain methods do not need transient excitation and time-resolved detection. In frequency domain methods, the sample is excited generally with a sine wave-modulated-light. The sample emits light at the same frequency and with a delay that depends on the lifetime of the sample. The decay time is calculated from the delay measured as a phase shift ($\phi$) between excitation and emission (Figure 1.b). Time domain methods require relatively expensive and complex equipment as well as an exponential decay fitting process limiting the use of these methods in real-time applications, in which results can be obtained at the time of measurement [1], [2]. On the other hand, the utilization of a basic function instead of curve fitting in frequency domain methods makes these methods favourable in real-time applications, e.g., observation of transient nature of flowing cells.
Therefore, frequency domain methods that allow measurements of the order of nanosecond or faster lifetimes are preferred in real-time applications [4]–[6]. Indeed, comparative studies between time and frequency domain methods have shown that they perform equally in terms of accuracy [7]–[9]. Additionally, the frequency domain methods allow measurement of the lifetime of samples with very low emission intensities since a lock-in amplifier can be employed. Lock-in amplifiers are more favourable than oscilloscopes and data acquisition cards, commonly used in time-resolved spectroscopy, due to high noise tolerance levels and very low voltage thresholds. The lock-in amplifier used in this work is the SR830 from Stanford Research Systems, Inc. (Sunnyvale, CA, USA) that can tolerate noise up to 100 dB and can detect a minimum voltage of 2nV whereas the minimum vertical sensitivity of a typical oscilloscope is around 2mV [10], [11].

Philip and Carlsson [9] theoretically investigated signal-to-noise performances of different frequency domain lifetime measurement methods. They demonstrated that sine as an excitation waveform is not optimal and that the use of square wave reduces the errors caused by scattered light, confirmed by other recent studies [7], [8]. However, the detected signal was processed by taking its Fourier transform to decompose the signal into its sine constituents in studies using square wave excitation [1], [3], [7] which is a time consuming process and limits the real-time usability of the method. Whereas a real-time lifetime measurement method for square-wave excitation exists in the time domain and it allows rapid lifetime determination, there are no methods in the frequency domain, to our knowledge. Although Harms et al. [12] obtained lifetime under square wave excitation by a lock-in amplifier, the excitation can be considered as sine wave since the excitation frequency was kept high to prevent the detection of harmonics by the lock-in amplifier.

We extracted a relation between the quarter-phase shift output (called as Y-output) of the lock-in amplifier and the lifetime of a sample excited by a square wave; thus, we have paved the way the usage of square wave in frequency domain real-time applications. The lifetime measurements were performed with the same setup used to obtain the photoluminescence measurements, consisting of a laser, a monochromator, a photodiode, and a lock-in amplifier. Samples used in this study are fabricated by magnetron co-sputtering technique and using the procedure [13].

2. Theory

When a sample is illuminated by a light pulse at $t=0$, the excited population exponentially decays to the ground state. This exponential decay is described as follows:

$$I(t) = I_0 * e^{-\frac{t}{\tau}}, \quad t > 0$$

where $t$ is the time, $I_0$ is the initial intensity, and $\tau$ is the lifetime of the sample. Because the excitation-emission mechanism behaves as a linear and time-invariant system in the absence of saturation and photobleaching, it can be characterized by its impulse response or its transfer function [14]. As it is well known from system theory, the convolution of the impulse response and input function
is equal to the output of the system. When the input is a square wave, the system's response becomes a piecewise function as follows:

\[
\text{Exc. Sig}(t) \otimes I(t) = \begin{cases} 
I_0 \left(1 - e^{-\frac{t}{\tau}}\right), & 0 \leq t \leq \frac{T}{2} \\
I_0 \left(e^{\frac{T}{2\tau}} - 1\right) e^{-\frac{t}{\tau}}, & \frac{T}{2} \leq t \leq T
\end{cases}
\] (2)

where \(T\) is the period of the excitation signal. This function is calculated assuming that the rising and decaying lifetimes are equal. Although they are inherently different, we provided the values of \(C_{up}\) and \(\phi\) at which this assumption is valid in Figure 2. Thus, theoretical (Figure 2a) and experimental (Figure 4a) results demonstrate that the assuming the rising and decaying lifetimes equal is feasible for a relatively wide range of \(C_{up}\) and \(\phi\). The rate equation for the first excited level of an upconverter sample can be described as [15]:

\[
\frac{dN_1}{dt} = \sigma \Phi (N_{Er} - N_1) - \frac{N_1}{\tau_1} - C_{up} N_1^2
\] (3)

where \(N_1\) is the population of the first level (in cm\(^{-3}\)), \(\sigma\) is the absorption cross-section (in cm\(^2\)), \(\Phi\) is the pump photon flux (in cm\(^2\)s\(^{-1}\)), \(N_{Er}\) is the number of erbium ions, \(\tau_1\) is the lifetime of the first excited state (in s) and \(C_{up}\) is the upconversion coefficient (in cm\(^3\)s\(^{-1}\)). The solution of the differential equation is more complex than the solution of the conventional emission function, i.e., the exponentially decaying function. Therefore, we solved the equation numerically (i.e., modelled for various values of \(C_{up}\) and \(\Phi\) in a practical range [15]) to investigate the upconversion coefficient and photon flux dependence of emission waveform. Figure 2.a shows \(R^2\) values found by comparing the rising and decaying parts of the emission waveform for various upconversion coefficients and photon flux intensities. \(R^2\)=1 suggests that the rise and fall times are identical, indicating that Equation 2 is valid. To better exhibit the dependency, some examples of emission waveforms are given in Figure 2.b and c. In addition to the system response, we mathematically modelled the output of the lock-in amplifier shown schematically in Figure 3 to complete the relation between the lifetime and the output.

![Figure 2](image_url)

**Figure 2.** (a) \(R^2\) values of rise-time and fall-time of photoluminescence emission depending on upconversion coefficient and photon flux, (b) The photoluminescence intensity dependency on upconversion coefficient at \(\Phi = 3 \times 10^{21}\), and (c) The photoluminescence intensity dependency on photon flux intensity at \(C_{up} = 1 \times 10^{-18}\).
The mathematical model of the Y output is:

\[ Y = \text{mean}(\text{wave} \ast \cos(wt + \theta_{\text{ref}})) \]  

where wave is the output signal of the detector, w is the modulation frequency of the excitation light and it is referenced to the lock-in amplifier, \( \theta_{\text{ref}} \) is the phase shift that can be introduced to the amplifier. The output of the low pass filter (Y output) is equal to the offset of the input signal. Therefore, the output can be found by integrating the product of the reference signal with the same frequency as the excitation signal and the piecewise function over one period. If we equalize the Y output of the lock-in amplifier to zero, the relation between lifetime and angle is derived as follows:

\[
Y = C_0 \left[ \int_0^{T/2} \left( 1 - e^{-t/\tau} \right) \cos(wt + \theta_{\text{ref}}) \, dt + \int_{T/2}^T \left( e^{-T/2\tau} - 1 \right) e^{-t/\tau} \cos(wt + \theta_{\text{ref}}) \, dt \right] = 0
\]  

The following relation can be obtained:

\[
\tan(\theta_{\text{ref}}) = \frac{-Btw}{2 + (\tau w)^2 + (2 - B)}
\]

\[
B = 2 - e^{-T/\tau} + e^{-T/2\tau}
\]

To sum up, first, the reference phase shift is adjusted until the output is zero. Then, the lifetime is found by using Equations 6 and 7.

**Figure 3.** Block diagram of the lock-in amplifier. The incoming signal with a phase shift (\( \theta_{\text{sig}} \)) is multiplied by the reference signal with the same frequency. The out is passed through a low pass filter.

3. Results

Here, the method described in detail in the previous section was used to measure photoluminescence lifetimes of erbium-ytterbium silicate samples with the highest obtained detected voltage as small as 6 \( \mu \)V_{rms}, which was smaller than the noise level of the detector. As mentioned earlier, our method was developed under the assumption of equal rising and decaying lifetimes, and they equalize at low upconversion emissions and low pump powers. However, increasing pump power enhances the signal-to-noise ratio, as demonstrated in Figure 4.b. The consequence of high pump power is inequality in rising and decaying lifetimes, as seen in Equation 3 and Figure 2. To determine the difference, we first measured the lifetime of the sample with the highest upconversion at high pump power. Later, its lifetime was also measured at low power. The difference between the lifetimes was 0.03 ms, which is much smaller than the measured lifetimes (i.e., 0.03ms << 2-3 ms), as seen in Table 1, and this small difference (0.03 ms) allows to use the suggested method at relatively high power. Moreover, the validity of our assumption is supported by Figure 4.a that shows no phase shift in Y-out with different pump powers. The assumption of equal rise and fall time is valid in our experiments as there is no phase difference with applied pump power. Table 1 shows the lifetime of the samples at the first excited state of erbium ions (corresponds to a wavelength of around 1540 nm). The lifetimes of the samples followed a trend where the increased concentration of ytterbium reduced the rate of energy transfer in the first excited state, thereby reducing non-radiative decay paths. Therefore, the lifetimes of erbium-ytterbium silicate samples increase with the ytterbium concentration.
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Figure 4. (a) The variation of the Y-out as a function of phase shift with different pump powers. An offset is applied to data points of different excitation laser powers for clarity. (b) Excitation power dependence of signal-to-noise ratio.

Table 1. The lifetime of the erbium-ytterbium silicate (Er$_x$Yb$_{2-x}$Si$_2$O$_7$) samples at the first excited state for various stoichiometry.

| x   | Lifetime (ms) |
|-----|---------------|
| 0.56| 3.1           |
| 0.75| 2.93          |
| 0.92| 2.75          |
| 0.96| 2.65          |
| 1.12| 2.50          |

4. Conclusions
A real-time, frequency domain measurement technique was constructed for fast (i.e., lifetime of a sample can be observed in a time corresponding to almost an excitation signal period), precise, and cost-effective detection of lifetime. The technique combined square wave excitation and a lock-in amplifier to measure lifetime under a constraint (equal rise and decaying lifetimes). The validity of the technique was discussed by demonstrating the dependence of the equality for different pump power and upconversion coefficient ranges. The main advantage of this method is that no equipment other than a lock-in amplifier, which is essential for photoluminescence spectroscopy, is required. The required emission intensity is minimized owing to very low detection voltage (2nV in this study) of lock-in amplifiers. Moreover, the constructed method does not introduce limitations on frequency, detection voltage, or lifetime. Finally, we measured lifetimes of upconverting erbium-ytterbium silicate samples.

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