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**Development and Investigation of an Automated
Temperature Calibration for Thermographic Phosphors**

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MASTER OF SCIENCE THESIS

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Abstract

This thesis achieves a semi-automatic temperature calibration for thermographic phosphors. Thermocouple temperature information and phosphorescence decay curves are recorded synchronized and continuously while the oven temperature is ramped across the entire temperature range. A LabVIEW interface was developed in this context and applied to calibrate two phosphors, CdWO_4 and $\text{Mg}_4\text{FGeO}_6\text{:Mn}$. These two thermographic phosphors have different temperature sensitive ranges, 294 K to 573 K for CdWO_4 phosphor, and 294 K to 973 K for $\text{Mg}_4\text{FGeO}_6\text{:Mn}$ phosphor. The *conventional* and *automatic calibrations* of CdWO_4 have been performed using the same experimental setup. Though in this thesis work only on *automatic calibration* of $\text{Mg}_4\text{FGeO}_6\text{:Mn}$ has been done, the *conventional calibration* presented in the article[1] was done under similar experimental condition. The automated results were compared to conventional calibrations showed no major difference neither for CdWO_4 nor $\text{Mg}_4\text{FGeO}_6\text{:Mn}$. Additionally, this thesis studies some factors which may affect the accuracy of CdWO_4 phosphor *automatic calibration* result. These factors include the relation between the phosphor response speed and thermocouple response speed, long exposure time for phosphor in high temperature environment, and laser induced heating effects. None of these factors showed a significant impact upon the obtained results within the area of investigation.

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1. Introduction

Temperature measurements are very important in combustion environment. Some combustion reactions are temperature-dependent, combustion processes release heat, and temperature affects radiation such as chemiluminescence, Planck radiation. Laser induced phosphorescence (LIP) is a technique which uses thermographic phosphors, such as CdWO_4 , $\text{Mg}_4\text{FGeO}_6:\text{Mn}$, and $\text{La}_2\text{O}_2\text{S}:\text{Eu}$. LIP technique is not only used for remote measurements of surface temperature, but also has a potential for sprays and even gas flow diagnostics[2, 3].The intensity of phosphorescence exponentially decays in time. The time of the phosphorescence intensity decay to $1/e$ of the initial emission intensity is referred to phosphorescence lifetime. Since the phosphorescence lifetime is temperature dependent, LIP technique can be a versatile alternative to thermocouples. In order to using a thermographic phosphor to determine temperature, a calibration of the phosphorescence lifetime as a function of temperature is necessary. Calibration can be done by heating an oven to a set of temperatures. Each time when the temperature reaches thermal equilibrium, phosphorescence decay curves are recorded and then evaluated to obtain the phosphorescence lifetime. This process is henceforth called *conventional calibration*, which takes long time and leaves temperature gaps depending on the chosen temperature step size. A faster and more precise calibration process can be achieved by introducing a LabVIEW interface. Using this approach, temperature information and phosphorescence decay curves are synchronized and recorded continuously while the oven temperature is ramped across the whole temperature range. This process will further be referred to as *automatic calibration*.

2. Theoretical Background

This chapter presents basic physical concepts in this thesis. Laser induced phosphorescence theory, principles of thermographic cadmium tungstate (CdWO_4) and $\text{Mg}_4\text{FGeO}_6:\text{Mn}$ phosphors which are utilized in this thesis.

2.1 Laser Induced Phosphorescence (LIP)

Accurate temperature measurements are very important for combustion researches and industrial applications such as in car engines or aircraft turbines. There are a lot of different approaches for temperature measurements, such as thermocouples, thermistors, and pyrometers. The advantage of laser induced phosphorescence temperature measurement is that temperatures can be obtained contact-free and with high precision for a wide range of temperatures up to 2000 K[4]. Thermographic phosphors can either be applied on top of surfaces by using, for example binding agents or seeded into liquids or gas flows.

Many thermographic phosphors are inorganic powders doped with rare earth ions such as $\text{Mg}_4\text{FGeO}_6:\text{Mn}$. They can emit radiation in the visible wavelength region, phosphorescence, for some time (typical μs -ms) after being excited by UV or near UV light (e.g from a laser). The principle of laser induced phosphorescence (LIP) is shown in figure 1. Molecules of the substance get excited from the ground state and then relax to lower vibrational states. Then the excited molecule undergoes intersystem crossing from an excited singlet state into a triplet state without radiation or phosphorescence progress, see figure 1. Theoretically, transition from triplet state to the ground state is forbidden which results into the characteristically prolonged lifetimes of phosphorescence which generally are much longer than 10^{-8}s [5].

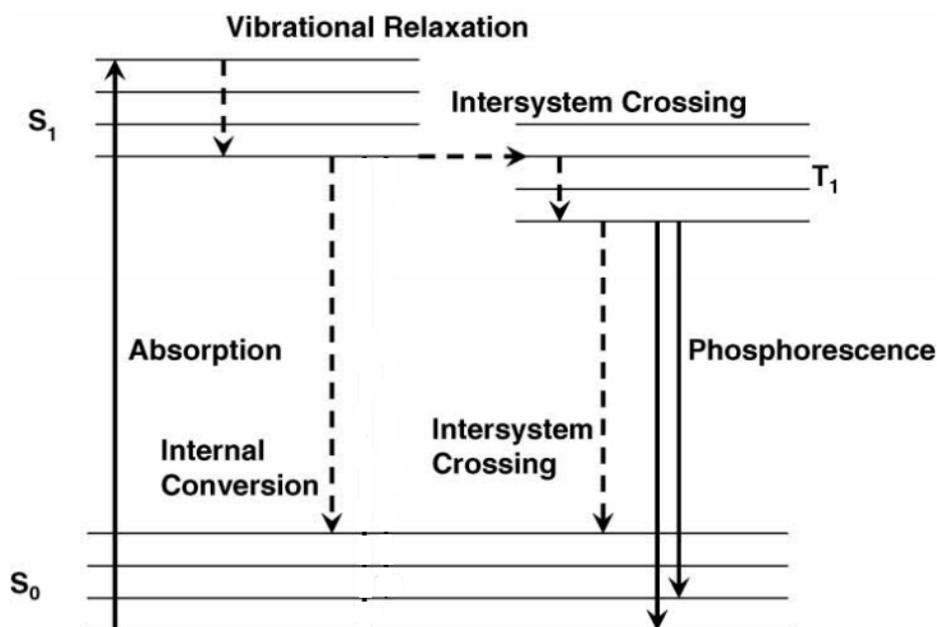


FIG.1: Partial energy level diagram for a photo luminescent molecule[6].

There are two common ways of using Laser induced phosphorescence (LIP). One method utilizes the phosphorescence lifetime decreases with temperature, the other one relies on the spectral shape of thermographic phosphorescence changing as function of temperature. In this thesis work, phosphorescence lifetime method is utilized. The emitted phosphorescence radiation decays exponentially in time. The extended afterglow of thermographic phosphorescence can in many cases be approximated by a single exponential decay:

$$I = I_0 \cdot e^{-\frac{t}{\tau}}$$

Where I_0 denotes the initial phosphorescence intensity, and τ is the phosphorescence lifetime.

2.2 Thermographic Phosphors

Thermographic phosphors are usually coated on a target surface. When they reach thermal equilibrium with the surface, they can be used to determine the surface temperature by using a calibration measurement that is performed under well controlled conditions.

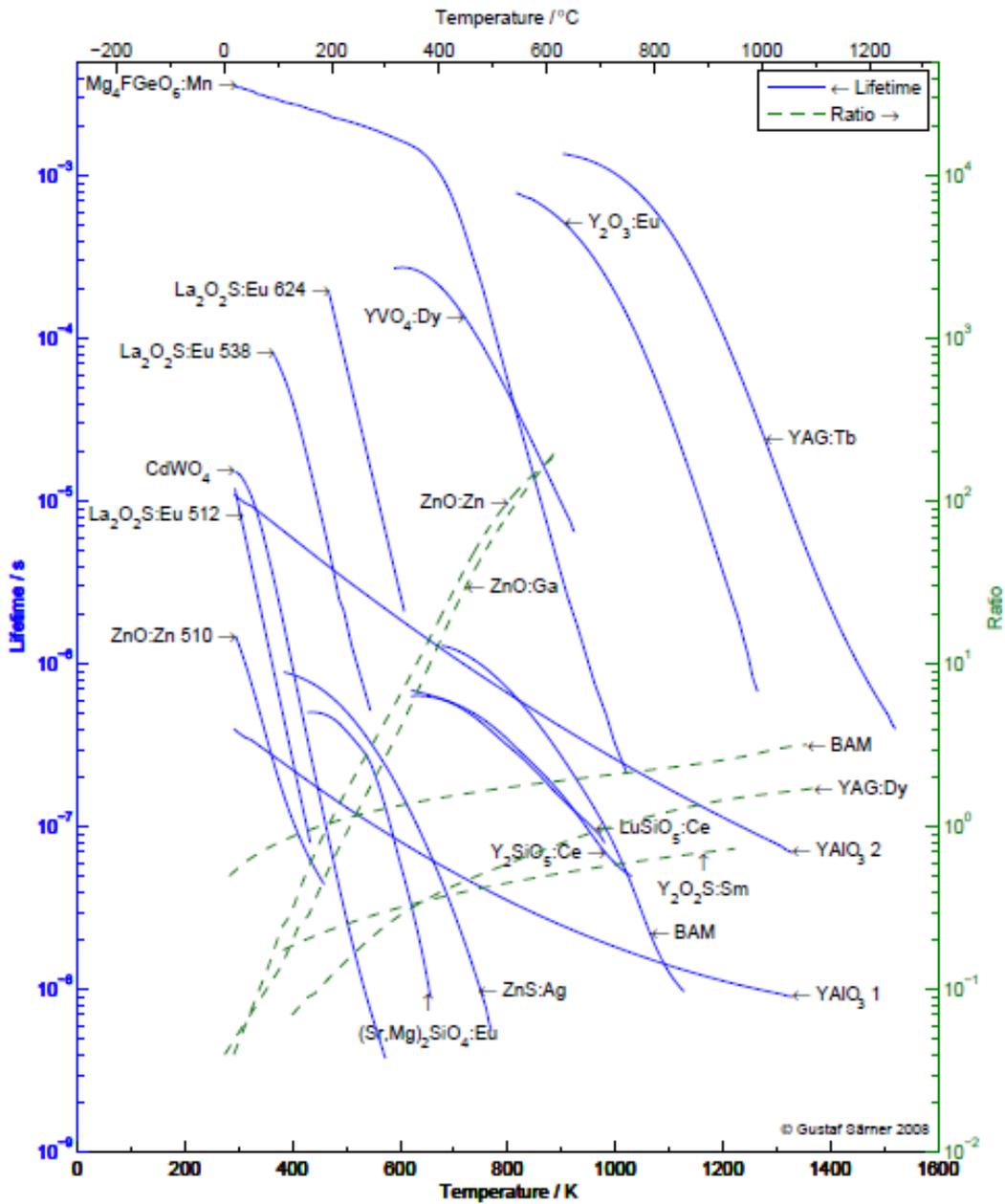


FIG.2: Temperature sensitivity ranges for different phosphors. The blue scale presents the decay-time dependence, whereas the green scale shows the intensity ratio of two phosphorescence wavelengths changing as a function of temperature[7].

2.2.1 CdWO₄

Cadmium tungstate (CdWO₄) has some advantages to using as a thermographic phosphor, such as chemical stability in radiation process, high absorption coefficient, and high radiation light yield[8]. It also has sufficiently short phosphorescence decay time, which is very useful for combustion environment where temperatures change very fast[9]. It absorbs light in a wide spectral region from 230 nm to 700 nm, see figure 3. Its phosphorescence emission is broadband and spans from 380 nm to

660 nm with a peak at about 480 nm, as shown in figure 4 with 298 nm excitation wavelength[10].

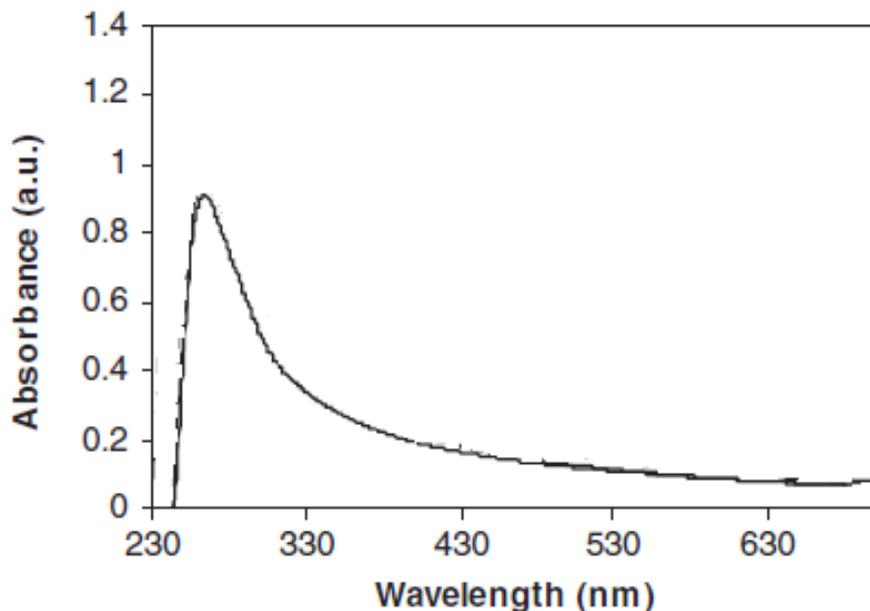


FIG.3:Absorption spectrum of CdWO₄ Phosphor[11].

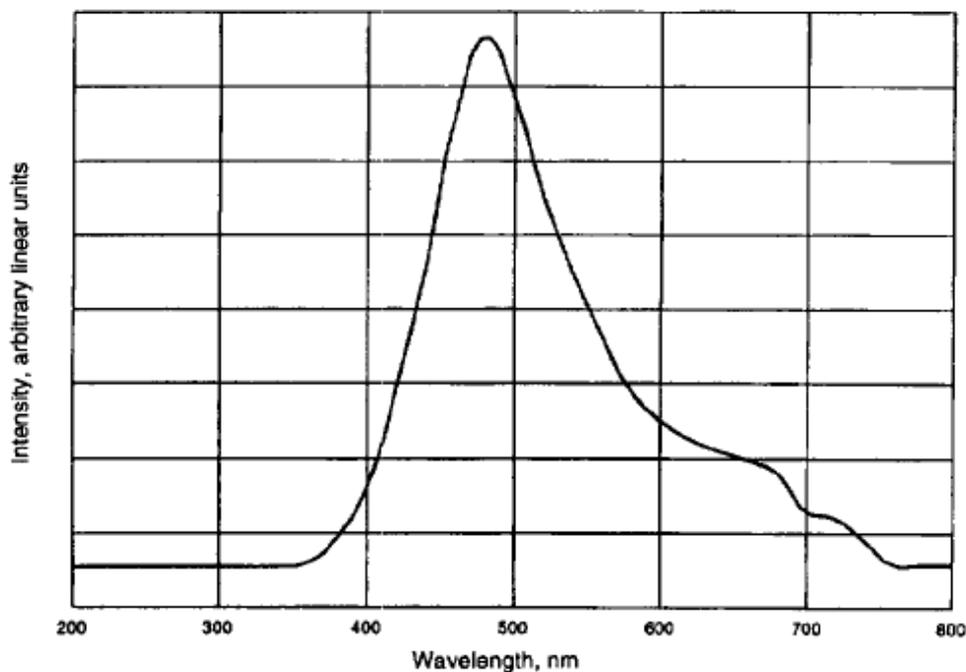


FIG.4:Emission spectrum of CdWO₄ phosphor[10].

The phosphorescence lifetime of CdWO₄ decreases with increasing temperature, see figure 5. Moreover, its phosphorescence intensity also decreases with increasing temperature. According to the temperature sensitivity range of CdWO₄ phosphor, calibration should be done around from 294 K to 574 K.

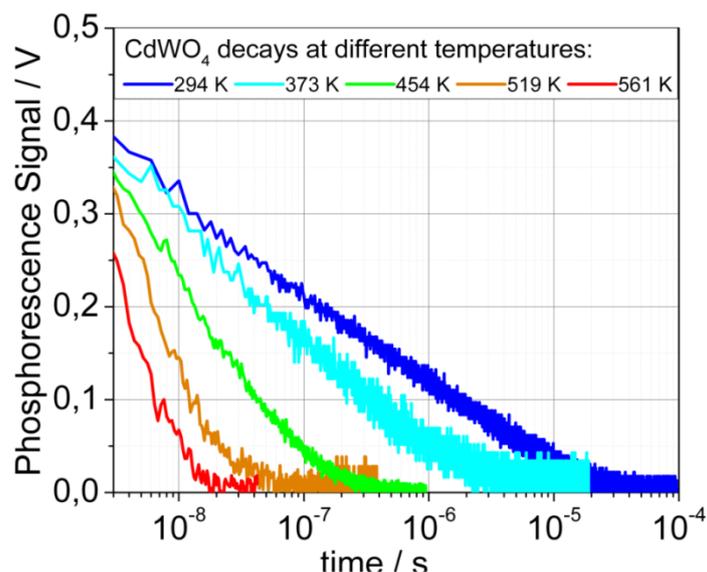


FIG.5: CdWO₄ phosphorescence decays of different temperatures with 266 nm excitation wavelength.

2.2.2 Mg₄FGeO₆:Mn

Magnesium fluorogermanate doped with manganese (Mg₄FGeO₆:Mn) phosphor is a thermographic phosphor and has an extraordinary temperature sensitive range from 13 K up to 1000 K [12]. After absorbing ultraviolet radiation, Mg₄FGeO₆:Mn phosphor emits phosphorescence which is in the deep red (620 nm to 680 nm) region [13]. Figure 6 shows the absorption spectrum of Mg₄FGeO₆:Mn at room temperature [14]. And figure 7 shows emission spectrum of Mg₄FGeO₆:Mn detected at room temperature with 355 nm excitation wavelength [12].

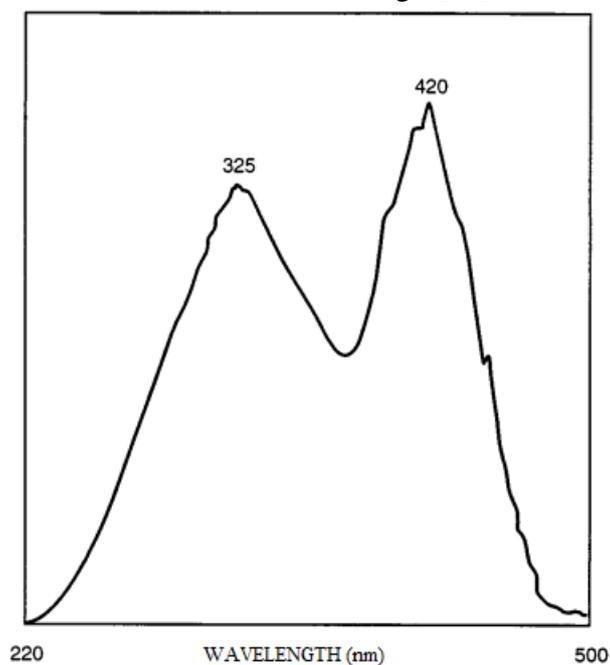


FIG.6: Absorption spectrum for Mg₄FGeO₆:Mn at room temperature [14].

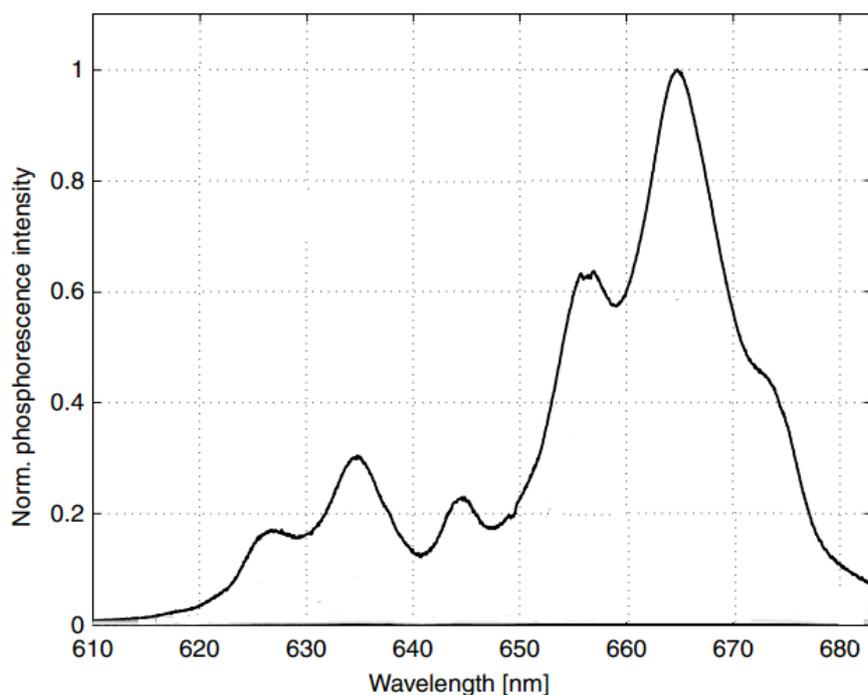


FIG.7: Emission spectrum of Mg₄FGeO₆:Mn[14]

The phosphorescence of Mg₄FGeO₆:Mn decreases with increasing temperature, see figure 8. Moreover, its phosphorescence intensity also decreases with increasing temperature. According to the temperature sensitivity range of Mg₄FGeO₆:Mn phosphor calibration should be done around from 294 K to 974 K.

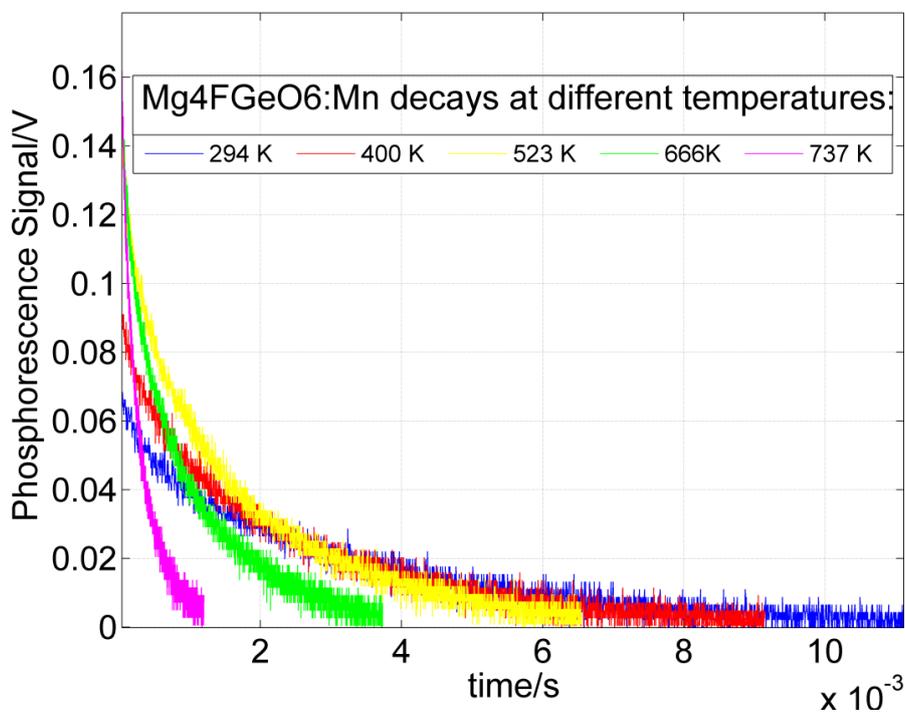


FIG.8: Mg₄FGeO₆:Mn phosphorescence 656 nm emission decays of different temperatures with 355 nm excitation wavelength.

3. Experimental Methods

This chapter provides details of the experimental setup and used experimental equipments.

3.1 Conventional and Automatic Calibration Measurement

This section presents the *conventional calibration measurement* process and *automatic calibration measurement* process separately. It also compares the *conventional calibration measurement* with the *automatic calibration measurement*.

3.1.1 Conventional Calibration Measurement

For the *conventional calibration measurement*, the oven must be set to thermal equilibrium at series of stable temperatures, which covers the whole temperature range (about 294 K to 574 K for CdWO₄ phosphor). This process takes up to several days upon completion depending on how much the temperature interval is chosen. A thermocouple is used to measure phosphor temperature. Once the oven reaches at thermal equilibrium, about 100 binary waveform files are saved which can be matched the average thermocouple temperature during the measurement time span. For the *conventional calibration measurement*, the sampling rate of oscilloscope can be modified at each temperature achieving the best trade-off between file size and resolution. Phosphorescence decay curves can be extracted and averaged from these saved waveforms. The standard deviation depends on the stability of oven temperature and shot-to-shot variations of waveforms. The temperature and waveform requiring is not synchronization, which leads certain error to the calibration.

3.1.2 Automatic Calibration Measurement

In order to compare results for *conventional calibration measurement* and *automatic calibration measurement*, the experiments for both methods have been performed with the same setup. In the *automatic calibration measurement*, the oven is ramped across the whole temperature range, while measurements are taken continuously with waveform recordings leading to a tighter grid of measurement points while greatly reducing the overall measurement time.

A LabVIEW interface is introduced to achieve *automatic calibration measurement*. The LabVIEW interface can acquire and process waveforms from the digital oscilloscope as well as matching them individually to thermocouple readings. The phosphorescence decay time becomes shorter and shorter with increasing temperature for both CdWO₄ and Mg₄FGeO₆:Mn phosphors. Regardless the length of a curve, a fixed number of sampling points is sufficient to fit an exponential function. That would mean that a short decay needs a higher sampling rate comparing with a long decay. However, for the *automatic calibration measurement*, the oscilloscope cannot

be controlled during the measurement. Therefore, the oscilloscope should always be used at highest possible sampling rate: sampling rate of 2.5 GS/s, time-base of 10.0 $\mu\text{s}/\text{div}$ for CdWO_4 . And for $\text{Mg}_4\text{FGeO}_6:\text{Mn}$ which has longer lifetime, 100 MS/s sampling rate and 2 ms/div time-base is enough, otherwise the memory of LabVIEW program will be full. It means that the LabVIEW program should define a *cutoff window* to getting rid of some points which are useless for fitting exponential function. More details of the *cutoff window* will be explained later in this thesis. Moreover, saving lots of points takes large disk space and long time. So the LabVIEW program also makes cutoff waveforms sparser accordingly before saving. The detail of this specific LabVIEW program is given in the Appendix II.

Figure 9 shows how the LabVIEW program deals with the waveforms. The original waveform is represented by blue points, and corresponding extracted phosphorescence decay is shown as red points, which has been dealt by the LabVIEW program. And the first green point is the start point of extracted phosphorescence decay curve, and the second green point is the end point of extracted phosphorescence decay curve. The window between these two points is referred as a *cutoff window*. Comparing these two curves, the sparsed phosphorescence decay curve still contains all necessary information to fit the phosphorescence decay time.

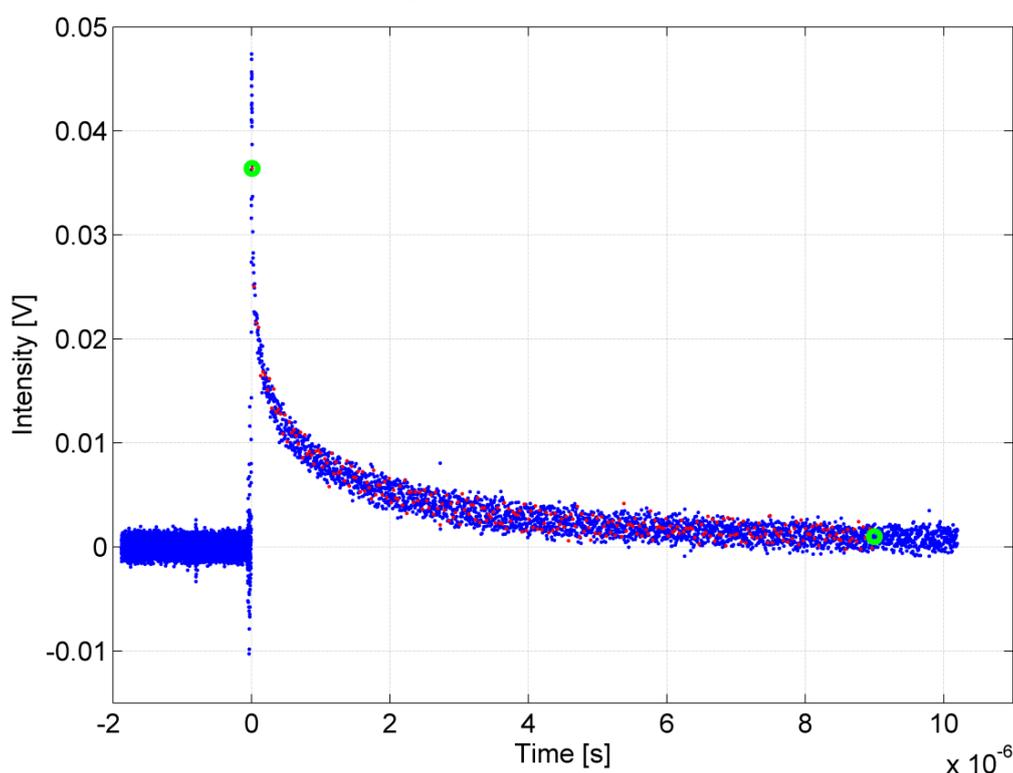


FIG.9: A waveform of CdWO_4 phosphorescence at room temperature, 294 K. The blue points are the original phosphorescence waveform. The red points are the phosphorescence decay curve which is altered by LabVIEW program. Two green dots indicated the edges of the fitting window.

3.2 Experimental Setup

This section shows the experimental setup both for CdWO_4 conventional and automatic calibration measurements. And the other experimental setup for $\text{Mg}_4\text{FGeO}_6:\text{Mn}$ automatic calibration measurement is also presented.

3.2.1 Experimental Setup for CdWO_4 - Conventional and Automatic Calibration Measurements

This experiment aims to detect phosphorescence decay curves at different temperatures both in conventional way and automatic way. A Nd:YAG laser, a digital oscilloscope, an oven, a thermocouple, a PMT detector, a power-meter, and several optical components are utilized in this experiment, shown in figure 10.

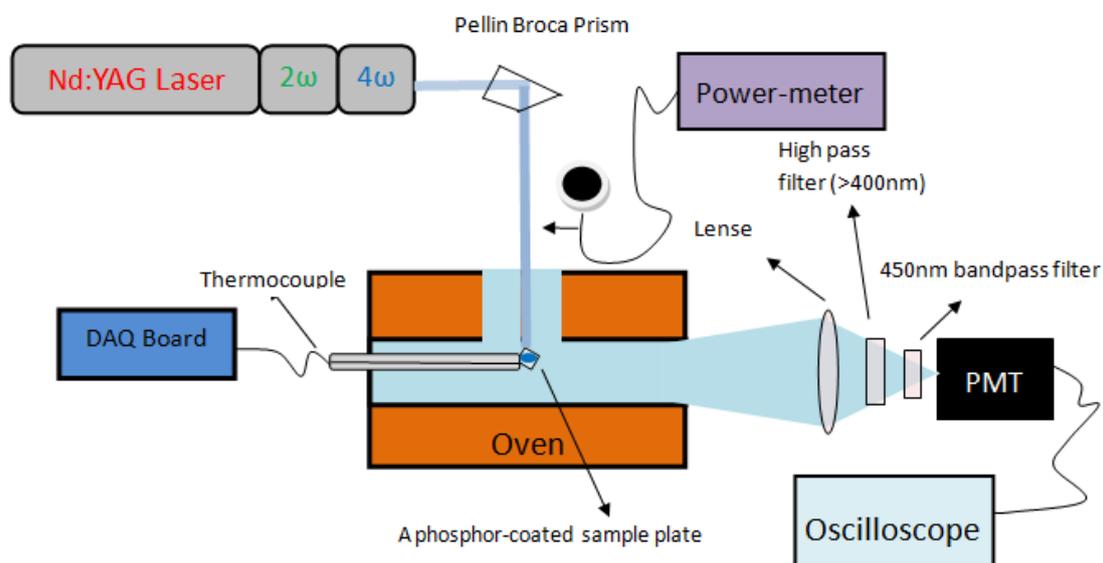


FIG.10: Experimental Setup for CdWO_4 phosphor calibration. A Nd:YAG laser is used to exciting the phosphor sample which is put in an oven. Laser power can be measured by a power-meter. The excited phosphorescence is guided and collected by some optical elements, such as lens, filters. Before the oscilloscope displays the decay curve, a PMT is used to amplify the signal. Moreover, phosphor temperature is measured by a thermocouple.

The Nd:YAG laser can be operated at 266, 532, or 1064 nm. It produces 10 Hz pulses with about 5 ns time duration using a Q-switch. Only 266 nm radiation is needed and utilized as excitation source for CdWO_4 phosphor. Most of the two longer wavelength orders have been consumed or filtered away by the two frequency doubling units shown in figure 10. However, a laser beam of 266 nm with spurious fractions of 532nm and 1064nm travelled through a Pellin Broca prism. The prism guides wavelengths into a different direction and helps separating 266 nm from the residual laser wavelengths. The pulse energy is limited to 5.0 mJ in order to prevent the phosphor coating from optical heating or burn-off, see section 4.3.3.2. Then the laser

beam directly hits a phosphor-coated sample plate which is placed inside a tube furnace. The phosphor-coated sample plate is placed inside the oven and at 45 degree to the oven tube in order to enable excitation and signal collection perpendicular to each other. The tip of a K-type thermocouple touches the back side of the thin metal phosphor substrate. A plano-convex lens is utilized to image the excited phosphorescence emission onto a PMT detector. In order to reduce scattered laser radiation (266 nm, 532 nm and 1064 nm), the phosphorescence passes through two different filters before hitting the PMT. The acceptance wavelength band of the first interference filter is 450 ± 20 nm, while only wavelengths greater than 400 nm can pass the second high-pass wavelength edge filter. Finally, the PMT detector converts the phosphorescence signal into an amplified electrical current, which is displayed and saved with a digital oscilloscope.

3.2.2 Experimental Setup for $\text{Mg}_4\text{FGeO}_6\text{:Mn}$ - Automatic Calibration Measurement

The experimental setup for $\text{Mg}_4\text{FGeO}_6\text{:Mn}$ *automatic calibration measurement* is almost the same as previously seen for the CdWO_4 calibration measurement. It is shown in figure 11.

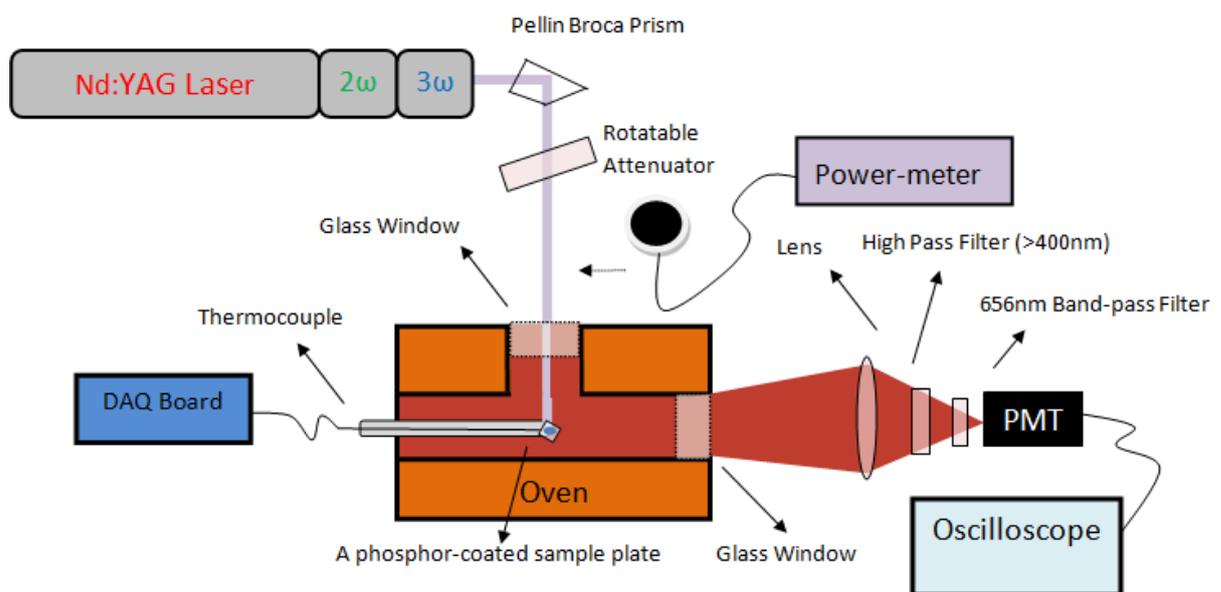


FIG.11: Setup for $\text{Mg}_4\text{FGeO}_6\text{:Mn}$ phosphor calibration.

For $\text{Mg}_4\text{FGeO}_6\text{:Mn}$, the Nd:YAG laser which emits 355 nm radiation is used, and a 656 nm band-pass filter is put in front of PMT detector. The phosphorescence yield rate for $\text{Mg}_4\text{FGeO}_6\text{:Mn}$ phosphor is lower than CdWO_4 phosphor, which means the laser should run with higher energy, 10 mJ. Due to avoiding burning phosphor sample by high laser power, a rotatable attenuator is utilized to adjust laser power before hitting the sample. Along with more experiments that have been done, it was found out that sealing the oven tube with two thick glass windows improved the oven temperature stability significantly, preventing air flow from and to the surroundings.

So this experimental setup is also referred as *window setup*, while the experimental setup for CdWO₄ calibration is referred as *non-window setup*.

3.3 Experimental Equipment

In this section, more details on laboratory equipment are provided.

3.3.1 Nd:YAG Laser

CdWO₄ is excited by 266 nm radiation from a Quantel Brilliant B pulsed Nd:YAG laser. This Nd:YAG laser produces 10 Hz pulses with pulse durations of about 5 ns by Q-switching. Subsequent frequency doubling and frequency quadrupling is used to generate 266 nm radiation. The process is that the fundamental wavelength radiation (1064 nm) passes through a frequency doubling harmonic generating crystal, generating 532 nm radiation accompanied by spurious 1064 nm radiation. Finally, after passing through the quadrupling unit, most of the 523 nm laser emission has been converted to 266 nm, shown in figure 12. However some leakage at 532 nm and 1064 nm cannot be fully avoided. The maximum energy per pulse for each of the wavelengths is: 850 mJ at 1064 nm, 400 mJ at 532 nm, and 90 mJ at 266 nm[15].

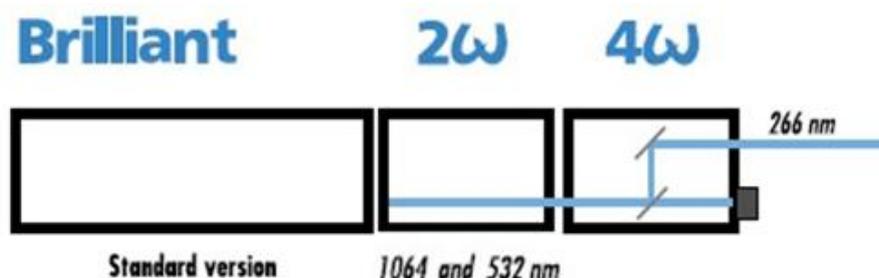


FIG.12: Principle of Brilliant Nd:YAG laser producing 266nm radiation[15].

For exciting Mg₄FGGeO₆:Mn, 355 nm radiation is needed. The pulse frequency and duration of the Quantel Brilliant B pulsed Nd:YAG laser is same as the laser which is used for exciting CdWO₄ phosphor. In order to obtain 355 nm radiations, 1064 nm fundamental radiation first goes through frequency doubling unit to get the doubling radiation, 532 nm wavelength. Then 1064 nm and 532 nm radiation pass together through a tripling unit to create 355 nm radiation, which is a nonlinear wave-mixing process, shown in figure 13. The maximum energy per pulse for 355 nm wavelength is 185 mJ[15].

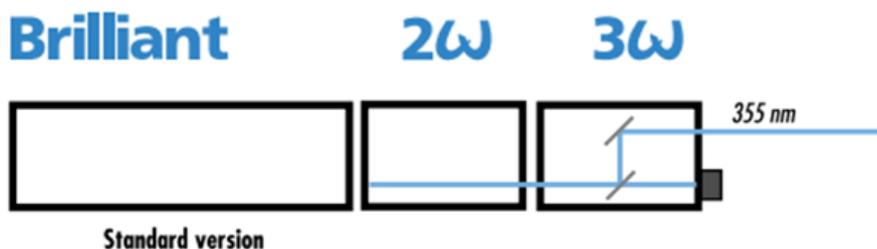


FIG.13: Principle of Brilliant Nd:YAG laser producing 355 nm radiation[15].

3.3.2 Oscilloscope

A LeCroyWaveRunner 6030A Oscilloscope is utilized to display and record phosphorescence decay curves. The maximum sampling rate of this oscilloscope is 5 GS/s. And there are four channels in this oscilloscope. One of them should be connected with Q-switch output from the Nd:YAG laser as a trigger signal. The input resistance of oscilloscope channels is set to 50 Ω . The phosphorescence signal which is amplified by PMT should be connected with another oscilloscope channel. The phosphorescence waveforms are saved as binary files onto the oscilloscope's hard disk.



FIG.14:A LeCroyWaveRunner 6030A Oscilloscope[16].

3.3.3 Thermocouple and DAQ Board

At this measurement, the thermocouple is of type K with a sensitivity approximate 41 $\mu\text{V}/\text{K}$. Type K thermocouple is made of two different alloys. One is chromel (90% nickel and 10% chromium), the other one is alumel (95% nickel, 2% manganese, 2% aluminum, 1% silicon). These two different metal conductors can produce a voltage value in its junction. This voltage is proportional to temperature difference between these two conductors. The sensitive range of type K thermocouples stretches from -473 K to +1623 K, with ± 2.2 K standard tolerance in 273 K to 1523 K range[17].

The tip of thermocouple is attached to the back of the phosphor-coated sample plate to provide an accurate temperature of the phosphor. And this thermocouple also connects with a DAQ board to read out temperature values on a computer. The DAQ board consists a NI USB-9211A Portable USB-Based DAQ for thermocouples (4 analog inputs at 24-bit resolution with 12 S/s sampling rate) and a NI USB-9162(C Series USB Single Module Carrier). By using the DAQ Assistant, the sampling rate and type of thermocouple is needed to be specified before the data can be acquired successfully.



FIG.15: NI USB-9211A Portable USB-Based DAQ for Thermocouples and NI USB-9162 C Series USB Single Module Carrier[18].

3.3.4 Power-meter

An Ophir Nova II laser power meter is utilized to measure laser power. The power meter absorbs the laser beam and converts it into heat. The thermal sensor of this power-meter is a pyroelectric measurement device. Pyroelectric type sensors are useful for measuring the energy of repetitively pulsed lasers at up to 25 kHz and are sensitive to low energies[19]. Pyroelectric sensors use a pyroelectric crystal that generates an electric charge proportional to the heat absorbed. The energy scale of this sensor is 2 mJ to 10 J, and measures laser pulse widths of up to 20 ms[19].



FIG.16: Ophir Nova II laser power meter. The left one is the sensor of the power-meter, and the right one is the readout device[19][20].

3.3.5 Photomultiplier Tube

To detect and amplify phosphorescence signal, a Hamamatsu H6780-04 Photomultiplier (PMT) is utilized. When phosphorescent light reaches the photocathode, the incoming photons are converted into electrons. These electron signals can be amplified by secondary electron emissions from the dynodes. An anode is used to collect these secondary electrons which were multiplied in the cascade process. The principle is shown in 17.

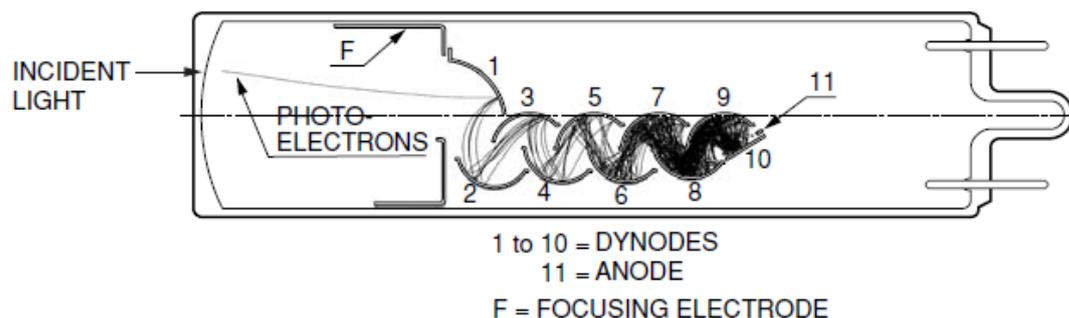


FIG.17: Principle of linear-focused type of electron multiplier[21].

For photomultiplier tube operation, a gradient voltage should be applied across the cathode and anode, in order to accelerate electrons. In practice, the inter-stage voltage for each electrode is supplied by using voltage-dividing resistors connected in between each dynode, as shown in figure 18.

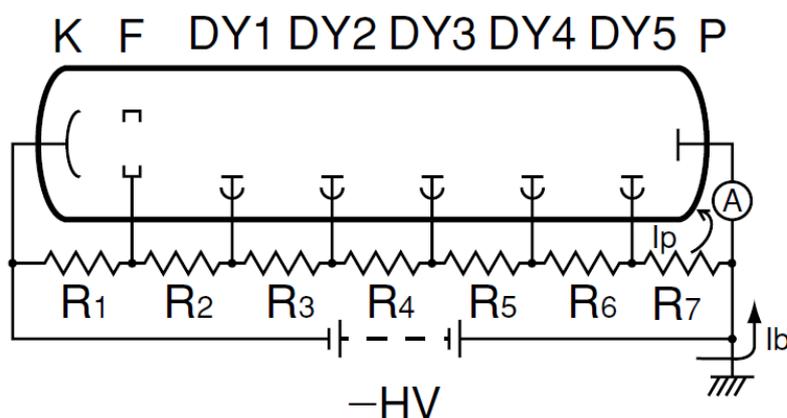


FIG.18: PMT external circuit, K (Cathode), F (electron focusing), DY1-DY5 (dynodes), P (Anode), R_1 - R_7 (resistors), I_p (anode current), I_b (divider current), HV (high voltage). Then output electron current goes through an external circuit[21].

Table 1 shows specific characteristics of a Hamamatsu H67880-04 Photomultiplier tube that was used in this work[22].

TABLE 1: Hamamatsu H67880-04 Photomultiplier tube specifications

Specification	Value	Unit
Spectral response	185-850	nm
Peak sensitivity wavelength	400	nm
Maximum output signal current	100	μA
Cathode radiant sensitivity	60	mA/W
Anode radiant sensitivity	$3e10^4$	A/W
Anode luminous sensitivity	75	A/lm
Rise time	0.78	ns

4. Results and Discussion

CdWO_4 temperature measurements results, have been obtained in two different ways, *conventional calibration* and *automatic calibration* are displayed in this chapter. And comparison of the *conventional calibration* and *automatic calibration* results is presented. It also discusses how fast the *automatic calibration* can be performed. Moreover, $\text{Mg}_4\text{FGeO}_6\text{:Mn}$ calibration done by *automatic measurement* is also shown.

This chapter also discusses some factors which may affect the accuracy of the CdWO_4 calibration.

4.1 Conventional and Automatic Calibration Measurements of CdWO_4

In this section, the results of *conventional* and *automatic calibration* for CdWO_4 are shown and compared. And the speed limitations of automatic performance are discussed.

4.1.1 Conventional Calibration Measurement of CdWO_4

Figure 19 shows the conventional CdWO_4 temperature calibration result. The oven has been set to 12 thermal equilibriums with around 25 K temperature interval. The whole measurement took 2 days upon completion.

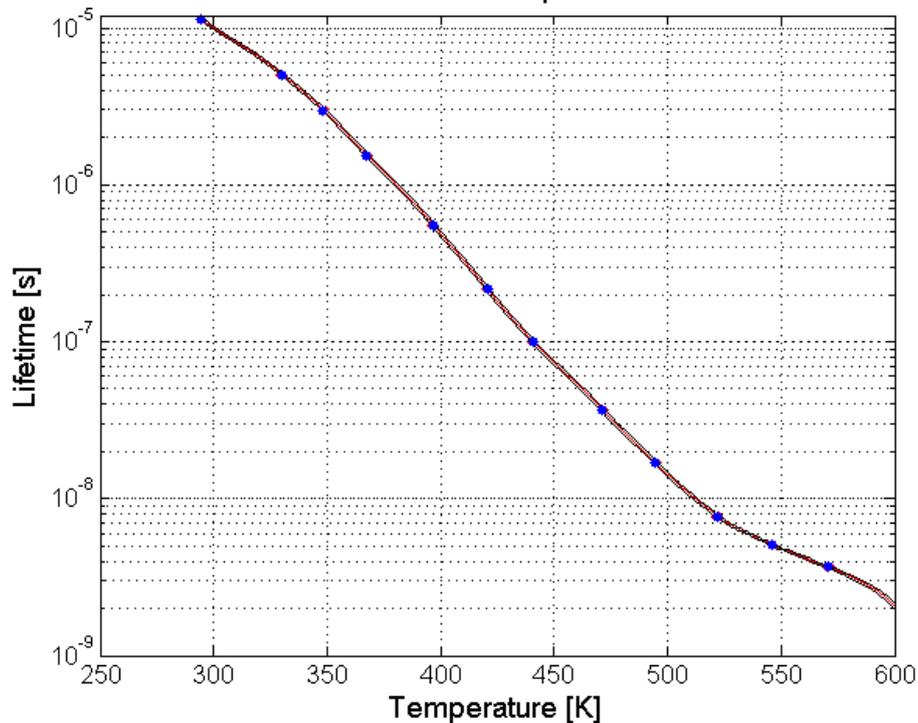


FIG.19: CdWO_4 *conventional calibration measurement* curve. The lifetime data (blue point) of each temperature is averaged over 100 individual decay curves. The red line is the fitting, which is created by a piecewise polynomial interpolation.

4.1.2 Automatic Calibration Measurement of CdWO₄

Figure 20 shows the CdWO₄ phosphor *automatic calibration* result. The waveforms and temperatures were continuously recorded with temperature intervals of around 0.33 K in between 2 measurements. The entire calibration was completed within 3 hours.

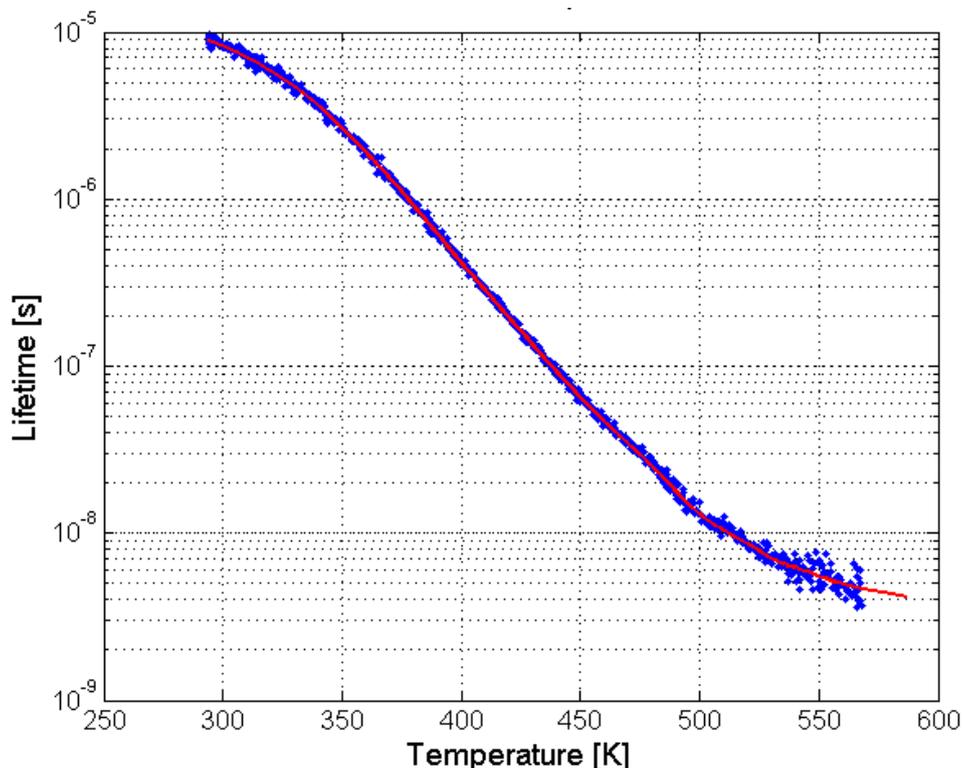


FIG.20: Automatic CdWO₄ temperature calibration measurement. The oven temperature has been ramped with 4 K/min and measurements of temperature and lifetime have been undertaken continuously with an acquisition speed of 5 samples/s. The blue points are the lifetimes from each acquired waveform, and the red line is a fitting of these blue points. The temperature interval of each blue point is around 0.33 K.

4.1.3 Comparison of Conventional and Automatic Calibration of CdWO₄

The *conventional* and *automatic calibrations* have been done in the same experimental setup and environment. It means that the power of laser, the gain of PMT, and the touching point between thermocouple and phosphor sample plate is the same. Moreover, the temperature range investigated is comparable within these two measurements. In these two measurements, the phosphor temperature is measured by a thermocouple, while phosphorescence lifetime of CdWO₄ is obtained from the oscilloscope waveform using MATLAB software. Figure 21 shows the comparison of *conventional* and *automatic calibrations*.

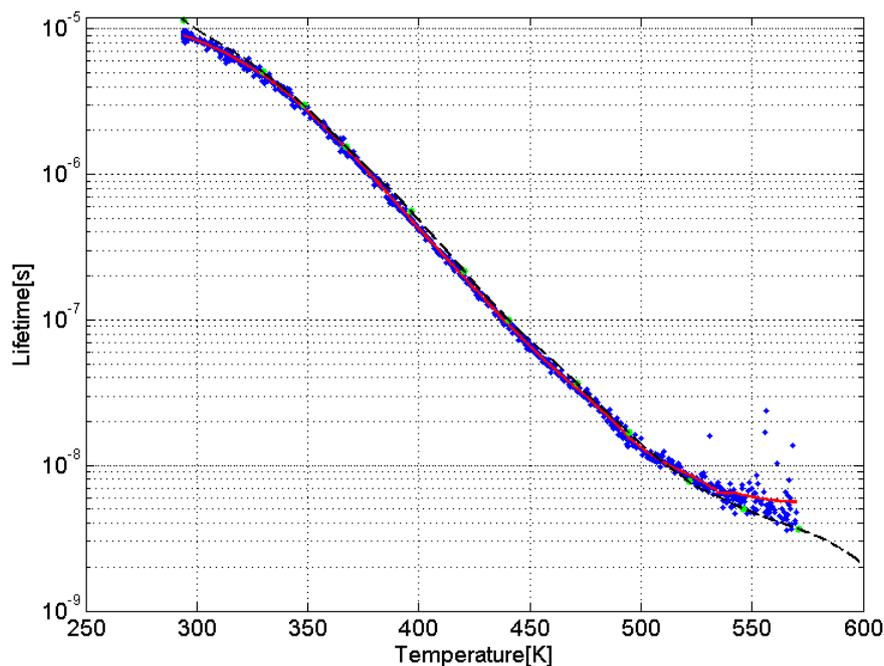


FIG.21: Comparison of *conventional calibration* and *automatic calibration measurement* results for CdWO_4 . Green points are *conventional measurement* data, and the black dashed line is a corresponding fitting curve. Blue points are *automatic measurement* data, and the red solid line is a corresponding fitting curve.

The conventional data almost overlaps with *automatic calibration* curve. CdWO_4 phosphor *conventional calibration measurement* takes up to 2 days, while CdWO_4 phosphor *automatic calibration measurement* only takes 3 hours. Moreover, different from the *conventional measurement*, an *automatic measurement* does not need to reach thermal equilibrium which is a time consuming process. The time of reaching thermal equilibrium at 525 K is in the order of around 5 hours, see figure 31 as an example. And the consuming-time is longer for higher temperature. The speed of *automatic measurement* is only limited by oven increasing temperature speed, which will be discussed in 4.1.4. According to figure 21, only 12 points (green points) are used to get fitting curve for the *conventional measurement*. Meanwhile, for *automatic measurement*, about 5000 points (blue points) are used to get fitting curve which gives more accurate fitting. In summary, the automatic process performs quicker and more accurate temperature calibration.

4.1.4 Time-consuming of Automatic Calibration Measurement

One important advantage of *automatic calibration measurement* is less time-consumption. There are, however, factors, that can affect the *automatic measurement* time. One main factor is oven increasing temperature speed, the other one is LabVIEW program loop speed.

4.1.4.1 Oven Increasing Temperature Speed

It is possible to set the temperature ramping speed to ≤ 4 K/min to do the calibration

measurement. For CdWO_4 the temperature range for calibration is around 294 K to 574 K, and for $\text{Mg}_4\text{FGeO}_6\text{:Mn}$ phosphor it is 294 K to 974 K. It means that the minimum time for a *automatic calibration* for CdWO_4 and $\text{Mg}_4\text{FGeO}_6\text{:Mn}$ phosphor is about 3 hours and 6 hours respectively.

4.1.4.2 LabVIEW Program Loop Speed

The LabVIEW program for *automatic calibration* contains a loop which acquires phosphorescence decay curve and phosphor temperature in a synchronized and continuous manner. The loop contains two main processes, one is *Temperature Acquiring Process*, and the other one is *Extract Decay Curve Process*, shown in figure 22.

Phosphor temperature acquiring speed, called *Temperature Acquiring Process*, is controlled by a DAQ board (NI USB-9211A) which is connected with the thermocouple. The maximum sampling rate of it is three samples per second for one thermocouple[23]. The speed for the temperature acquiring process is constant during the whole calibration. Acquiring, processing and saving an oscilloscope waveform is a time-consuming process, called *Extract Decay Curve Process*. The time of extracting a decay curve can vary. Regardless the performance of computer, the *saving waveform data LabVIEW process* governs the *extract decay curve process* speed. It means the big saving data size can slow down the speed.

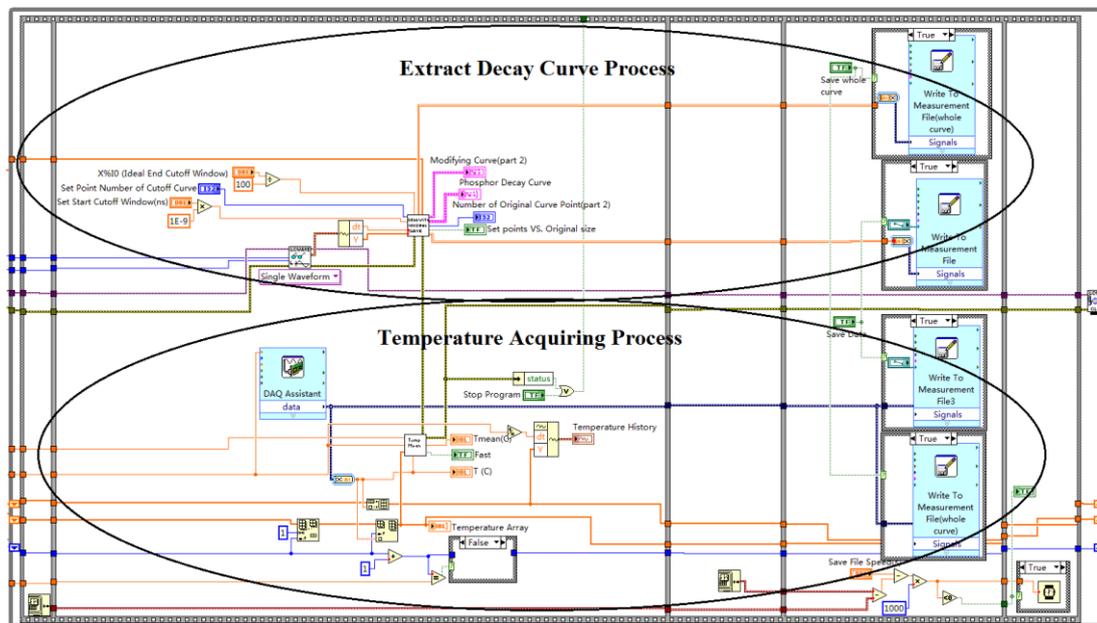


FIG.22: The block diagram of the main loop of LabVIEW program for automatic calibration. This program contains two processes, *Extract Decay Curve Process* and *Temperature Acquiring Process*, which are marked by black circles.

The main loop synchronizes the two processes: *Temperature Acquiring Process*, and *Extract Decay Curve Process*, so its speed is governed by the slower process and

varies for each recording. For this *automatic calibration measurement*, it is enough to take a thousand waveforms. Thus, an input parameter *Time interval between 2 File(s)* is used to slow down the main loop speed, shown in figure 23.

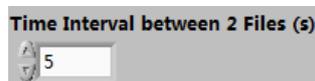


FIG.23: The snapshot of the user front panel of *Time interval between 2 Files(s)*.

For this thesis, the time interval between 2 files is set 5 s for CdWO_4 phosphor *automatic calibration*. This means if the loop speed is faster than 5s, the sequent loop will wait until 5 s have passed before running another acquisition loop. Otherwise, the next loop performs immediately. If someone wants to do a fast measurement, the speed limitation should be considered. For example, to investigate the wall temperature of a truck engine running at 1200 rpm, an acquisition speed of 10 samples/s would be needed to measure once during every engine cycle. This is also the repetition rate of the laser, meaning that for processes in need of sampling rates of 10Hz or faster, the Laser pulse rate is taking over as a limiting factor.

In any other case, the consuming time of the whole measurement is limited by the loop speed and oven increasing temperature speed. For the case of CdWO_4 and $\text{Mg}_4\text{FGeO}_6\text{:Mn}$ phosphor, the oven increasing temperature speed limitation governs the data acquisition time for *automatic calibrations*.

4.2 Automatic Calibration Measurement of $\text{Mg}_4\text{FGeO}_6\text{:Mn}$

Figure 24 shows that the *automatic calibration* result of $\text{Mg}_4\text{GeO}_6\text{:Mn}$. The temperature sensitive range of $\text{Mg}_4\text{GeO}_6\text{:Mn}$ is 294 K to 973 K, which is much wider than that of CdWO_4 . So $\text{Mg}_4\text{FGeO}_6\text{:Mn}$ can be applied on higher temperature combustion environment measurement. During this *automatic calibration measurement*, the waveforms and temperatures were continuously recorded with temperature intervals of 0.67 K. The entire process took around 6 hours.

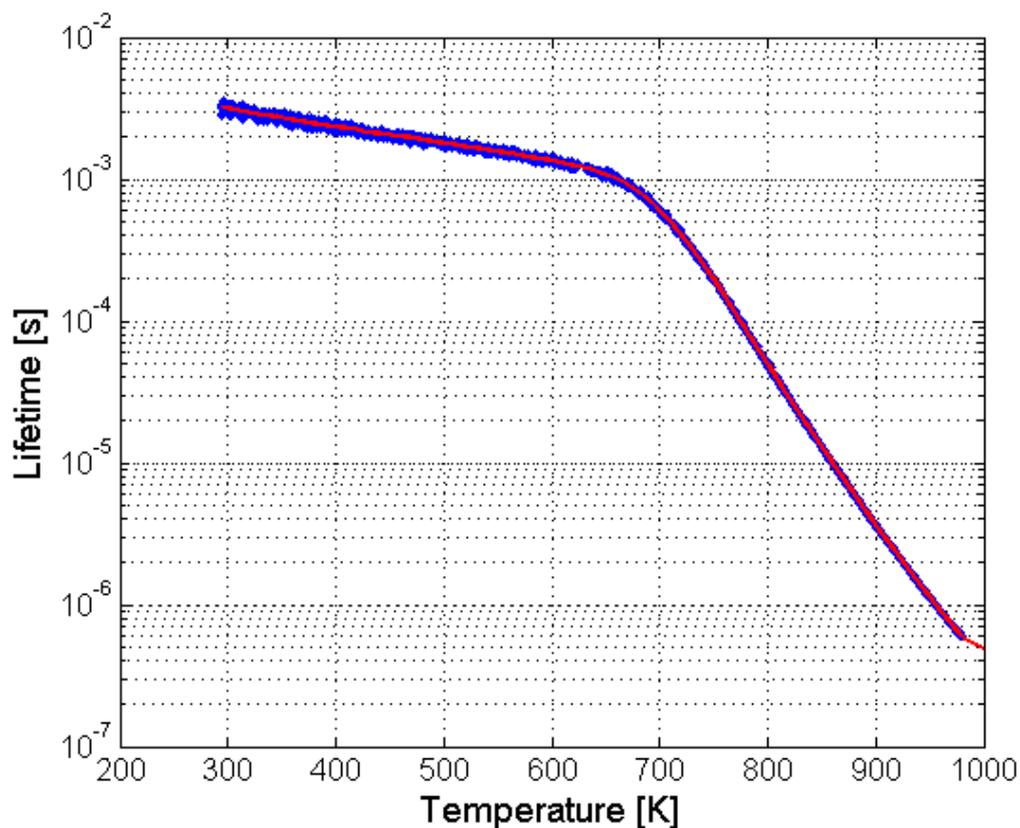


FIG.24: Mg₄FGeO₆:Mn *automatic calibration measurement*. The blue dots are the measured data, and the red line is a fitting curve. The oven has been ramped at 2 K/min and measurements of temperature and lifetime have been undertaken continuously. The blue points are the lifetimes from each acquired waveform, and the red line is a fitting of these blue points. The temperature gap in between 2 measurement points is about 0.67 K on average.

Though *conventional calibration* of Mg₄FGeO₆:Mn has not been done in this thesis. Article[1] has done the conventional calibration of Mg₄FGeO₆:Mn under experimental condition which is similar to that of the automatic calibration of Mg₄FGeO₆:Mn in this thesis. Comparing the results of these two methods, figure 24 and figure 25, there is no significant difference.

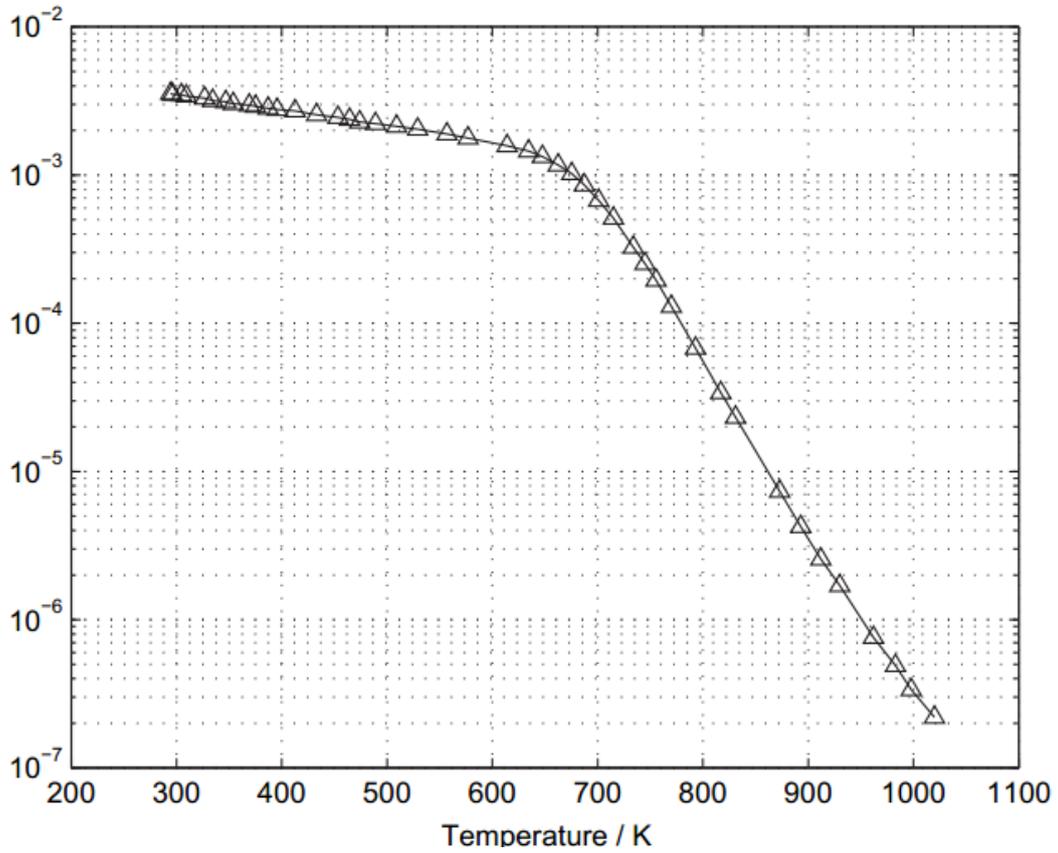


FIG 25: Temporal response to temperature for the 656 nm line of $\text{Mg}_4\text{FGeO}_6:\text{Mn}$. [1]

A comparison of *automatic calibration* results from CdWO_4 and $\text{Mg}_4\text{FGeO}_6:\text{Mn}$ are given in figure 26. As mentioned before, they have different temperature sensitivity ranges, and are used for different applications.

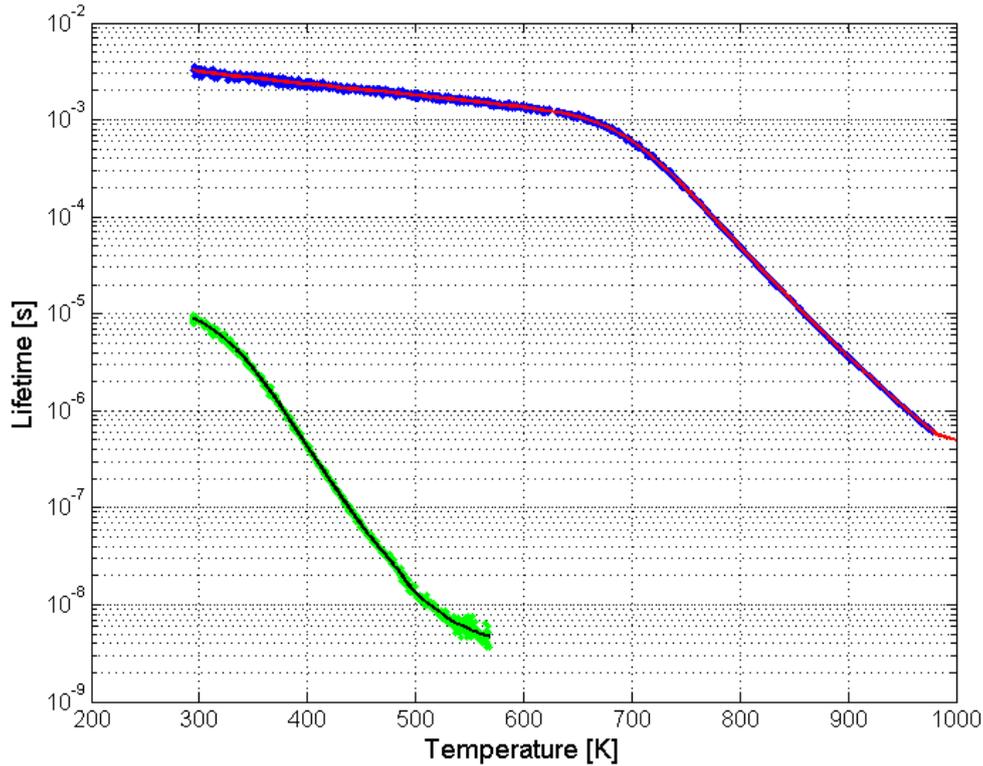


FIG.26: *Automatic calibration* of CdWO_4 and $\text{Mg}_4\text{FGeO}_6:\text{Mn}$. The green points are CdWO_4 measurement data, and the black line is corresponding fitting. The blue points are $\text{Mg}_4\text{FGeO}_6:\text{Mn}$ measurement data, and the red line is corresponding fitting.

4.3 Affecting Accuracy Factors

This section examines some factors which may affect the accuracy of the CdWO_4 calibration result. They are intensity of phosphorescence, response time of CdWO_4 and thermocouple, phosphor exposure time in high temperature, and laser induced heating.

4.3.1 Intensity of Phosphorescence

For CdWO_4 phosphor calibration, in high temperature the decay time standard deviation increases, as shown in figure 20. One reason is that the intensity of phosphorescence decreases with increasing temperature. The phosphorescence intensity is higher at 564 K than the intensity at room temperature, shown in figure 27. The $\text{Mg}_4\text{FGeO}_6:\text{Mn}$ phosphor behaves the opposite way, the intensity increases with increasing temperature, shown in figure 28. Intensity variations affect the accuracy of the fitting procedure as lower intensities also have a lower signal-to-noise ratio.

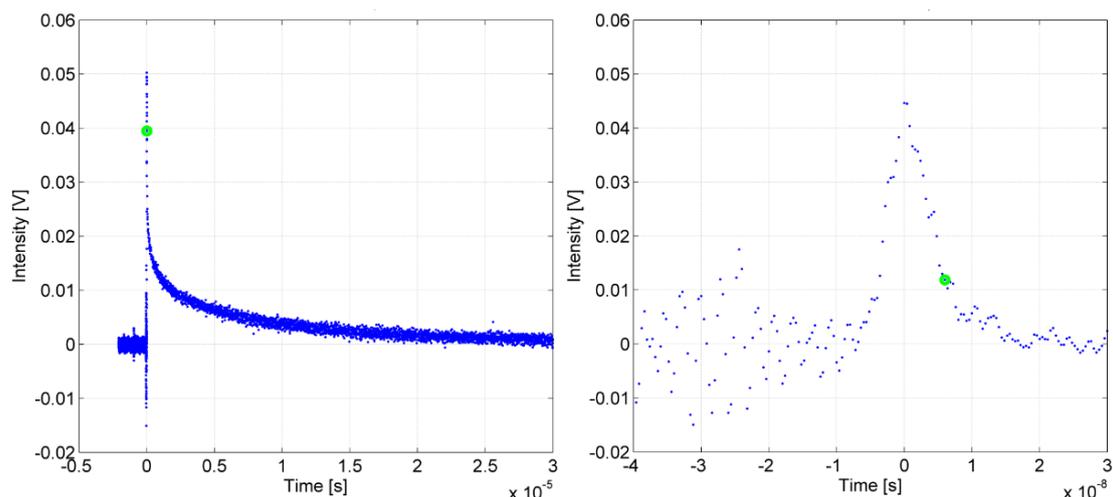


FIG.27: The left graph is a saved waveform of CdWO_4 phosphor at room temperature, 294 K. And the graph on the right is a saved waveform at high temperature, 569 K. The green dot marks the initial phosphorescence intensity at the start of the decay time fitting window, which is 0.0395 V for the left graph (294 K), and 0.0119 V for the right graph (569 K).

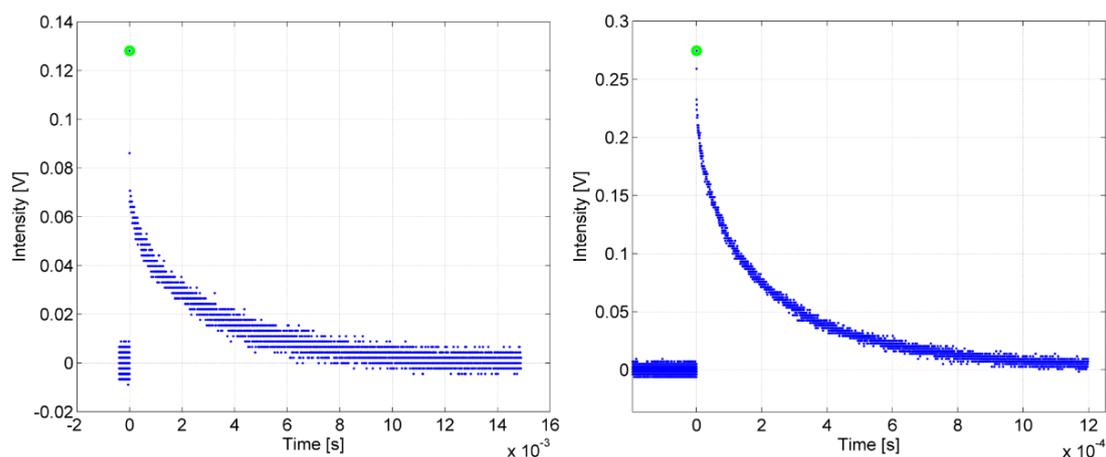


FIG.28: The left graph is a saved waveform of $\text{Mg}_4\text{FGeO}_6:\text{Mn}$ phosphor at room temperature, 294 K. And the graph on the right is a saved waveform at high temperature, 666 K. The green dot marks the initial phosphorescence intensity at the start of the decay time fitting window, which is 0.1281 V for the left graph (294 K), and 0.2745 V for right graph (666 K).

The phosphorescence intensity of CdWO_4 decreases with rising temperature, which is a characteristic of most thermographic phosphors, shown in figure 29 upper one. And lower intensity lead to worse precision, which is a result of the property of detection system, such as PTM. However, for $\text{Mg}_4\text{FGeO}_6:\text{Mn}$ phosphor, the intensity increases with increasing temperature, shown in figure 29 lower one.

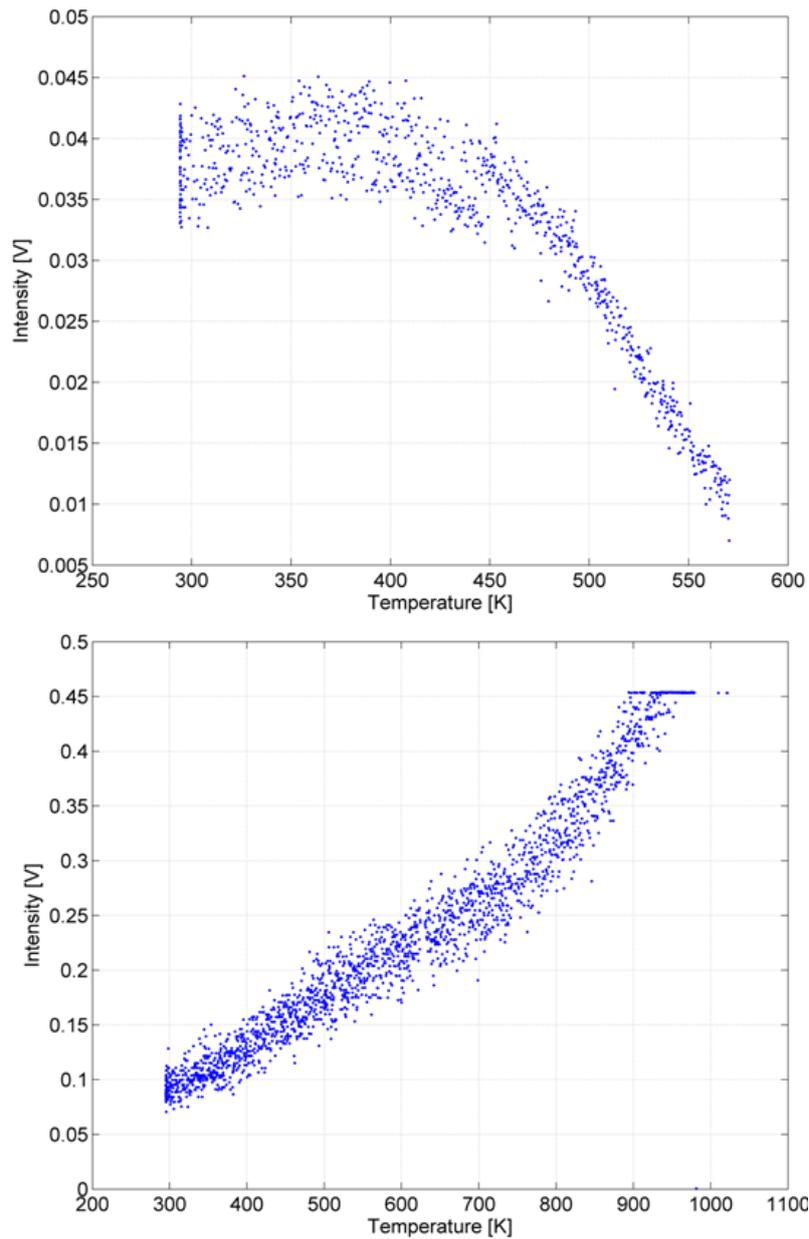


FIG.29: Phosphorescence peak intensity changes with increasing temperature. The temperature is read from thermocouple. The upper one is for CdWO₄ phosphor, and the lower one is for Mg₄FGeO₆:Mn phosphor.

4.3.2 Response Times of CdWO₄ Phosphor and Thermocouple

Whether the CdWO₄ phosphor and the thermocouple reacts equally fast to physical temperature changes is very important in order to determine the maximum heating rate during automatic temperature calibration of a phosphor. This affects the accuracy of the calibration result.

Temperature oscillations are a good way to examine whether sensitivities of phosphor and thermocouple are the same or not. During these temperature oscillations, it is observed how the phosphor temperature changes follow thermocouple temperature

changes. Temperature oscillations are created by manually controlling oven heating or cooling speed. Temperature information from the thermocouple can directly be read out whereas the phosphor waveforms still need to be converted into temperatures using an earlier calibration which is believed to be taken under slow enough heating rates. Figure 30 (a)-(d) shows results from four oscillation experiments which both contain phosphor temperature and thermocouple temperature.

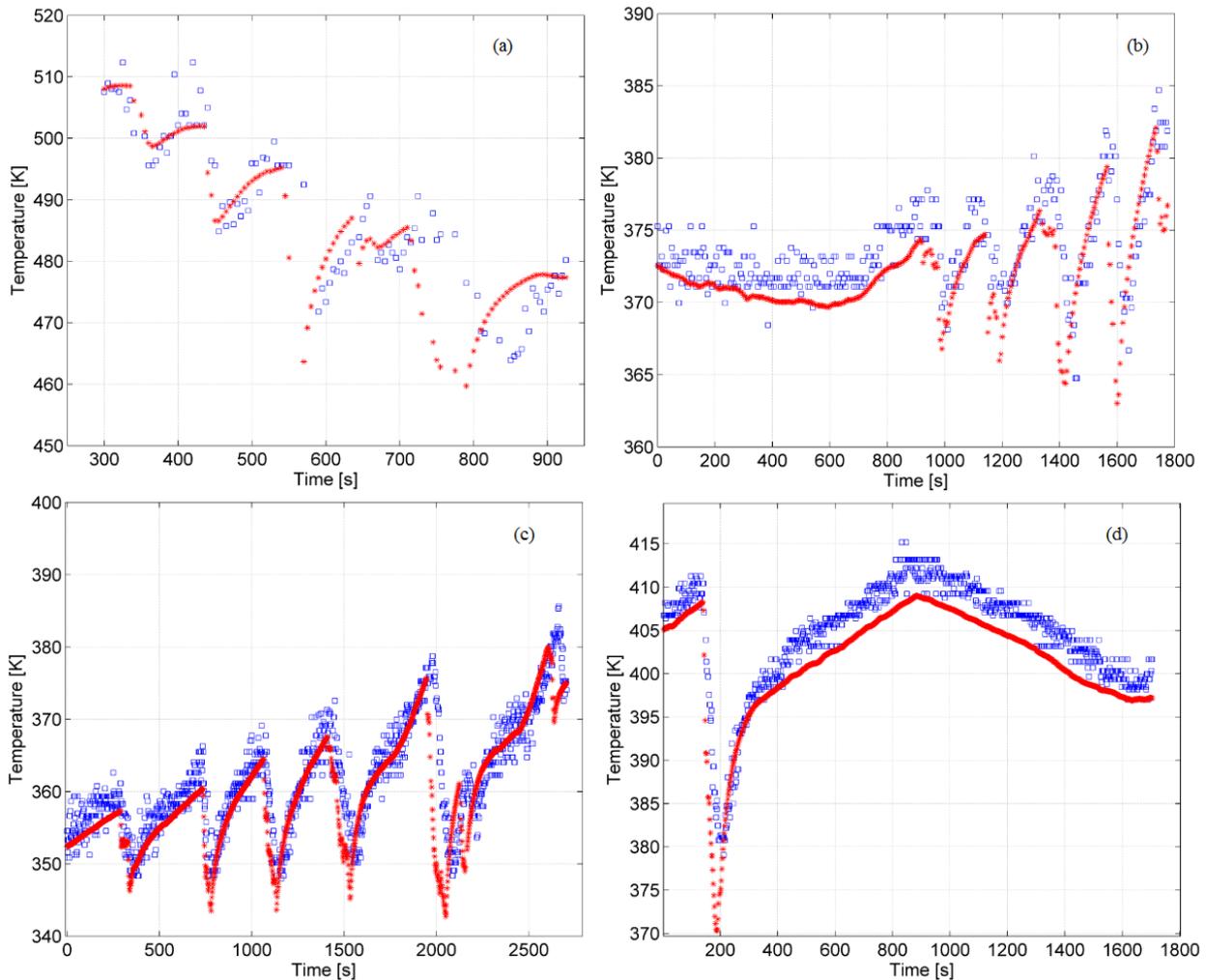


FIG.30: Thermocouple temperature and phosphor temperature of four different temperature oscillation processes, (a) to (d). The blue squares are phosphor temperature, while the red points are thermocouple temperature.

Figure 31 shows that thermocouple response speeds, and corresponding phosphor response speeds which are manually extracted from figure 30. According to figure 31, the phosphor response speed almost linearly responds with thermocouple response speed, especially in our interesting region, 0-4 K/min.

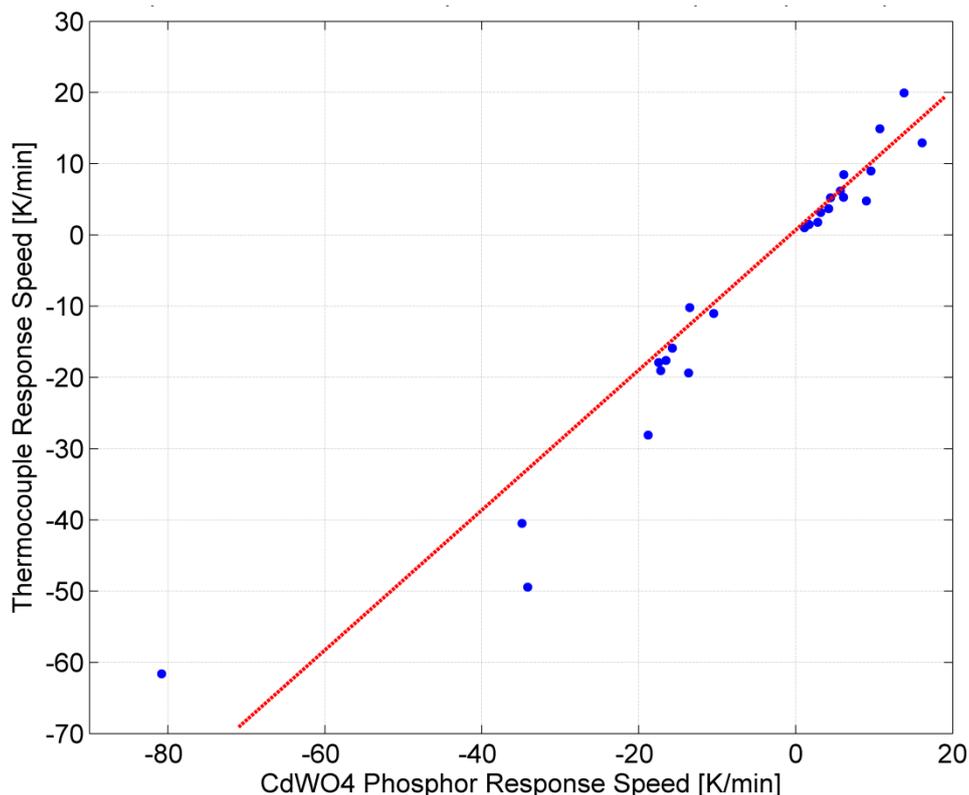


FIG.31: Comparison of thermocouple response speed and thermocouple response speed for different oven increasing or decreasing speeds (blue dots), taken from figure 30. The red line corresponds to a linear fit.

4.3.3 CdWO₄ Phosphor and Thermocouple Temperature Off-set

Figure 30 (a) and (d) shows that phosphor temperature roughly matches the thermocouple temperature. However, figure 30 (b) and (c) show that the phosphor temperature sometimes is above and below of the thermocouple temperature. Many factors may lead to this phosphor and thermocouple temperature off-set. In this thesis work, two possible factors are investigated further. One is irreversible changes of the phosphor due to long-time heat treatment. The other one is laser induced heating.

4.3.3.1 Long Exposure Time for Phosphor at High Temperature Environment

In order to finding out whether the CdWO₄phosphor will change its emission characteristic after long exposure at high temperature environment, a new coating of CdWO₄is put into the oven at constant high temperature, around 520 K for 25 hours. Phosphorescence decay curves and thermocouple temperatures are recorded continuously during the first 15 hours, and then are recorded again after an 8-hour break. According to the CdWO₄temperature calibration, the lifetime of phosphor gives the temperature information. Figure 32 shows the temperature information both from CdWO₄ phosphor and thermocouple.

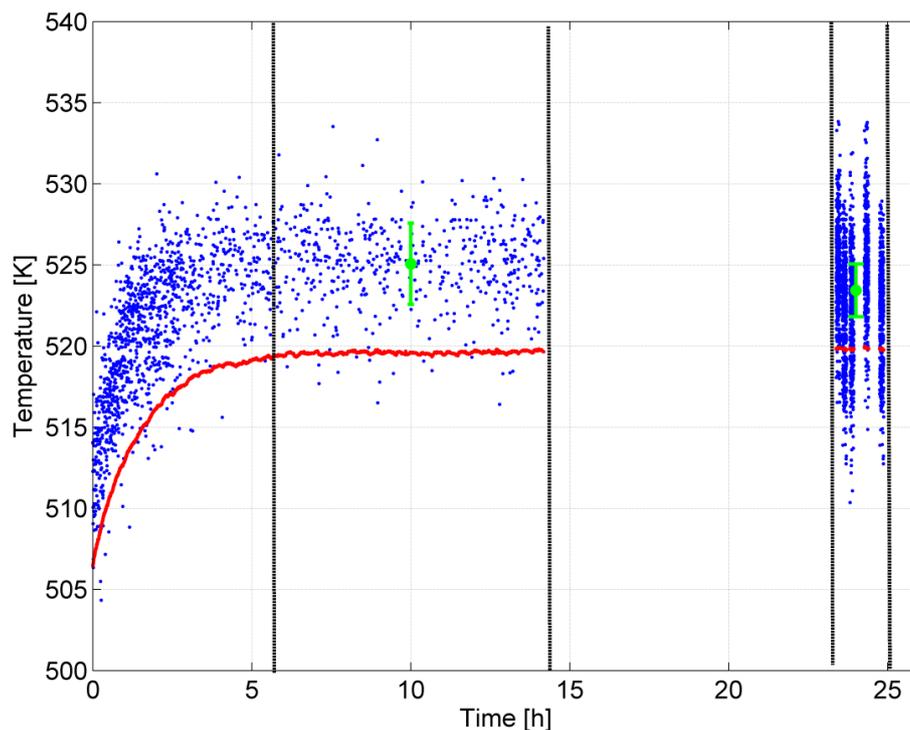


FIG.32: Phosphor temperature and thermocouple temperature recorded during 25 hours in high temperature environment at 520 K. The red data represent the thermocouple temperature, and the blue data correspond to the phosphor temperature. The first green point is the mean phosphor temperature with standard deviation between 6 to 14 hours (marked by first two dashed black lines). The other green point is the mean phosphor temperature with standard deviation during the last 2 hours (marked by last two dashed black lines).

The first green point in figure 32 is the mean phosphor temperature between 8 to 15 hours (marked by two dashed black lines). The value of this point is 525.1 K with standard deviation is 2.5 K, while the value of the other mean point is 523.5 K with standard deviation of 1.6 K. The reference thermocouple mean temperature is 519.6 K and 519.9 K respectively. The thermocouple temperature only changes 0.3 K. So the thermocouple indicates that the oven temperature has not changed particularly during the 8 hour to 25 hour time interval. The phosphor may have changed its lifetime corresponding to the mean temperature changes 1.6 K. But the error bar of these two mean temperature points are overlapping which means the change of phosphor is probably not significant.

The mismatch of phosphor temperature and thermocouple temperature of figure 32 is due to this measurement is done by *window setup*. It means the thermocouple temperature was read out by using a *window setup system*, while the phosphor temperature analysis was performed using an *automatic calibration where no windows were present*. The positions of these two glasses windows are shown in figure 11. The two windows block cold room air going into the oven, so that the oven temperature is more stable. Both phosphor and thermocouple are feeling the same temperature for *no window setup* calibration. But the temperature in the oven gets

hotter if windows are applied. The following assumption is used to explain why the thermocouple temperature is lower than phosphor temperature:

For *non-window calibration measurement*, thermocouple temperatures and corresponding phosphorescence lifetimes are:

$$\begin{array}{l} T_1 \xrightarrow{\text{Corresponds}} \tau_1 \\ T_2 \xrightarrow{\text{Corresponds}} \tau_2 \end{array} \quad (1)$$

where $T_1 < T_2$

For *window measurement*, a thermocouple temperature and corresponding phosphorescence lifetime is:

$$T_1 \xrightarrow{\text{Corresponds}} \tau_2 \quad (2)$$

where T_1 is temperature, and τ_2 is lifetime.

By using calibration result (1), τ_2 gives temperature information T_2 which is bigger than thermocouple temperature information T_1 . It leads to the mismatch between thermocouple temperature and the phosphor temperature during the *window measurement*.

4.3.3.2 Laser Induced Heating

In order to know whether the laser induced heating will affect the calibration result, 1 mJ and 5 mJ laser energies are test separately upon a phosphor coated test target. First, the pulsed Nd:YAG laser was run at 5 mJ energy, which is the maximum laser energy for around 7 minutes at 327 K oven temperature. During this process, both thermocouple temperature and phosphor waveform was recorded. After that, the laser was turned off allowing the sample in the oven to cool down from the laser induced heat. This process had been repeated three times. Figure 33 shows thermocouple temperature trends of these repeated three times with 5 mJ laser energy.

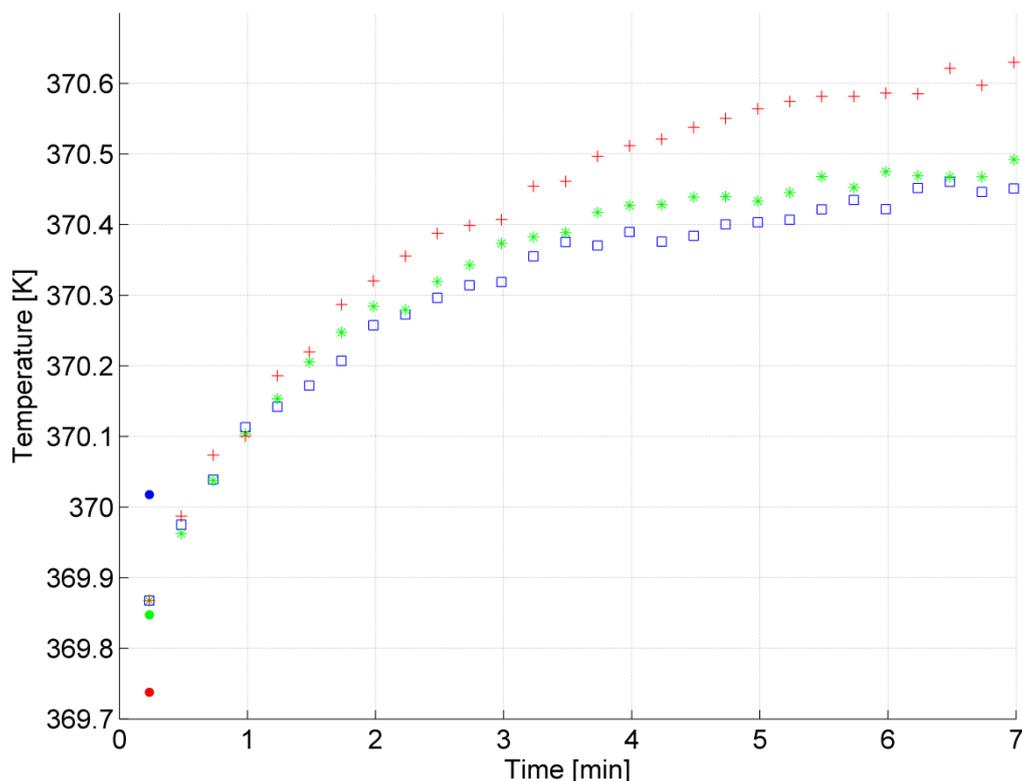


FIG.33: Thermocouple temperatures within 7 minutes of 5 mJ laser energy exposure during three measurements. These three measurements were shifted at the same start point, which is the mean start temperature of these three measurements. Original point means the real start temperature of each measurement, marked by filled dots.

The thermocouple temperature trends of these three measurements are almost the same. It means that 5 mJ laser energy induces the same heat. Figure 34 shows how the phosphor temperature is increased by 1 K by the laser induced heating at 5 mJ laser energy. At high temperature environment, the temperature difference between the inside of the oven and the surrounding air temperature is bigger. Heat exchange takes place faster to reach equilibrium. So if the oven temperature increases the laser induced heating effect will be reduced.

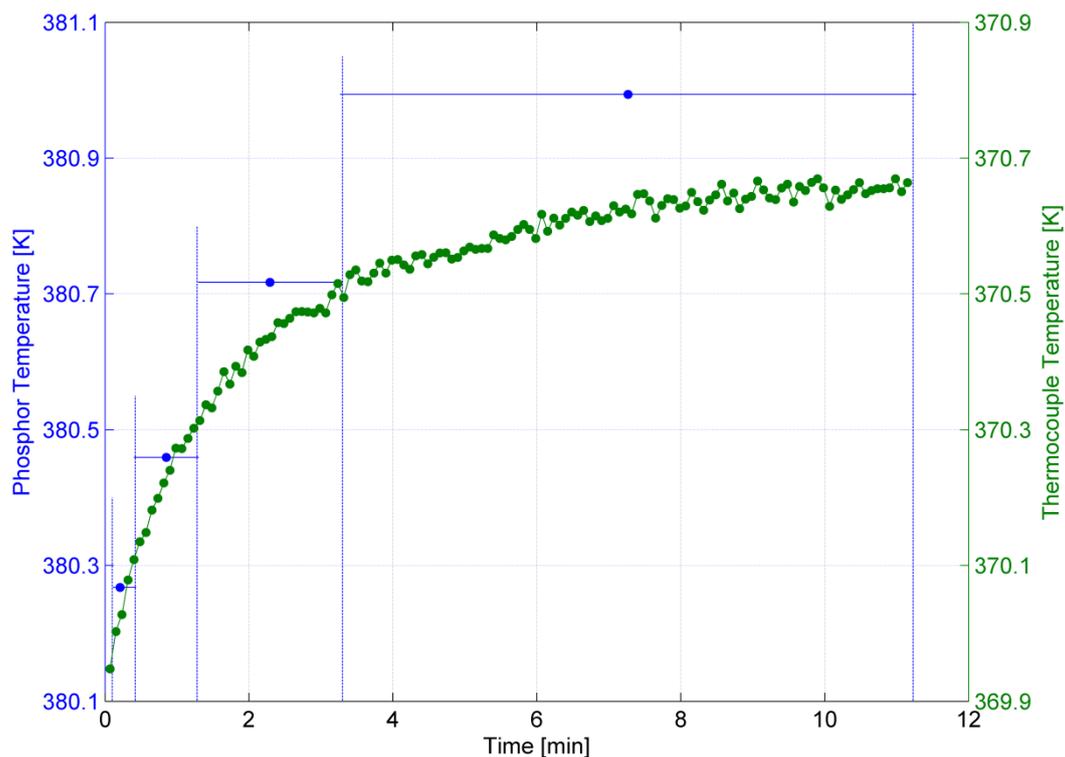


FIG.34: Thermocouple temperature and phosphor temperature is shown as a function of time while being exposed to 5 mJ laser energy. The green points are the thermocouple temperature data and the blue points are the mean temperatures of the phosphor data at certain time range. Each time range is marked by two blue dash lines.

In another experiment, the CdWO_4 phosphor calibration is done using 1 mJ laser energy. According to figure 35, for 1 mJ laser energy, the overall temperature change is in the order of 100 mK only and no clear dependence on the laser interaction time could be found. The trends rather relate to oscillations originating from the active temperature control in the oven that tries to maintain a steady temperature by regulating the heating current.

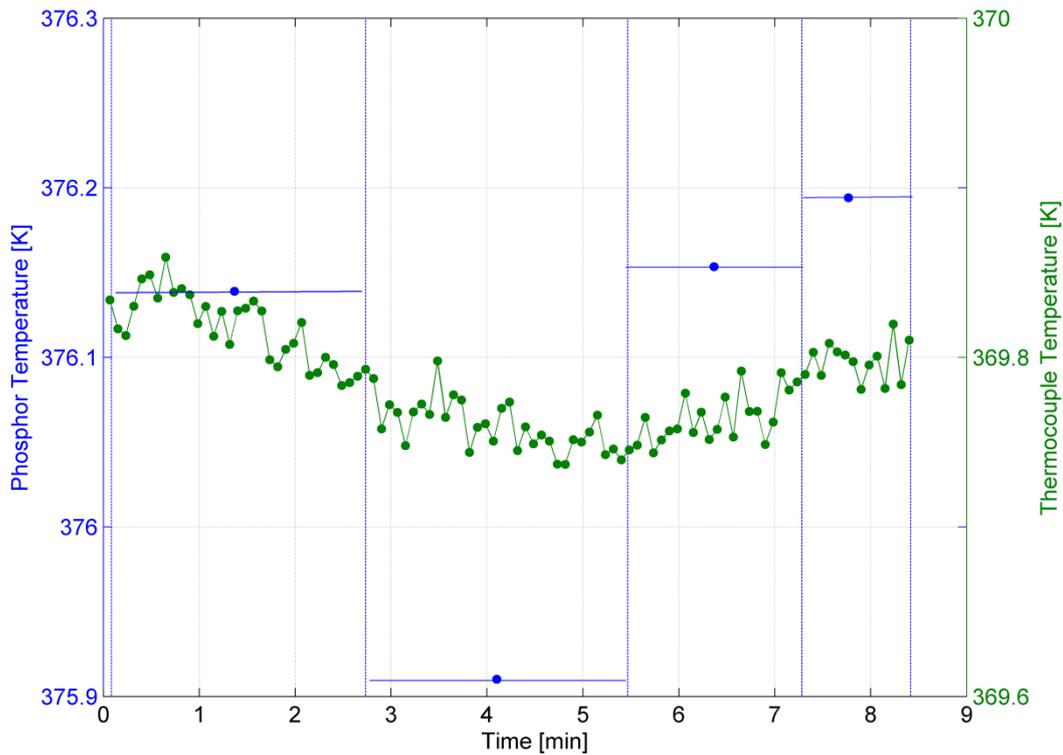


FIG.35: Thermocouple temperatures and phosphor temperatures are shown within a 9 minutes time interval of 1 mJ laser energy exposure. The green points are the thermocouple temperature data and the blue points are the mean temperature of phosphor from of corresponding time ranges. Each time range is marked by two blue solid lines.

4.3.4 Effects of Experiment Operation Parameters

Figure 30 shows that the phosphor temperature does not follow the thermocouple temperature in the same way. Such as the figure 30 (a) shows that the phosphor temperature is higher than thermocouple temperature, while the figure 30 (d) shows the opposite way. Before operating the experiment system for each measurement process, we first adjusted gain of PMT, and energy of laser manually. It causes laser energies and peak values to be different for four oscillation processes. The peak value means the peak voltage of phosphorescence signal which is displayed on the oscilloscope.

In order to find out if different laser energies, or different the peak values could cause different relations of phosphor and thermocouple temperatures, five measurements were done keeping laser energy constant, and the other five measurements were done by keeping the PMT peak voltage constant. However, it is impossible to adjust the laser power and peak value to be completely constant, due to the energy of running laser slightly fluctuating. Table 2 shows the experimental parameters of each measurement. No.1 to No.5 measurements were done by keeping laser energy constant which was set around 1.00 mJ, shown in table 2: laser energy before

measurement (mJ). And No.6 to No.10 were done by keeping peak value constant which was set around 39.0 mV, shown in table 2: peak intensity (mV).

TABLE2: The experimental parameters of 10 different measurements.

No. of measurement	Laser energy before measurement (mJ)	Laser energy after measurement (mJ)	Gain of PMT	Peak intensity (mV)
1	0.99	1.00	3.5	35.7
2	1.04	1.01	3.5	37.5
3	1.01	1.08	3.5	36.5
4	0.98	0.93	3.5	36.0
5	1.01	0.95	3.5	38.8
6	1.15	1.20	3.5	39.7
7	1.12	1.15	3.5	39.3
8	1.11	1.07	3.5	37.8
9	1.10	1.07	3.5	39.1
10	1.01	0.90	3.5	38.7

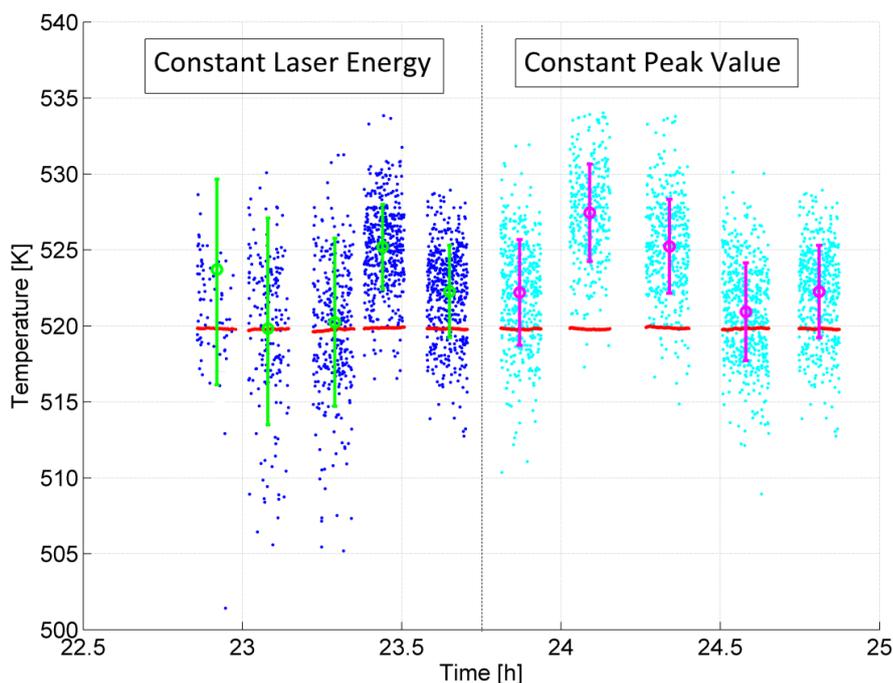


FIG.36: The left 5 measurements are done by constant laser energy. The right 5 measurements are done by constant peak value. Red points are thermocouple temperatures, the first five sets of blue points and last five set of cyan points are phosphor temperature data. Meanwhile, the green and magenta dots are the mean temperature of each set of phosphor temperature, with their standard deviation as an error bar.

The No. of measurement 1 to 10 are corresponding to each set of data and mean value of figure 36 from left to right. All mean values should be almost the same for all

different measurements, since the oven temperature is kept at constant temperature. But according to figure 36, keep the laser energy constant or peak voltage constant, even though the mean values are random. So we can't conclude that the different laser energies and different peak values affect or do not affect the phosphorescence lifetime.

5. Conclusion and Outlook

The *automatic calibration* is faster and more accurate than the *conventional calibration*. The speed of automatic calibration is not infinitely fast. For this work, the oven speed (max 4 K/min) is the main limitation.

Additionally, some factors which may affect the accuracy of the *automatic calibration* are examined: long time exposure in high temperature environment for CdWO₄, laser induced heating, and comparison of the phosphor response and thermocouple response. These factors did not significantly affect the calibration result. Some unknown factor(s) lead to the phosphor temperature sometimes above and sometimes below the thermocouple temperature.

According to this thesis work, there are several directions for further studies. First of all, as mentioned before, a *cutoff window* in a LabVIEW program is used to determine which part of original acquiring waveform is extracted as phosphorescence decay. And the phosphorescence lifetime then is evaluated from the decay curve. It means how to define the cutoff window will affect the value of lifetime. Figure 9 shows a typical *cutoff window*, the start point and the end point of window are the green points. The *cutoff window* which is defined in this thesis is relatively a good way. The start of cutoff window is the point of 6 ns after laser peak, and the end of it is the first point below certain percentage of initial phosphorescence intensity. The percentage is determined by LabVIEW program user. However, it is not a perfect way to define the cutoff window, because it does not only depend on the characteristic of the waveform which is the intensity is exponential decay, but also depends on the noise level of the waveform.

Moreover, to achieve the *automatic calibration*, the LabVIEW interface is introduced. Although LabVIEW is useful to synchronously recording the temperature and acquiring phosphorescence decays, the while loop is used in our LabVIEW program. Due to loop structure is slow, the speed of this LabVIEW program is slowed down by using while loop structure. LabVIEW needs all kinds of loops where other program just as MATLAB can have smarter algorithms for example to create a vector. And the LabVIEW software is installed on the digital oscilloscope, LeCroy WaveRunner 6030A. The configuration of the oscilloscope is not very high, such as CPU, Memory and hard disk. And the oscilloscope always runs LabVIEW program with acquiring the waveform. The LabVIEW program speed is limited by the oscilloscope low configuration. Actually, one way to solve this problem is to install the LabVIEW on another computer. By changing the LabVIEW connection way, LabVIEW can be used to control the oscilloscope acquiring wave.

At this thesis work, the *automatic calibration* actually is not completely automatic. The oven increasing temperature speed is not stable during the whole measurement. So we should adjust the oven speed during the whole measurement when the speed

changed. Further study can find out a way to make the oven increasing temperature speed is kept the same throughout the whole measurement.

Appendix I Program Documentation

The LabVIEW program does not only acquire waveforms and temperature, but pre-processes the waveforms as well. The flow chart, figure A1, clearly shows what this program does.

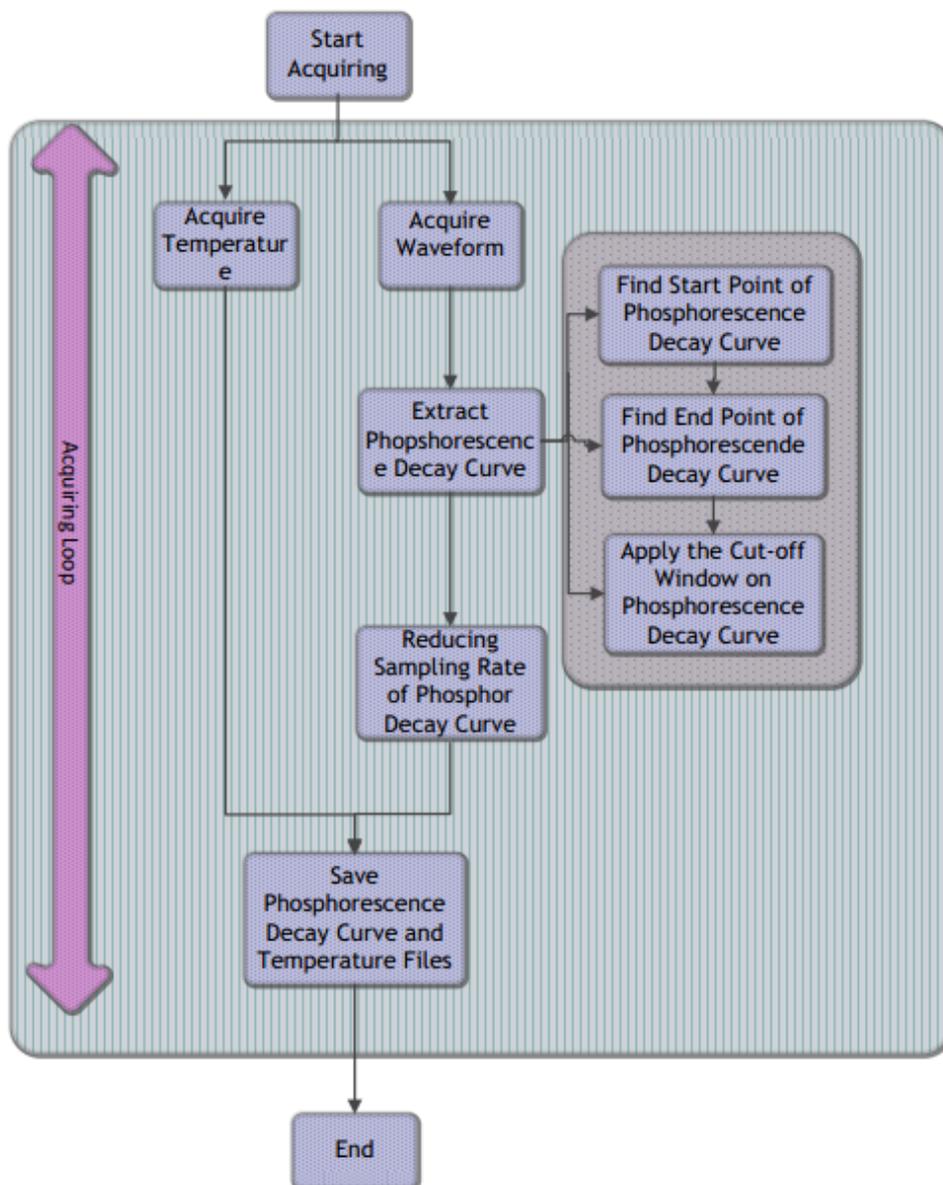


FIG A1: The flow chart of LabVIEW program.

The figure A2 shows the front panel of LabVIEW program, called *Phosphor Project*. One part is referred as *Oscilloscope Controls*, which acquires the phosphor decay curves. To acquire the phosphor decay curve from the oscilloscope, the *VISA Resource name* should be set to 'LCRY0604P17643' for this oscilloscope communication. *Source* and *Timeout* specifies the trace channel and minimum timeout setting to read one channel from the instrument. The residual two buttons *Reset?* and *Perform Auto Setup?* are used for the initial test. They control to *True*, and then run the VI to find the signal. Leave both set to *False* (light is off and button is dark green)

for subsequent runs.

As mentioned earlier, this program does not only acquire the oscilloscope curves, but also deals with the curve as well. This part is referred as *Waveform Parameter Controls*. *Set Cutoff-time after Peak(ns)*, *Set last Vector Element to save as a Fraction of the Cutoff Value(%)* and *Data points after Cutoff (samples)* determines how to cut and modify the original acquired curve, which is the phosphor decay curve that can be evaluated later. *Set Cutoff-time after Peak(ns)* is used to determine where is the first point to cutting the original waveform. If this is set to 6 ns, it means the start point is the first point 6 ns after the waveform intensity peak. *Set last Vector Element to save as a Fraction of the Cutoff Value(%)* is used to determine where is the last point to cutting the original waveform. If this is set 0.5, it means the first point whose value is smaller than $0.5\% * I_0$, the I_0 is the intensity of original waveform. Due to the first and last points are determined, the original waveform is cutting to a new decay curve with enough phosphorescence lifetime information. *Data points after Cutoff (samples)* is used to determine how to sparse the cut decay curve.

The DAQ board reads the temperature of the oven. And the acquiring temperature speed (max speed is 3 temperatures/second) can be changed from the DAQ Assistant setting from Block Diagram. *Maximum Heating Rate (°C/min)* is used to trigger a warning in case the real speed goes higher than the value specified here. *Rate of T(Hz)* controls the thermocouple acquiring data rate.

For further evaluation, the temperatures and all curves during a measurement should be saved. *Time Interval between 2 Files(s)* specifies the saving speed and *Save Data* is a button to control saving files. When this program is running, pressing the *Stop Program* button will stop running it. And *File Path of Waveform* and *File Path of Temperature* specify the file paths of saving data by the user.

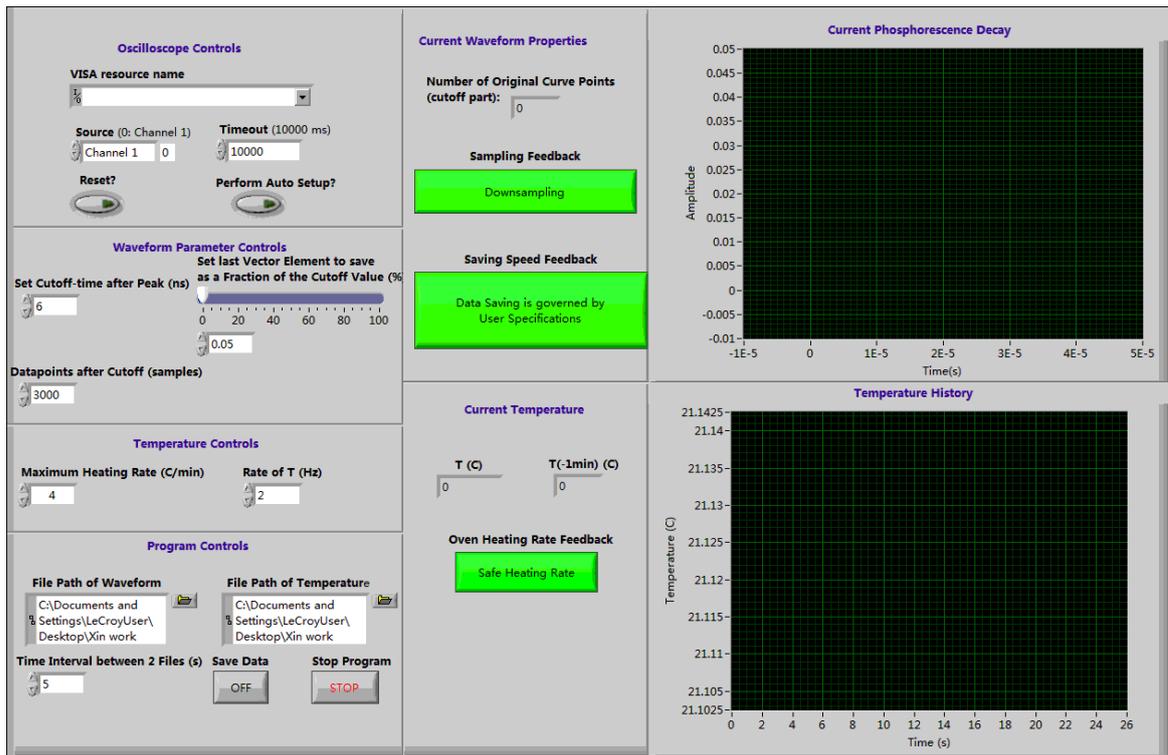


FIG A2: The front panel of Phosphor Project.vi

Appendix II LabVIEW Program for Automatic Measurement

The automatic measurement is controlled by a LabVIEW program, which is called 'Phosphor Project.vi'. This program acquires oven temperature from DAQ board which is contacted with a thermocouple and oscilloscope waveform at the same time. Moreover, this program only saves phosphor decay information from original waveforms. This LabVIEW program contains a LeCroyScope driver which is used to acquire waveforms from oscilloscope offered by National Instruments, and lots of subVIs which are used to extract phosphorescence decay curve. The details of the subVIs are described as follows:

Deal with original waveform (SubVI).vi deals with the oscilloscope waveform in a specific way. At first, the noise level and laser peak of the curve is captured, and the phosphorescence decay curve is extracted and sparsed according to the users input parameters. And the rest part of the waveform is thrown away. The thrown part only contains noise points which come after phosphorescence decay goes down to noise base line. There are seven subVIs, *Set zero base line (SubVI)*, *Filter & Baseline (SubVI)*, *Set Filter Peak Zero (SubVI)*, *Get first part of original curve (SubVI)*, *Set Peak Zero Original (SubVI)*, *Set start of cutoff window (SubVI)*, and *Set and modify cutoff curve (SubVI)*. The details of them are described below.

Set zero base line (SubVI) helps user to adjust the curve to a zero base line. The zero base line is determined like this: the mean value of last 20 points of the curve which are noise level points are set as zero.

Filter & Baseline (SubVI) filters the part of original curve. Filtered part of original curve is from peak to end of it. The filter type here is set 'Smoothing' and filter specifications is set 'Moving average'-'Rectangular'-'Half-width of moving average: 50'. This means the original curve is filtered by smoothing filter with FIR (Finite Impulse Response) method. And for a half-width of 50, the full width of the moving-average filter is $1+2 * 50=101$ samples.

However, the intensity of filtered curve becomes smaller comparing with original curve, so that the filtered one shifts in vertical direction. As the filtered and original curves should overlap for determining cutoff window, this program also adjusts the filtered curve in a zero base line. The zero base line is determined like in this way: the mean value of last 20 points of the curve which are noise level points are set as zero.

Set Filter Peak Zero (SubVI) and *Set Peak Zero Original (SubVI)* sets peak of filtered curve and peak of original curve to zero which is referred to as time. So that these two curves will match each other in horizontal direction.

Get first part of original curve (SubVI) separates the curve into two parts. The first part of the curve composes the all noise points before phosphorescence comes and

laser peak. The other part is all rest points of the waveform.

Set start of cutoff window (SubVI) determines where the start point of the cutoff window is. This cutoff window is used to determine the time between when the phosphorescence comes and when it decays to zero level.

The phosphorescence comes after the laser excitation, a certain delay time should be considered as when phosphorescence decay curve starts. Different phosphor samples and experimental environment lead to different decay times, the user should set it in front panel in specific situation. In this automatic calibration, 6ns is used for separating the laser peak and when phosphorescence comes.

Set and modify cutoff curve (SubVI) determines how to set the cutoff window and modify this cutoff curve to keep less points. The start of window point is determined by *Set start of cutoff window (SubVI)*. The end of this cutoff window is determined by a parameter: Set last vector element to save as a fraction of the cutoff value (%).

Ideally, the end of this cutoff window should be a point which equal to the percentage, Set last vector element to save as a fraction of the cutoff value (%), multiplying with I_0 . However, due to noise effect, it is hard to find a right point to satisfy this condition. Considering the first point less which is than $X\%I_0$ in original curve is used as end of cutoff window, this point always comes too early before the phosphorescence drop to zero due to noise effect. As filtered curve reduce noise effect, the first point less than $X\%I_0$ from smoothing filtered curve is found instead.

The horizontal length between this point and start of window point is phosphorescence decay time. So apply this time at original curve to find the point for end of cutoff window. This SubVI is composed by four SubVIs, *Set end of cutoff window value (SubVI)*, *Cutoff end index (SubVI)*, *Get the cutoff curve (SubVI)*, and *Keep less points of cutoff curve (SubVI)*. The details of these four subVI are described below.

- a) *Set end of cutoff window value (SubVI)* determines value of cutoff window for filtered curve.
- b) *Cutoff end index (SubVI)* gives the length of cutoff window from filtered curve.
- c) *Get the cutoff curve (SubVI)* determines the cutoff window for original curve.
- d) *Keep less points of cutoff curve (SubVI)* modifies the cutoff part of original curve by keeping the same shape of curve with less points. If the number of points is less than user's setting, all points will be kept.

Acquiring the oven temperature is another important part of this LabVIEW program. The temperature is recorded from DAQ Assistant. Before measurement, DAQ Assistant should be set suitable parameters, such as input range of thermocouple, thermocouple type and record rate. The Figure A3 shows the setting of DAQ Assistant.

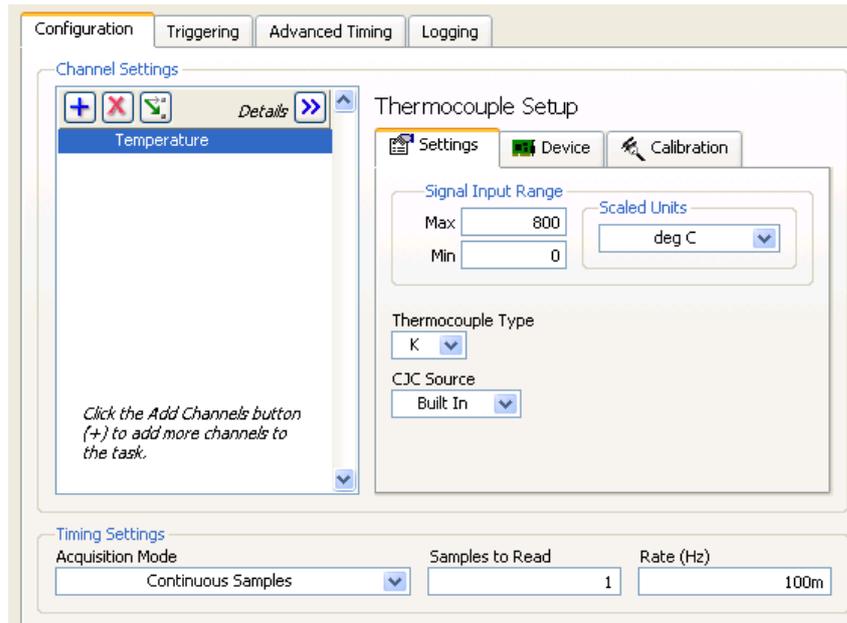


FIG A3: Setting of DAQ Assistant for Phosphor Project.vi.

Saving files is another important function of this LabVIEW program due to later evaluation. Both the temperature recording and modified curve array would be saved as txt-files. Users can specify their way of saving temperatures by double-clicking the *Write To Measurement File* button.

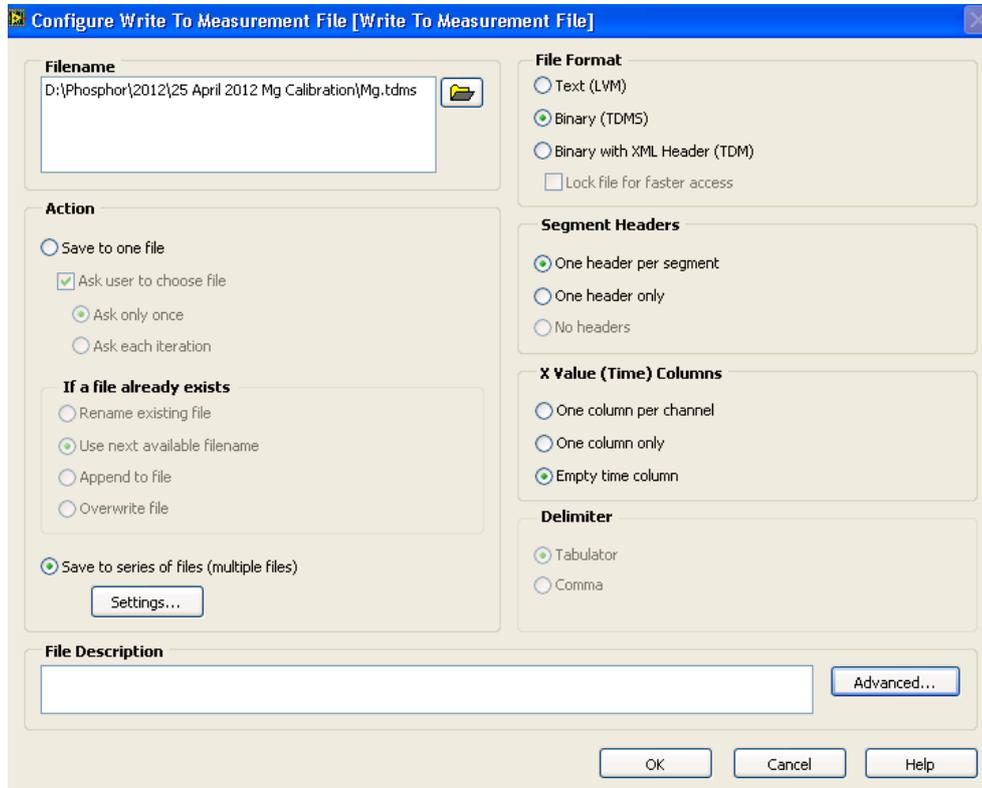


FIG A4: Specific saving files way.

Appendix III Specification of Automatic Measurement

For this automatic measurement, some parameters should be set to successfully extract CdWO_4 phosphorescence decay curve and make sure that the oven heating speed is within a safe region (max 4 K/min). As these parameters might influence the outcome of obtained measurement data, all program parameters used during this work are summarized below.

The parameters for filter are shown:

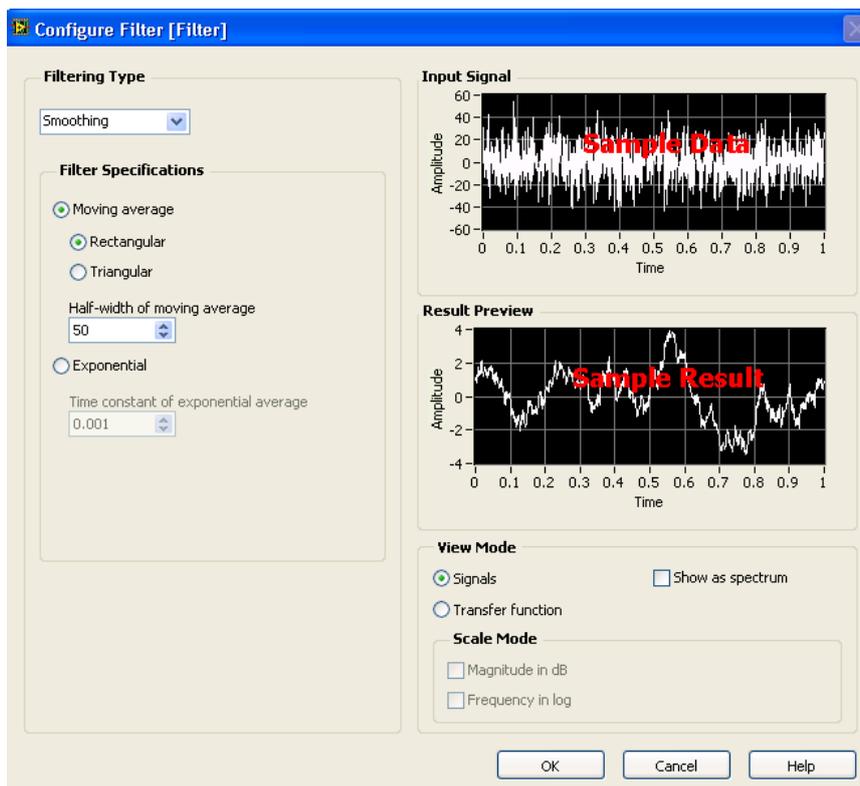


FIG A5: Filter setting for both CdWO_4 phosphor and $\text{Mg}_4\text{FGeO}_6:\text{Mn}$ automatic measurements.

The parameters in Front Panel of Phosphor Project.vi are shown:

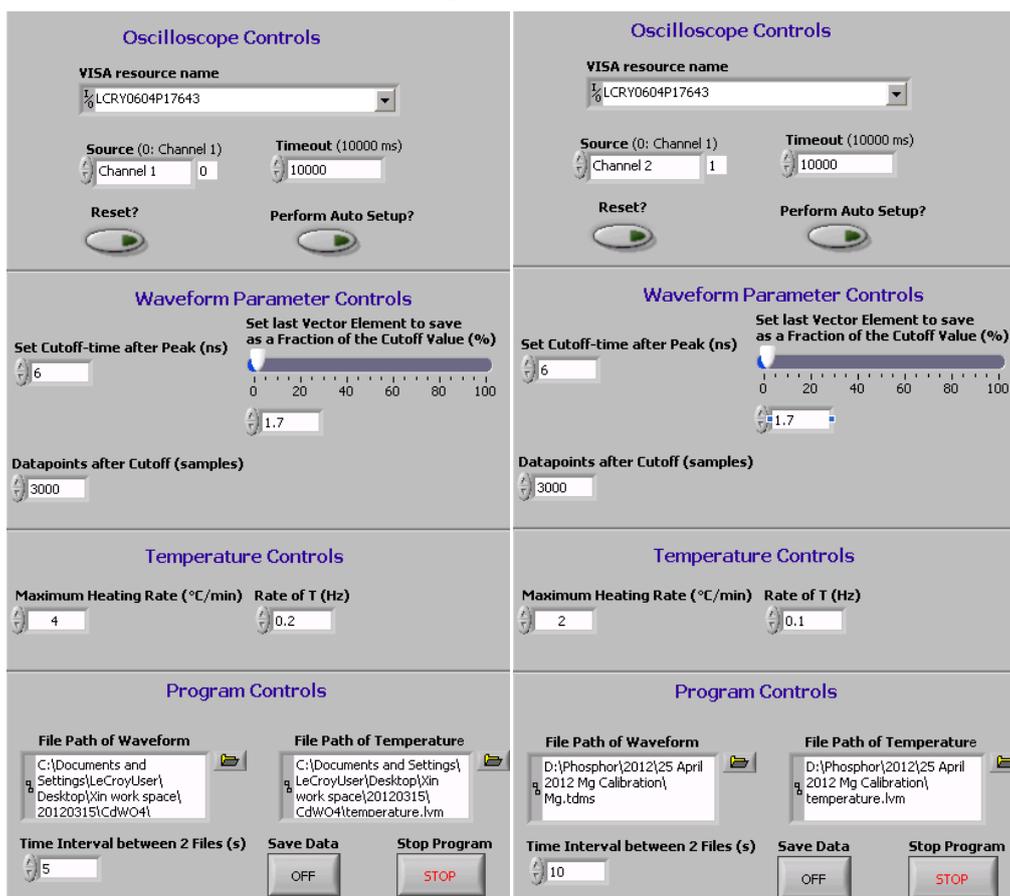


FIG A6: The parameters in Front Panel of Phosphor Project.vi. The left figure is for CdWO₄ phosphor calibration and right figure is for Mg₄FGeO₆:Mn phosphor calibration.

The parameters for DAQ are shown:

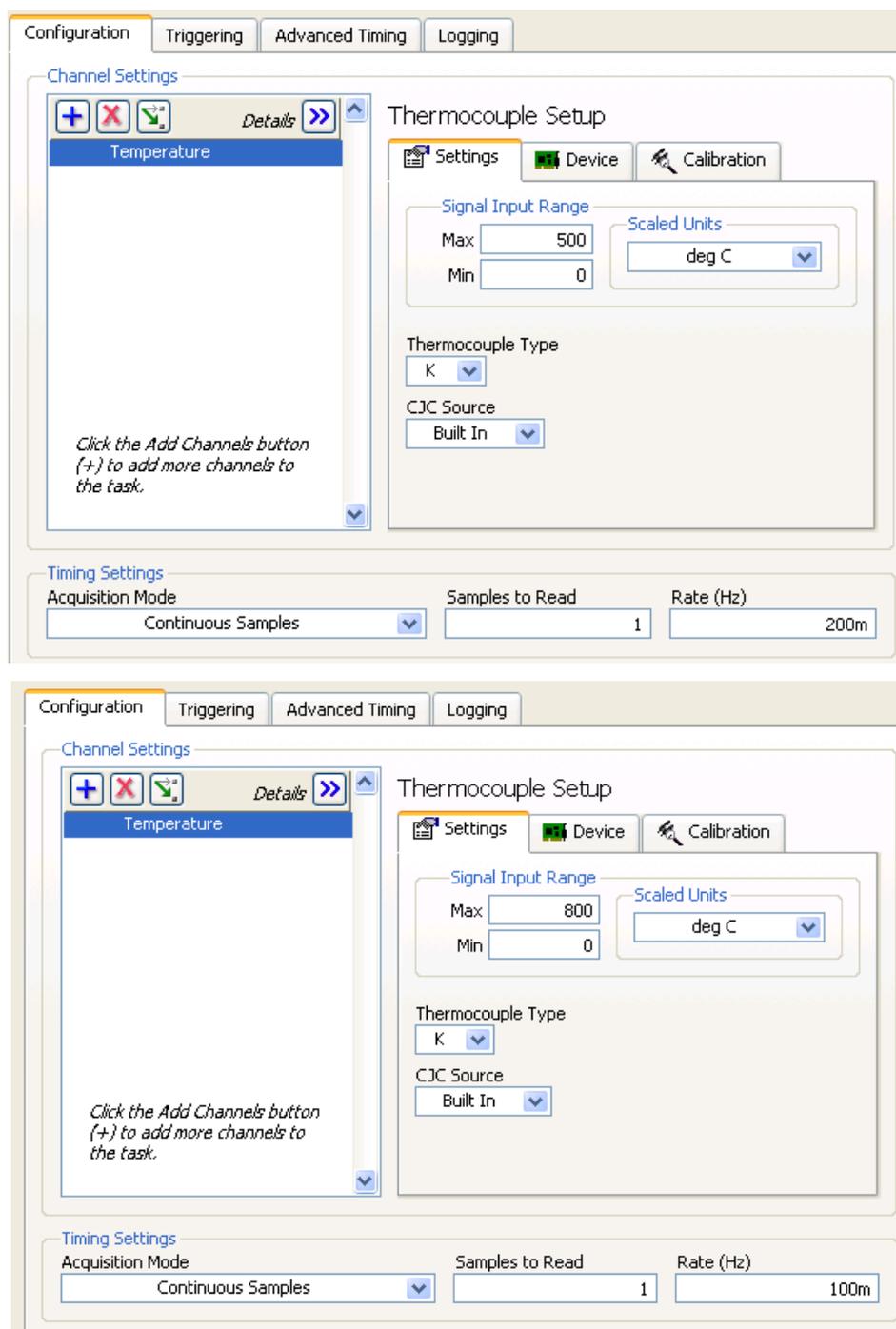


FIG A7: The parameters for DAQ board. The upper one is for CdWO_4 phosphor calibration and lower one is for $\text{Mg}_4\text{FGeO}_6:\text{Mn}$ phosphor calibration.

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