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**Development of a Thermoluminescence -
Radioluminescence Spectrometer**

(Desenvolvimento de um Espectrômetro de
Termoluminescência - Radioluminescência)

Ribeirão Preto - SP

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LEONARDO VINÍCIUS DA SILVA FRANÇA

**Development of a Thermoluminescence -
Radioluminescence Spectrometer**

Dissertation presented to Faculty of Philosophy, Sciences and Literature of the University of São Paulo, as part of the requirements for acquirement the grade of Master of Sciences.

Concentration area:

Applied Physics to Medicine and Biology

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“Our mouths were filled with laughter, our
tongues with songs of joy. Then it was said
among the nations, ‘The Lord has done great
things for them’.”

Psalms 126:2-3

RESUMO

FRANÇA, L. V. S. **Desenvolvimento de um Espectrômetro de Termoluminescência - Radioluminescência**. 2018. 83 f. Dissertação (Mestrado - Programa de Pós-Graduação em Física Aplicada à Medicina e Biologia) - Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Ribeirão Preto - SP, 2018.

Nesse trabalho, inicialmente as técnicas de radioluminescência (RL) e termoluminescência (TL) são apresentadas. A radioluminescência é a luminescência imediata emitida por um material quando exposto à radiação ionizante. A termoluminescência é a luminescência emitida por um material previamente exposto à radiação quando este é aquecido. Conceitos de bandas de energia, defeitos em cristais e os diferentes processos de ionização que ocorrem na matéria quando exposta à radiação ionizante são brevemente discutidos a fim de apresentar os mecanismos envolvidos na RL e TL. A utilização das técnicas na caracterização de materiais e na dosimetria é reportada, justificando a importância do instrumento desenvolvido.

As partes mecânicas/estruturais e uma descrição de cada componente do instrumento são descritos. O algoritmo implementado para controle do instrumento e aquisição de dados é também descrito. O desenvolvimento do instrumento possibilitou a geração de rampas de temperatura com uma boa performance, atingindo até 500°C com variações de até 2°C ao utilizar taxas de aquecimento entre 0.5°C/s e 5°C/s. Calibrações do espectrômetro óptico utilizado na aquisição da luminescência e do sistema de irradiação foram executadas. Por fim, testes de aquisição de espectros de RL e TL foram realizados. Os testes de RL foram realizados utilizando vários materiais cujos espectros de emissão são bem conhecidos pela literatura, a saber, óxido de alumínio dopado com carbono $\text{Al}_2\text{O}_3\text{:C}$, oxissulfeto de gadolínio dopado com

térbio $\text{Gd}_2\text{O}_2\text{S:Tb}$, óxido de ítro dopado com európio $\text{Y}_2\text{O}_3\text{:Eu}$ e borato de cálcio dopado com disprósio $\text{CaB}_6\text{O}_{10}\text{:Dy}$. Para o teste dos espectros de TL, o $\text{Al}_2\text{O}_3\text{:C}$ foi utilizado. Os resultados dos espectros de RL e TL mostraram concordância com a literatura, indicando que o instrumento desenvolvido é comparável a outros instrumentos em operação de outros grupos, tornando os nossos resultados confiáveis.

Palavras-chave: 1. Termoluminescência. 2. Radioluminescência. 3. XEOL. 4. Espectroscopia. 5. Controle de Temperatura. 6. Cintiladores. 7. Dosimetria.

ABSTRACT

FRANÇA, L. V. S. **Development of a Thermoluminescence - Radioluminescence Spectrometer**. 2018. 83 f. Dissertation (M.Sc. - Postgraduate Program in Applied Physics to Medicine and Biology) - Faculty of Philosophy, Sciences and Literature, University of São Paulo, Ribeirão Preto - SP, 2018.

In this work, initially the radioluminescence (RL) and thermoluminescence (TL) techniques are presented. The radioluminescence is the prompt luminescence emitted by a material under ionizing radiation exposure. The thermoluminescence is the luminescence emitted by a material previously exposed to ionizing radiation when excited by heat. Energy bands concepts, defects in crystals and the different processes of ionization that take place in matter when exposed to ionizing radiation are briefly discussed in order to present the mechanisms involved in RL and TL processes. The usage of the techniques in characterization of materials and dosimetry is reported, legitimating the importance of the instrument developed.

Mechanical and structural parts as well as a description of each component of the instrument are fairly described. The implemented algorithm for controlling the instrument and acquiring data is also discussed. The development of the instrument enabled us to generate temperature ramps with a quite good performance, reaching temperatures up to 500 °C with deviations up to 2 °C, having used heating rates between 0.5 °C/s and 5 °C/s. Calibrations of optical spectrometer used in light collection and irradiation system were carried out. Lastly, TL and RL spectra tests were performed. The RL tests were carried out using several materials which emission spectra are well known by literature, namely, carbon-doped aluminium oxide $\text{Al}_2\text{O}_3\text{:C}$, terbium-doped gadolinium oxysulphide $\text{Gd}_2\text{O}_2\text{S:Tb}$, europium-doped yttrium oxide $\text{Y}_2\text{O}_3\text{:Eu}$ and dysprosium-doped calcium borate $\text{CaB}_6\text{O}_{10}\text{:Dy}$. For the

TL spectra test, the aluminium oxide doped with carbon $\text{Al}_2\text{O}_3\text{:C}$ was used. The results of RL and TL spectra tests showed a good agreement with the literature, pointing out that the instrument developed in this work is comparable to others instruments in operation from others research groups, making our results reliable.

Key-words: 1. Thermoluminescence. 2. Radioluminescence. 3. XEOL. 4. Spectroscopy. 5. Temperature control. 6. Scintillators. 7. Dosimetry.

CONTENTS

List of Figures	xiii
List of Tables	xvi
Acronyms	xvii
1 Introduction	1
2 Radioluminescence and Thermoluminescence: theoretical aspects	5
2.1 Interaction of ionizing radiation with matter	5
2.2 Energy bands, defects on crystals and a RL mechanism	8
2.3 A kinetic model for RL phenomenon	10
2.4 A thermoluminescence model	12
3 The Thermoluminescence-Radioluminescence Spectrometer Construction	19
3.1 Instrument modelling and design	19
3.2 Heating system	22
3.3 Light collection system, irradiator and environment shielding	25
3.4 Data acquisition and control software	26
4 Results and discussions I: Temperature ramps and plateaus	29
4.1 Inspection of temperature measurements	29
4.2 Temperature control: ramps and plateaus	32
5 Results and discussions II: Feasibility of RL and TL spectra	41
5.1 Wavelength calibration and spectral resolution	41

	xii
5.2 X-ray tube calibration	45
5.3 Radioluminescence tests	46
5.3.1 Radioluminescence versus integration time	50
5.4 Implementations on λ -TL software	53
5.5 λ -TL spectra test	56
6 Conclusions and future perspectives	60
6.1 Further steps	60
References	67

LIST OF FIGURES

1.1	Example of the usage of an intensifying screen in a radiographic imaging procedure	1
1.2	The most important inorganic scintillator materials discovered before 2003	2
1.3	Some key thermoluminescent materials commercially used in different applications.	4
2.1	Total photon linear attenuation coefficient, defined as the fractional change in the number of photons per unit thickness of material transversed (ICRU, 1998d), and attenuation coefficient due to various interaction processes in water calculated using the database from the US National Institute of Standards and Technology (Hubbell and Seltzer, 2004).	6
2.2	Radioluminescence mechanism for materials with high band-gap and having a large number of defects in the crystal lattice	9
2.3	The energy level diagram of two electron trapping states and two types of hole recombination centers.	11
2.4	Scheme showing the trapping of the charge carriers after the irradiation and the following thermal excitation and light emission, in the OTOR model	14
2.5	Profiles of trapped electron population n , probability p of excitation and the glow curve as a function of T during heating.	15
2.6	Change in temperature at TL peak T_m of glow curves with change in activation energy trap E	16
2.7	Change in temperature at TL peak T_m with change in frequency factor s	17

2.8	Change in glow curves with change in heating rate β	17
3.1	Design of the TL-RL spectrometer	20
3.2	Flowchart showing the modes of operation of the TL-RL spectrometer	21
3.3	Design of the heating planchet	22
3.4	Thermocouple probe inserted on the heating planchet	23
3.5	Circuit diagram of the electronic components	24
3.6	(a) <i>Ocean Optics</i> spectrometer, model <i>USB2000</i> . (b) <i>Moxtek</i> x-ray tube	25
3.7	<i>USB2000</i> spectrometer, <i>Ocean Optics</i> with components	26
4.1	Digital thermometer used for the temperature calibration of the TL- RL spectrometer	30
4.2	(a) Temperature calibration curve of the TL-RL spectrometer. (b) Measurement of room temperature for testing the cold junction com- pensation	31
4.3	Temperature ramp using a proportional gain of 5	33
4.4	(a) Temperature ramp using a proportional gain of 30. (b) Temper- ature ramp using a integral time of 0.5 min.	34
4.5	Temperature ramp using a derivative time of 0.1 min.	35
4.6	(a) Temperature ramp using a rate of 0.5 °C/s. (b) Temperature ramp using a rate of 1 °C/s.	36
4.7	(a) Temperature ramp using a rate of 3 °C/s. (b) Temperature ramp using a rate of 5 °C/s.	37
4.8	Temperature plateau at 500 °C	39
5.1	Mercury-Argon calibration source <i>HG-1 Ocean Optics</i> . Model used in the wavelength calibration	42
5.2	Spectral lines from HG-1 calibration source.	43
5.3	(a) Correlation between HG-1 and recorded wavelengths. (b) Plot showing the wavelength shifts for the five lines recorded.	44
5.4	Calibration of X-ray source.	45

5.5	Examples of $\text{Al}_2\text{O}_3\text{:C}$ dosimeters in pellet and film shapes used in RL measurements as well as TL spectra acquisition	46
5.6	Radioluminescence spectrum of the aluminium oxide doped with carbon dosimeter	47
5.7	RL spectrum of $\text{Gd}_2\text{O}_2\text{S:Tb}$ phosphor.	48
5.8	RL spectrum of $\text{Y}_2\text{O}_3\text{:Eu}$ phosphor	49
5.9	RL spectrum of $\text{CaB}_6\text{O}_{10}\text{:Dy}$ phosphor	50
5.10	Radioluminescence spectra of $\text{Al}_2\text{O}_3\text{:C}$ dosimeters for different integration times	51
5.11	(a) Radioluminescence spectra amplitudes of $\text{Al}_2\text{O}_3\text{:C}$ dosimeters for different integration times. (b) RL spectra amplitudes of a $\text{Al}_2\text{O}_3\text{:C}$ dosimeter over 30 s of acquisition time	52
5.12	Interface of the software implemented in <i>Labview</i> for collecting λ -TL spectra	54
5.13	Table showing how λ -TL spectra data is saved	55
5.14	Single spectrum of $\text{Al}_2\text{O}_3\text{:C}$ λ -TL spectra corresponding to the highest TL emission (182°C)	57
5.15	λ -TL $\text{Al}_2\text{O}_3\text{:C}$ expressed as a 3D contour map	58
5.16	Contour map plot showing the emission spectra of blackbody radiation from heating planchet	59
6.1	Example of linear variable bandpass filter, 400-700 nm range, that will be used in the development of the new optical spectrometer . . .	61
6.2	(a) Modelling of the new optical spectrometer. (b) Modelling seen from another angle	62

LIST OF TABLES

3.1	Components of the spectrometer <i>USB2000</i>	27
4.1	Fitting parameters of ramps generated by the temperature control software. The standard deviations for intercepts and slopes were smaller than 0.12% and 0.018%, respectively. In these results we are not taking into account the inaccuracies from thermometer, thermocouple and electronics.	38
4.2	Averages and standard deviations of the temperature plateaus at 500 °C	39
5.1	HG-1 emission lines with the corresponding recorded ones and the FWHM for each line.	43

ACRONYMS

FWHM	Full Width at Half Maximum
IR	Ionizing Radiation
Kerma	Kinetic energy released in matter
OSLDs	Optically Stimulated Luminescent Dosimeters
OTOR	One-Trap-One Recombination center
PID	Proportional Integral Derivative
RL	Radioluminescence
TL	Thermoluminescence
TLDs	Thermoluminescent Dosimeters
XEOL	X-ray Excited Optical Luminescence
λ -TL	Wavelength-resolved Thermoluminescence

INTRODUCTION

Radioluminescence is the prompt luminescence emitted by a material when exposed to ionizing radiation. Sometimes the radioluminescence (RL) is referred as X-ray excited optical luminescence (XEOL). Although not referring as radioluminescence or XEOL, the phenomenon was firstly reported at 1896, in the year following the discovery of the X-rays by Röntgen. He recognized that the X-rays could be used for screening the condition of our bones. However, he noticed that the absorption of the X-rays by photographic films was very inefficient and hence arose the need of finding a converter of X-rays to visible light which are better absorbed by radiographic films. In the same year, Thomas A. Edison found that calcium tungstate CaWO_4 among

Figure 1.1: Example of the usage of an intensifying screen in a radiographic imaging procedure. The intensifying screen as the name suggests intensify the absorption of the X-rays by the radiographic film. Extracted from [1]

more than 8000 chemicals exhibited that feature with a quite good yield of luminescence [2]. In an attempt to enhance the absorption efficiency of the radiographic films, Mihajlo I. Pupin, a physicist and Serbian immigrant in the United States of America [3], carried out a series of experiments using CaWO_4 covering the films and found that the exposure time of the films could be reduced efficiently, from one hour to a few seconds, giving rise to the well known intensifying screens [4]. Figure 1.1 depicts an example of the usage of an intensifying screen in a radiographic imaging procedure.

The emergence of the CaWO_4 in the use for enhancement of X-ray absorption by radiographic films was the first of a series of materials to be used as scintillators or X-ray phosphors. A scintillator is a radiation detector that emits light when excited by ionizing radiation. A phosphor is a solid material that converts certain types of energy in light. Depending upon the energy to be converted, the luminescence receives special names, namely, electromagnetic (often ultraviolet) radiation, pho-

Figure 1.2: The most important inorganic scintillator materials discovered before 2003. Extracted from [5]

toluminescence; beam of energetic electrons, cathodoluminescence; electric voltage, electroluminescence; mechanical energy, triboluminescence; X-rays, X-ray luminescence; energy of a chemical reaction, chemiluminescence and so on [1]. The CaWO_4 was used almost exclusively for 75 years. However this status changed with the discovery of the rare-earth phosphors in the early 1970s, enabling researchers to engineer materials with improved X-rays absorption and higher X-ray-to-light conversion efficiencies [6]. Figure 1.2 depicts the most important inorganic scintillator materials discovered before 2003.

* * *

Thermoluminescence is the luminescence induced by heat excitation of a material previously exposed to ionizing radiation. The phenomenon of thermoluminescence (TL) was possibly first reported by Robert Boyle in 1663, when he noticed a luminescence from a diamond by placing it on a warm part of his body for a while and he also observed the phenomenon when stimulated the luminescence by heating with a hot iron [7]. In spite of TL phenomenon be firstly interpreted as a direct conversion of heat into light, Du Fay, a French Chemist [8], reported in the first half of 17th century that thermoluminescence can be reactivated by light exposure and hence the heat only stimulated the luminescence [7]. Becker (1974) reported that the first careful investigation of radiation induced TL was performed by Wiedmann and Schimidt (1895) using an electron beam and was the first reported artificial type of TL, whereas the earlier observations occur on natural TL, i.e., excitation by natural radioactivity in the environment [7].

Since then many efforts have been done to develop the knowledge in this area in many applications ranging from basic science, dosimetry, archeological dating and even food irradiation [9–12]. Since the emergence of the TL and the possible applications of the thermoluminescent materials, lots of materials have been discovered as having thermoluminescent properties. Figure 1.3 depicts some key thermoluminescent dosimeters which properties have been fairly investigated. This table shows the dose range in which the dosimeters can be used and the thermal fading of each dosimeter. The thermal fading is the decrease in luminescence over the time for a

material previously irradiated, stored and protected of excitation sources.

Materials	Type of dosimeter	Useful range	Thermal fading
LiF:Mg, Ti	TLD-100	10 μ Gy–10 Gy	5–10% per year
LiF:Mg, Cu, P	TLD-100H	1 μ Gy–20 Gy	3% per year
⁶ LiF:Mg, Ti	TLD-600	10 μ Gy–20 Gy	Negligible
⁶ LiF:Mg, Cu, P	TLD-600H	Neutron sensitive 1 μ Gy–20 Gy	Negligible
CaF ₂ :Dy	TLD-200	0.1 μ Gy–10 Gy	16% total in 2 weeks
CaF ₂ :Mn	TLD-400	0.1 μ Gy–100 Gy	15% total in 3 months
Al ₂ O ₃ :C	TLD-500	0.05 μ Gy–10 Gy	3% per year

Figure 1.3: *Some key thermoluminescent materials commercially used in different applications. Extracted from [13]*

* * *

The instrument developed in this work enables us to explore the two techniques and hence the combination of them can be a multipurpose tool. This combination allows us to investigate radioluminescent or/and thermoluminescent properties and this can lead us to establish models for the trapping centers involving the luminescent processes. In addition to this, thermal quenching of RL signal can be investigated and models for different materials can be proposed. Furthermore, the knowledge of the emission spectrum can be useful to optimize the collection of light in standard light detectors. The instrument also gives us the opportunity to search for new radioluminescent materials, since their usage in real time dosimetry has been suggested [14–16].

RADIOLUMINESCENCE AND THERMOLUMINESCENCE: THEORETICAL ASPECTS

In this chapter, the radioluminescence and thermoluminescence phenomena are briefly described. The role of the ionizing radiation in the RL and TL processes is discussed. The concept of energy bands in insulator and semiconductor materials is introduced and the importance of crystal defects in RL and TL processes is presented. Some qualitative aspects of RL and TL are briefly discussed.

2.1 Interaction of ionizing radiation with matter

Ionizing radiations are characterized by having enough energy to excite and ionize atoms of matter with which they interact [17]. The interaction of ionizing radiation with matter is a process of transfer of energy and measuring this process is fundamental to the radiation dosimetry and radiation instrumentation as well [18]. Depending on the form of ionization, there are two types of ionizing radiation, i.e., the directly and indirectly ionizing radiations. The directly ionizing radiations are the charged particles. These particles ionize matter directly through the coulomb interactions with the atomic electrons. The indirectly ionizing radiations are the neutrons and photons (X-rays and γ -rays). The neutrons ionize matter by releasing charged particles through elastic/inelastic scattering and nuclear interactions. These charged particles will eventually interact with atomic electrons and hence ionize the matter.

As for neutrons, X-rays and γ -rays ionize matter indirectly by releasing charged particles. However, in this case the charged particles are created mainly by three processes, namely, photoelectric effect, Compton scattering and electron-positron pair production. In the photoelectric effect, a photon interacts with an electron from the inner shells of the atom and the electron is ejected with an energy equal to the difference between the photon energy and the energy needed to release the electron from the atomic nucleus (binding energy). In Compton scattering, the incident photon interacts and releases an electron from outer shells (low binding energy), generating a secondary photon with a lower energy. The weakly bound electron is released with an energy equal to the difference between the incident and released photon energies minus the binding energy of the electron. In electron-

Figure 2.1: Total photon linear attenuation coefficient, defined as the fractional change in the number of photons per unit thickness of material transversed (ICRU, 1998d), and attenuation coefficient due to various interaction processes in water calculated using the database from the US National Institute of Standards and Technology (Hubbell and Seltzer, 2004). This graph shows that photoelectric effect dominates in the low photon energy region, whereas the Compton effect dominates in the intermediate photon energy range. The probability of pair production increases for photon energies larger than 1.022 MeV. Extracted from [19].

positron pair production, a photon with energy higher than 1.022 MeV ¹ interacts with the atomic nucleus via its field electric field, creating an electron and a positron with kinetic energies corresponding to part of the excess of energy carried by the incident photon [19]. The Figure 2.1 depicts the different energy ranges in which each process is dominant. That behaviour is dependent on the atomic number of the different elements that make up the crystal.

Two quantities that are fundamental in the interaction of ionizing radiation with matter are Kerma and absorbed dose. Kerma, acronym for Kinetic Energy Released in Matter, is a quantity defined for an absorbing medium when photons (X-rays or γ -rays) or neutrons strike it. Kerma is the kinetic energy transferred from the photons (or neutrons) to charged particles (electrons) in the medium per unit of mass of the medium, i.e.,

$$K = \frac{dK_{tr}}{dm}, \quad (2.1)$$

expressed in units of Gray (Gy, $1\text{ Gy} = 1\text{ J/Kg}$) or rad ($1\text{ Gy} = 10^2\text{ rad}$). The absorbed dose quantifies the amount of energy absorbed by the matter per unit of mass of the medium. This quantity can be associated to any type of IR and may be estimated in any medium, i.e., human body related or not. Mathematically, the absorbed dose can be expressed as

$$D = \frac{d\varepsilon}{dm}, \quad (2.2)$$

where $d\varepsilon$ is the energy imparted by IR to matter in a volume element of mass dm and its units are the same for Kerma (Gy or rad). It is important to make clear the difference between Kerma and absorbed dose: Kerma is related to the kinetic energy that electrons receive by the IR in the medium, while the absorbed dose is related to the energy deposited by these electrons in the medium.

An amount of dose is never delivered to an absorbing medium at once. The dose rate of a radiation source striking an absorbing medium at a specific time t is

¹This energy corresponds to the rest mass of the electron or the positron, since both have the same rest mass.

given by

$$\dot{D} = \frac{dD}{dt}. \quad (2.3)$$

Two factors that cause different dose rates for a specific source: first one, the distance between source and target. Unless the medium between source and target be vacuum, attenuation processes occur. By interacting with the intermediate medium, the radiation transfers energy to it. Furthermore, for a point source, the beam of particles diverges as the distance increases. Second one, the nature of the ionizing radiation (energy). The higher the energy of the beam of particles, the higher is the kinetic energy delivered to the absorbing medium. Then, the higher energy of the beam of particles, the higher the dose rate in the absorbing medium. The absorbed dose and the dose rate are two important parameters in thermoluminescence and radioluminescence, respectively. This will be demonstrated in the next sections.

2.2 Energy bands, defects on crystals and a RL mechanism

Electrons in a single atom exhibits discrete energy levels. However, when we consider an ensemble of atoms and they are brought together to form a crystal, the energy levels of the isolated atoms split into $(2l + 1)N$ closely space levels, where N is the number of atoms in the crystal and $(2l + 1)$ is the degeneracy of each level [20]. These are a quasi-continuous distribution of energy levels in such a way that can be treated as continuous band of allowed energy states separated by forbidden energy bands. These bands are shared by the entire crystal and the two highest energy bands are called valence band and conduction band. The valence band is the highest filled energy band and the conduction band is the available energy band above the valence band. The separation between the valence band and the conduction band is called band-gap, and depending on its width a material may be an insulator (large band-gap) or a semiconductor (intermediate band-gap). The conductors do not have forbidden energy bands, which explains why electrons move freely throughout the crystal.

The distribution of the electrons in the available energy levels follows the

Pauli's exclusion principle, i.e., each energy state can be occupied by a single electron only. Furthermore, the electrons fill the energy levels starting from the lower energy level up to the valence band. Electrons in the valence band may be excited to the conduction band if the energy of excitation is equal or higher than the band-gap of the material. The excitation can be a heat source, an UV/visible light source, ionizing radiation and so on. If the excitation source is the ionizing radiation, the radioluminescence or thermoluminescence may take place.

As these ionization processes occur, a large amount of electron-hole pairs are created in the crystal until the ionizing radiation lose its total energy in the crystal. The electrons and holes can eventually recombine radiatively or non-radiatively. Non-radiative recombinations are mainly related to lattice vibrations of the crystal (phonon production). When recombination is prompt and radiative, the radioluminescence takes place. Here, the defects on crystal structures play an important role. In general, defects are distortions on crystal lattice of materials that allow electrons or holes be trapped on these sites. In other words, defects on crystals produce the formation of states before not allowed. In terms of energy, electron traps are situated close to conduction band and the hole traps close to valence band. Electrons on traps can eventually be released by light or heat excitation. If this excitation

Figure 2.2: Radioluminescence mechanism for materials with high band-gap and having a large number of defects in the crystal lattice. Extracted from [19].

is followed by light emission, Optically Stimulated Luminescence (OSL) or Thermoluminescence (TL) takes place. Unlike these defects, the defects responsible for RL process lies in the mid-gap region and they can trap electrons following holes trapping or vice-versa, and the electron-hole pairs decays to valence band emitting light. These defects are called recombination centers. Figure 2.2 depicts a mechanism for materials with high band-gap and having a large number of defects in the crystal lattice in which the radioluminescence may take place [19]. This mechanism sums up the radioluminescence process since the creation of electrons and holes by ionizing radiation until the radiative recombination.

2.3 A kinetic model for RL phenomenon

Here we present a kinetic model for the RL phenomenon². This model is basically a set of equations that governs the dynamics involving trapping and recombination centers during excitation by ionizing radiation. A scheme for this model is shown in Figure 2.3. In this model, two types of electron traps are present, namely, one in which radiative processes occur through light excitation of electrons (OSL), and the other in which electrons can not be released by light excitation. In addition to the electron traps, two types of recombination centers are present, i.e., one in which RL process occur and the other in which a non-radiative competitive process takes place.

Let M_1 be the concentration of radiative recombination centers with $m_1(t)$ concentration of holes occupying them, M_2 be the concentration of non-radiative recombination centers with $m_2(t)$ concentration of holes occupying them, N_1 be the concentration of electron traps which electrons can be released by light excitation, with $n_1(t)$ concentration of electrons occupying them and N_2 be the concentration of electron traps which electrons can not be released by light excitation, with $n_2(t)$ electrons occupying them. Consider n_c and n_v as the concentrations of electrons and holes in the conduction and valence bands, respectively. These concentrations are

²This model was proposed by Pagonis *et al.* for the carbon-doped aluminium oxide $\text{Al}_2\text{O}_3 : \text{C}$, a well known dosimeter which luminescent properties have been fairly investigated [21]. In spite of that, this model satisfy successfully our needs.

Figure 2.3: The energy level diagram of two electron trapping states and two types of hole recombination centers showing the possible transitions. Extracted from [21].

expressed in units of cm^{-3} . Let X be the rate of production of electron-hole pairs, in units of $\text{cm}^{-3}\text{s}^{-1}$, which is proportional to the excitation dose rate. Consider B_1 and B_2 as the trapping probability coefficients of free holes in centres 1 and 2, respectively. Let A_{m_1} and A_{m_2} be the recombination probability coefficients for free electrons with holes in centres 1 and 2, A_{n_1} be the retrapping probability coefficient of free electrons into the electron trap N_1 and A_{n_2} be the retrapping probability coefficient of the free electrons into the competing trapping state N_2 . These probability coefficients are expressed in units of $\text{cm}^{-3}\text{s}^{-1}$. The equations governing the RL process during excitation are

$$\frac{dm_i}{dt} = -A_{m_i}m_in_c + B_i(M_i - m_i)n_v, \quad (2.4)$$

$$\frac{dn_i}{dt} = A_{n_i}(N_i - n_i)n_c, \quad (2.5)$$

$$\frac{dn_v}{dt} = X - B_2(M_2 - m_2)n_v - B_1(M_1 - m_1)n_v, \quad (2.6)$$

$$\frac{dn_c}{dt} = X - A_{n_1}(N_1 - n_1)n_c - A_{n_2}(N_2 - n_2)n_c - A_{m_1}m_1n_c - A_{m_2}m_2n_c, \quad (2.7)$$

where the index i in equations 2.4 and 2.5 corresponds to $i = 1, 2$. The RL intensity

$I(t)$ is related to transitions involving the radiative recombination center, i.e., m_1 and hence is given by

$$I(t) = A_{m_1} m_1 n_c. \quad (2.8)$$

The set of these seven equations is solved analytically in [21]. Here, we just want to present two practical aspects of this model. As described in this cited work, for short irradiation pulses, we can expand $I(t)$ as a Taylor series about $t = 0$, i.e.,

$$I(t) = C_1 + C_2 t + O(t^2), \quad (2.9)$$

where C_1 is given by

$$C_1 = I(0) = A_{m_1} m_{10} n_{c0} = \frac{A_{m_1} m_{10} X}{A_{n1} N_1 + A_{n2} N_2 + A_{m1} m_{10}}, \quad (2.10)$$

where $m_{10} = m_1(0)$ and $n_{c0} = n_c(0)$. From 2.10, the initial RL intensity is proportional to the dose rate, since X is the rate of production of electron-hole pairs, as described by Pagonis *et al.* [21].

Solving C_2 coefficient from equation 2.9, Pagonis *et al.* concluded that for a constant dose rate, the RL intensity increases linearly with time [21]. A quantitative analysis for the increase of RL intensity with time will be reported in section 5.3.1.

2.4 A thermoluminescence model

As already defined, the thermoluminescence is the luminescence emitted by a material previously exposed to ionizing radiation when excited by heat. As in RL, TL takes place in crystals which have defects in their structure. Unlike RL, here the recombination centers as well as charge carrier (electron or hole) traps have important roles. The traps are responsible for storing the electrons and holes so that they can remain in these states over ages, until be excited by heat.

Here, we present a simple model for thermoluminescence, in which one type of electron trap is presented and also one type of hole recombination center, i.e., a center that first captures a hole and eventually can trap an electron. This model is

known as one-trap-one recombination center (OTOR), and it is described in most of textbooks on TL or OSL [7, 19, 22]. In spite of the simplicity of the model, some qualitative aspects of TL can be explored³. Figure 2.4 depicts a scheme showing the trapping of the charge carriers after the irradiation and the following thermal excitation and light emission, in the OTOR model.

In this model, three different processes can occur, namely, excitation, retrapping and recombination. Excitation takes place when electrons trapped in their defects are released to conduction band during heating. As the name suggests, the retrapping occur when free electrons once released from their traps and moving freely in conduction band are captured again by their traps. The recombination takes place when electrons in conduction band recombines with holes trapped in the recombination centers, emitting light. The set of equations governing these processes are

$$R_{ex} = ns \exp\left(-\frac{E}{kT}\right), \quad (2.11)$$

$$R_{ret} = n_c A_n (N - n) \quad (2.12)$$

and

$$R_{rec} = n_c A_h h. \quad (2.13)$$

R_{ex} , R_{ret} and R_{rec} are the excitation, retrapping and recombination rates, respectively. N and n are the total and the filled concentration of the electron traps, n_c is the concentration of the electrons in the conduction band, h is the concentration of the available recombination centers, s is the frequency factor⁴, E is the activation energy of the trap, which is also called the trap depth, T is the sample temperature and k is the Boltzmann constant. A_n and A_h are the retrapping and the recombination coefficients, respectively. Under thermal stimulation, the concentration of filled

³We are presenting the model as it is described by Sunta [22].

⁴The frequency factor is appropriately called the ‘attempt to escape frequency’, i.e., it is the rate in which electrons in their traps are released.

Figure 2.4: Scheme showing the trapping of the charge carriers after the irradiation and the following thermal excitation and light emission, in the OTO model. Extracted from [22].

electron traps changes according to

$$n(t) = n_0 \exp(-pt), \quad (2.14)$$

where n_0 is the initial concentration of filled electron traps and p is the transition probability per unit time for the trapped electron to escape to the conduction band under thermal stimulation. Furthermore, the probability of thermal stimulation of the electron to the conduction band (or hole to the valence band) is described by the Boltzmann factor, i.e.,

$$p = s \exp\left(-\frac{E}{kT}\right), \quad (2.15)$$

since the defect can be considered in equilibrium with the thermal reservoir represented by the crystal [19].

Considering the re trapping and recombination rates, the fraction F of the electrons which produces luminescence during heating is given by

$$F = \frac{R_{rec}}{R_{rec} + R_{ret}} \quad (2.16)$$

Randall and Wilkins assumed that the retrapping may be negligible ($R_{ret} = 0$) [22]. For this model the TL emission intensity is given by

$$I = cR_{ex} = -c\frac{dn}{dt} = cns \exp\left(-\frac{E}{kT}\right), \quad (2.17)$$

where dn/dt comes from equations 2.14 and 2.15. T is given by $T = T_0 + \beta t$ and c is a constant representing the optical efficiency factor relating the luminescence output to the electron release rate and the measuring instrument's efficiency to collect the light [22]. Assuming that $c = 1$, since this only changes the TL intensity, and assuming that the sample is heated in a linear heating rate ($dT/dt = \beta$), the equation 2.17 can be rearranged to

$$\frac{dn}{n} = -\left(\frac{s}{\beta}\right) \exp\left(-\frac{E}{kT}\right) \quad (2.18)$$

Integration this equation and taking the equation 2.17 into account, the TL intensity can be written as

$$I(t) = n_0 s \exp\left(-\frac{E}{kT}\right) \exp\left[-\int_{T_0}^T \left(\frac{s}{\beta}\right) \exp\left(-\frac{E}{kT'}\right) dT'\right] \quad (2.19)$$

Figure 2.5: Profiles of trapped electron population n , probability p of excitation and the glow curve as a function of temperature T during heating. Input parameters used are $E = 1 \text{ eV}$, $s = 1013 \text{ s}^{-1}$, $\beta = 1 \text{ K/s}$. Initial value of n is 1017 cm^{-3} . Extracted from [22].

This equation is the expression for the TL glow curve, i.e., the curve that relates the TL intensity with the temperatures. Figure 2.5 depicts the profiles of trapped electron population n , probability p of excitation and the glow curve as a function of temperature T during heating. As we can see, as the trapped electron population decreases, the TL intensity is increased up to a maximum value, following the intensity decaying. In agreement with the n curve, the p curve shows that the probability of thermal stimulation of the trapped electrons reaches its higher values at higher temperatures.

From equation 2.19, we can extract some qualitative aspects of TL glow curves. The glow peak shifts to higher T as E increases. Figure 2.6 depicts the effect of the activation energy of the trap E in the TL glow curves. Higher value of E means stronger binding of the trapped charge [22]. Furthermore, for given values of E and β , the glow peak shifts to lower T as s is increased. Figure 2.7 illustrates this effect. Higher s means faster escape of the trapped charge from the excited state of the trap and hence lower the temperature at TL peak [22]. In addition, for given values of E and s , the peak temperature T_m increases as heating rate β is increased. Figure 2.8 depicts the effect of heating rate in TL glow curves. This effect is valid for materials that do not exhibit thermal quenching in higher heating

Figure 2.6: Change in temperature at TL peak T_m of glow curves with change in E . The glow curves were recorded for $E = 0.5, 0.75, 1, 1.25$ and 1.5 eV. Extracted from [22].

Figure 2.7: Change in temperature at TL peak T_m with change in s . The glow curves were recorded for $s = 10^{13}$, 10^{12} , 10^{11} , 10^{10} and 10^9 s^{-1} . Extracted from [22].

rates [22]. At last, n_0 has no effects in the peak temperature T_m nor in shape of glow TL curves. This means that the peak features are independent of radiation dose given to the sample. This result is the reason for the usage of thermoluminescence as a dosimetric technique [22].

Figure 2.8: Change in glow curves with change in β . The glow curves were recorded with heating rates $\beta = 2$ and 4 K/s and plotted with normalized intensity. Extracted from [22].

In thermoluminescence measurements, the control of temperature is a quite important task. In research of materials, the determination of the temperature of glow curves must be performed to characterize the material. Usually it is desirable that the temperature of the peak of the glow curve be well above the room temperature to warranty thermal stability of the chage traping center of the dosimeters. Temperatures around 200 °C are a good compromise between thermal stability and practical instrumentation.

THE THERMOLUMINESCENCE- RADIOLUMINESCENCE SPECTROMETER CONSTRUCTION

The development of the TL-RL spectrometer is divided in two parts. The first one concerns about the instrument structural arrangement, description of main components, electronics involved and the control/data acquisition system, including implemented software. The second one deals with the tests carried out to evaluate the performance of the instrument. This chapter is focused on the first part.

The instrument modelling and design are reported. These steps are important due to the multi-modality operation of the instrument, i.e., radioluminescence in room temperature reading, radioluminescence in high-temperatures reading and thermoluminescence spectra acquisition. The electronic components involving heating system are briefly described, showing their roles in the instrument functioning. The x-ray tube used for irradiation samples before TL measurements or during RL measurements is presented. The light collection system, i.e., the optical fiber spectrometer is described, showing its main features. At last, the acquisition board for controlling the instrument and recording data is reported. The general view of implemented software is described without going deep in details.

3.1 Instrument modelling and design

The spectrometer was designed to carry out thermoluminescence measurements as well as radioluminescence. Thus, the instrument had to be designed so that we

would be able to heat the sample, irradiate it and collect the emitted light from the sample induced by x-rays or heat. Therefore, the positioning and accommodation of all parts are of crucial importance in the instrument to optimize its performance.

For attending these requirements, an aluminum basis was built. This basis holds the x-ray tube, optical fiber with lens and a sample drawer together. The drawer contains the heating planchet and its construction is similar to standard thermoluminescence readers. For making the instrument design (Figure 3.1), we used the software Blender, a free and open 3D modeling software. Some components of the heating system are not shown on the design as well as board acquisition and electronic components. Details about the several components of the instrument will be given throughout the text.

Through the instrument design, one can see the possibility of performing radioluminescence as well as thermoluminescence measurements. Furthermore, the

Figure 3.1: Design of the TL-RL spectrometer showing its main components: aluminum basis (1); drawer with heating planchet (2); x-ray source (3); lock-sensor (4); optical fiber spectrometer (5) and acrylic box (6).

Figure 3.2: Flowchart showing the different modes of operation of the spectrometer: radioluminescence spectra, thermoluminescence spectra and radioluminescence in high temperatures. Besides TL spectra, we are able to read the TL by integrating the luminescence of the different wavelengths.

positioning of x-ray tube and heating planchet enable us to carry out another type of measurement: radioluminescence as function of the temperature, with temperatures ranging from room temperature up to 500°C. This type of measurement will be subject of future works. Figure 3.2 depicts the different modes the spectrometer can be operated and the order of operation for each mode. In TL measurements, the x-ray source can be used for irradiating the sample before the reading but an external source with others features can be used as well.

3.2 Heating system

For heating the samples, we used a planchet made of Fecralloy, an Iron-Chromium alloy with high oxidative resistance [23] with dimensions of 44mm x 17mm x 1mm. The design of the planchet is depicted in Figure 3.3. The planchet shape was made as a spring for preventing possible deformation during thermal cycles. It was also machined at its center to hold the powder sample and to be a guide for maintaining samples at the more suitable position for the best performance in light collection and x-ray irradiation. The wiring underneath the planchet is a K-type thermocouple and its rounded probe was inserted close to the sample position through a small orifice created in the planchet. The largest the contact surface of the thermocouple probe with the object the more accurate is the temperature measurements of the object. Thus, the orifice was created for increasing the surface contact of the thermocouple probe with the planchet (Figure 3.4).

The planchet edges are fixed by upper and lower metal blocks through allen screws. These blocks are necessary to promote a good electrical and thermal contact holding the planchet through screws in one side and copper rods with 5mm diameter that conduct the high electric current to the planchet in the other side. The distance between the rods is 44mm.

Figure 3.3: *Design of planchet receptacle made in black anodized aluminum. The wires represent the K-type thermocouple. The white parts are Teflon insulators surrounding the copper rods that provide the electric current to the planchet.*

Figure 3.4: *Thermocouple probe inserted on the heating planchet.*

A cleaning drawer was inserted under the planchet for cleaning in the case of material spilled. In view of part of the sample may be lost in the sample gathering, the circular holder also allows us to insert powder on circular metal plates as well. Nevertheless, the thermal contact between sample and planchet is lowered and that causes a superestimation of the temperature in TL glow curves. Thus, the preferable type of samples to be used in this instrument is in pellet or disc shapes.

A modified 2kW microwave-oven transformer is used for generating the high electric current to be transmitted by the metal rods to the planchet. Microwave transformers are usually used as an elevating transform to provide high voltage to magnetron. For ramp generations there is a need of high current and low voltage, thus the secondary was removed and a 4 turns of AWG wiring with 6.4 mm diameter was wound to produce a step down transformer capable to deliver a current up to 60A. Microwave oven transformers have the primary and secondary windings easily accessible making the removal and rewinding of the secondary relatively easy and also the magnetic circuit is of good quality allowing high efficiency. A universal phase angle controller *FC11AL/2* plays a special role on this system: it is the device responsible for controlling the input voltage of transformer and this produces the voltage through the planchet. The heating system is triggered by a PID software controller.

Due to the low voltage on millivolt order of the thermocouple output and for a better control of temperature, an amplifier was used. An integrated circuit *AD595* was chosen for making a linear voltage amplification. Moreover, this component

provides a cold compensation junction excluding the need of measuring the room temperature and enabling us to make a correct measurement of temperature on a planchet. Figure 3.5 shows the circuit diagram of the electronic components involved in the heating system. The *OEM-6009* component in the circuit is the acquisition board used for applying a variable voltage¹ to the *FC11AL/2* and for receiving the voltage amplified by the *AD595*. The voltage output from acquisition board did not trigger the *FC11AL/2* properly. Therefore, a high-input impedance operational amplifier, *TL071*, was used.

Figure 3.5: Circuit diagram showing the heating system operation. *T1* supplies the controller with a 12V AC. *F1* is a 10 A high speed fuse. *R1* and *R2* are 50 k Ω and 250 Ω , respectively. *C1* is a 0.1 μ F. *T2* delivers an alternating current up to 60 A to the planchet. The resistor inside the heater represents the planchet and *TC* is the K-type thermocouple.

¹By software control, the acquisition board applies a variable voltage ranging from 0 to 5V DC in order to maintain the temperature increasing according to the pre-configured parameters, i.e., rate temperature and final temperature.

3.3 Light collection system, irradiator and environment shielding

In the light detection system, we used a fiber optic *Ocean Optics* spectrometer, mod. *USB2000* (Figure 3.6a). This spectrometer is based on a CCD detector, ILX511 linear silicon CCD array, *Sony*, with 2048 pixels, 250:1 signal-to-noise ratio and 200–1100 nm range. According to the CCD detector specifications, the slit size of 25 μm and the grating used, the spectrometer exhibits a spectral resolution of $\sim 1.4\text{ nm}$ (FWHM). Figure 3.7 depicts the components of the spectrometer and Table 3.1 describes their functions. For enhancing light collection, a convergent lens was located before the detector. Several measurements were carried out for choosing the position closer to focal length. The polished aluminum enclosure where the sample is placed also helps to reflect light towards the lens working as an integrating sphere.

In all types of dosimetry using luminescent materials, it is desirable to relate the dosimetric parameter with the higher possible intensity of luminescence. Initially, the spectrometer was intended to be used for dosimetric purposes. In view of that, its slit was enlarged using a drill of 200 μm diameter in order to enhance the optical sensitivity. However, as the spectrometer slit is enlarged, its spectral resolution is reduced. The spectral resolution is the least wavelength shift in which two spectral peaks can be resolved by a spectrometer. Thus, in order to quantify the new spectral resolution of the modified spectrometer, a experiment was carried out. This experiment is reported in the next chapter (Section 5.1).

Figure 3.6: *Ocean Optics spectrometer, model USB2000 used in the TL-RL spectrometer (a) and the 50 kV x-ray tube model used in the TL-RL spectrometer (b).*

Figure 3.7: *USB2000 spectrometer, Ocean Optics, with components. In Table 3.1 is described the components and their functions. Extracted from manual of USB2000+ spectrometer. Available at [24].*

A compact design *Magnum 50 kV* x-ray source, *Moxtek* (Figure 3.6b), was used for sample irradiation. This source produces a current up to 0.20 mA and is coupled to a 29 cm flexible cable. This module is connected to a home made power supply that controls the voltage (kV_p) and tube current. A timer and others safe features are also presente allowing the control of the exposition time, total time of using of the x-ray tube for possible preventive maintenance and interlock of the door. Furthermore, the x-ray source has a stable output so that we are able to make precise calibrated measurements.

An acrylic box was built mainly for radiation protection. Besides, the box let the others parts, i.e., X-ray source and optical spectrometer better arranged and even gives a robust appearance to the TL-RL spectrometer. A lock sensor is in contact with box door allowing radiation exposure just while the box is closed.

3.4 Data acquisition and control software

For temperature control and data acquisition, an *OEM-6009* board acquisition, *National Instruments*, with 14-bit analog inputs and 12-bit analog outputs, and the *Labview* software, *National Instruments*, were chosen. This board is not suitable for making accurate thermocouple measurements due to its poor voltage resolu-

Table 3.1: *Components of the spectrometer USB2000. Extracted and adapted from manual of USB2000+ spectrometer. Available at [24].*

Item	Name	Description
1	SMA Connector	Secures the input fiber to the spectrometer. Light from the input fiber enters the optical bench through this connector.
2	Slit	A dark piece of material containing a rectangular aperture, which is mounted directly behind the SMA Connector. The size of the aperture (25 μm) regulates the amount of light that enters the optical bench and controls spectral resolution.
3	Filter	Restricts optical radiation to pre-determined wavelength regions. Light passes through the Filter before entering the optical bench.
4	Collimating Mirror	The Collimating Mirror focuses light entering the optical bench towards the Grating of the spectrometer. Light enters the spectrometer, passes through the SMA Connector, Slit, and Filter, and then reflects off the Collimating Mirror onto the Grating.
5	Grating	The Grating diffracts light from the Collimating Mirror and directs the diffracted light onto the Focusing Mirror.
6	Focusing Mirror	Receives light reflected from the Grating and focuses the light onto the L2 Detector Collection Lens.
7	L2 Detector Collection Lens	The L2 Detector Collection Lens (optional) attaches to the Detector to increase light-collection efficiency. It focuses light from a tall slit onto the shorter Detector elements.
8	CCD Detector	Collects the light received from the Focusing Mirror or L2 Detector Collection Lens and converts the optical signal to a digital signal.
9	LVF Filters	Optional Linear Variable Filters (LVF) construct systems with excellent separation of excitation and fluorescence energy. LVF-L Linear low-pass filters fine tune the excitation source for maximum signal with minimum overlap. LVF-H high-pass filters are available for the detection side. These filters are optional and are not included in our spectrometer.

tion. However, the usage of *AD595* amplifier improves the voltage resolution of the thermocouple excluding the need of using specific boards for thermocouple measurements. This board reads the thermocouple voltage and indirectly applies a potential difference to the planchet simultaneously.

For creating the temperature ramps and plateaus, a PID algorithm was built. This algorithm is the key factor for the heating control system. PID algorithms for controlling temperature has been widely used [25–27]. The PID controller reads the thermocouple voltage and comparing to a pattern of setpoint temperatures controls the applied voltage on the planchet. The algorithm was implemented so that the

pattern of setpoints can be generated from the parameters - rate temperature and final temperature - chosen by the user on the software interface. Furthermore, the software implementation enables the user to choose a temperature ramp generation or a temperature plateau followed by ramp. For PID software might work a set of parameters is supposed to be chosen: proportional gain, integration time and derivative time. The choice of the PID parameters for the generation of temperature ramps and plateaus is reported in the next chapter.

The spectrometer software used was provided by *National Instruments* and adapted for our purposes. This software is compatible with several spectrometers (*Ocean Optics*) and for enhancing the performance of processing and data acquisition we have eliminated all parts that *USB2000* spectrometer is not dependent on. The control under integration time of spectra acquisition ranges from 3 ms to 65 s. Furthermore, another software, *SpectraSuite* (*Ocean Optics*) may be used for spectra acquisition. This software does not need the use of *Labview* and hence its use is easy and straightforward.

RESULTS AND DISCUSSIONS I: TEMPERATURE RAMPS AND PLATEAUS

Here the performance of the heating system is reported. Firstly, a test for verifying the reliability of room temperature reading was carried out, following temperature calibration for higher temperatures. After that, a procedure to determine the choice of PID parameters in the control of temperature ramps was performed. Using different heating rates, the temperature ramps were generated and an analysis about their performance is discussed. Similarly, temperature plateaus for the highest temperature limit of the system were generated and we present a brief analysis about their feasibility.

4.1 Inspection of temperature measurements

As described in the datasheet, the integrated circuit differential amplifier *AD595* is supposed to provide a cold junction compensation, giving an accurate measurement of the thermocouple probe (hot junction) and its output should have a $10\text{ mV}/^{\circ}\text{C}$ response. However, different electronic components and instruments as a whole exhibit different responses. In view of that, an inspection of temperature measurements was carried out in order to account for the deviation from the datasheet values and to enable us to know if the temperature in the planchet is read accurately. The inspection we performed consists in a temperature calibration and a following comparison with expected results.

In an instrument calibration, the larger the acquired dataset the more accurate is the calibration. Furthermore, the time response of the reference instrument

and non-calibrated instrument should be taken in account in order to avoid some mistakes in the calibration. In the acquisition of *AD595* voltages, the software was configured to collect 10 samples every second. A digital thermometer, manufactured to operate specifically with K-type thermocouples and having a ~ 1 s response time was used as the reference instrument. This response time means that the instrument averages an array of values over that time. Hence, the software was configured so that the planchet could be heated slowly.

The planchet was heated from room temperature up to 500°C over ~ 8 minutes and since this instrument does not have an output port to collect the data, a camera recorded the temperatures from the thermometer directly connected to the K-thermocouple and the *AD595* voltages. Figure 4.1 depicts the digital thermometer used in the calibration and also shows the *AD595* output reading and the corresponding temperature, assuming the *AD595* output response of $10\text{ mV}/^{\circ}\text{C}$ or, equivalently, $100^{\circ}\text{C}/\text{V}$. A dataset of 46 data points in 10°C steps were used in the calibration (Figure 4.2a). The slope of data points indicate that the *AD595* exhibited a response of $10.2\text{ mV}/^{\circ}\text{C}$, showing a small variation of 2% from datasheet value.

Figure 4.1: Digital thermometer used for the temperature calibration of the TL-RL spectrometer. The picture was taken while the room temperature stability was recorded (See the text).

Figure 4.2: (a) Temperature calibration curve. The voltages and temperatures were acquired from 50 °C up to 500 °C over ~ 8 minutes. (b) Measurement of room temperature for testing the cold junction compensation.

In addition, the intercept value showed a good agreement with the datasheet ($0^{\circ}\text{C} \rightarrow 2.7\text{mV}^1$), since we have to consider the inaccuracies of the calibration method and electronic components. The AD595 has a calibration error of $\pm 1^{\circ}\text{C}$ at room temperature. The thermometer has an uncertainty of 0.5% and its response time generates an error due to the averaging of temperatures over the reading. Moreover, there is an error associated to the thermocouple and that depends mainly on possible electrical interference and on purity of metals used in the thermocouple wires. Therefore, we have demonstrated that *AD595* response is in agreement with the expected datasheet value.

For testing the cold junction compensation, room temperature was recorded by reading the temperature from software. The measurement was carried out over 60 s for verifying the stability of room temperature measurements. While the digital thermometer indicated a temperature of $\sim 24.6^{\circ}\text{C}$ (Figure 4.1), the software showed a temperature between 24.4°C and 24.7°C (Figure 4.2b). This confirms that the *AD595* is providing cold junction compensation as expected.

4.2 Temperature control: ramps and plateaus

As described in the Chapter 3, it is indispensable to have an accurate control of temperature in thermoluminescence measurements. Ramps from room temperature up to 500°C were acquired in different temperature rates. In spite of the properties of the heating planchet enable us to achieve temperatures higher than 500°C , the blackbody radiation emitted by the planchet becomes a point of concern. Furthermore, 500°C is a quite good temperature limit for recording TL spectra, since the most thermoluminescent materials exhibits light emission in the region below 500°C . A quantitative analysis about the blackbody radiation emitted by the heating planchet will be presented in the next chapter (section 5.5).

By selecting the temperature rate and the final temperature, the software generates a ramp profile that is the reference for the PID controller. This controller adjusts the ramps according to the profiles generated in the software and the PID

¹Considering the voltage range, we can assume that this is approximately zero. Thus, $0^{\circ}\text{C} \rightarrow 0\text{mV}$.

parameters. Initially, the ramps exhibited large oscillations ($\pm 15^\circ\text{C}$). For enhancing their accuracy, the PID parameters were optimized until we achieve acceptable results. It was observed that as we change the PID parameters we change how the applied voltage on the planchet varies with time.

Several ramps were generated for analysing the effects of the PID parameters on their performance. For each parameter, two different ramps were generated and all ramps were generated up to 250°C using a rate of 3°C/s . Figures 4.3–4.5 depict the results obtained. The plots contain the experimental data and the expected ramps, having considered an accurate measurement of the initial temperatures. The larger table on graphs shows the fitting parameters of the experimental data and the smaller one shows the PID parameters used. K_c is the proportional gain, T_i is the integral time in units of minute and T_d is the derivative time in units of minute as well. Using a proportional gain of 5 the ramp exhibited oscillations of up to 15°C around the expected ramp (Figure 4.3). Maintaining the time parameters and increasing the proportional gain to 30, the oscillations did not exceed 7°C (Figure 4.4a). Using the proportional gain of 30 and increasing the integral time to 0.5 min, we had a large enhancement in the performance of ramps (Figure 4.4b). The

Figure 4.3: The ramp using a proportional gain of 5 exhibited variations of up to 15°C

Figure 4.4: (a) Increasing the proportional gain from 5 to 30 the variations did not surpass 7°C. (b) Effects of the integral time in the performance of temperature ramps. Changing the integral time from 0.01 min to 0.5 min causes a large enhancement in the ramp performance, exhibiting a deviation of up to 1.5°C from expected ramp.

Figure 4.5: Effects of the derivative time in the performance of temperature ramps. The increase of the derivative time from 0.001 min to 0.1 min causes a large discrepancy from the expected ramp.

largest deviation between the experimental and expected ramps was 1.5 °C. and the slope showed agreement with the selected temperature rate. At last, increasing the derivative time to 0.1 min the ramp exhibited total discrepancy from the expected ramp (Figure 4.5).

Initially the PID parameters were chosen for all range of temperatures but the precision and accuracy of ramps were not acceptable at certain ranges of temperature. After so many attempts, we selected a set of parameters for three different ranges: the first one, from initial temperature to 60 °C, the second one, from 60 °C to 230 °C and the third one, from 230 °C to 500 °C.

For performing an analysis of the ramp data points, four different ramp rates, i.e, 0.5, 1, 3 and 5 °C/s were selected, and three tests were carried out for each rate. The Figures 4.6 and 4.7 depict some of the ramps recorded. The sequential generation of ramps following cooling is responsible for the different intercepts of the ramps. The slopes of the ramps showed agreement with the selected rates. For each ramp, we select the regions with the largest oscillations to determine the

Figure 4.6: (a) Temperature ramp using a rate of 0.5°C/s. The inset is the plot in a higher resolution showing the largest temperature deviation ($\sim 1.3^\circ\text{C}$) from the expected ramp. (b) Temperature ramp using a rate of 1°C/s. The inset shows the largest temperature deviation of about 2°C

Figure 4.7: (a) Temperature ramp using a rate of 3°C/s. The inset is the plot in a higher resolution showing the largest temperature deviation ($\sim 1^\circ\text{C}$) from the expected ramp. (b) Temperature ramp using a rate of 5°C/s. The inset shows the largest temperature deviation of about 1.7°C

largest temperature variations from the fits, since the fits can be considered as the reproduction of the theoretical ramps. As depicted in the insets of the graphs, the deviations were not larger than 2 °C. In the Table 4.1 is shown the fitting parameters obtained for each ramp. The statistical fitting parameters demonstrate the good performance on temperature ramps generation. Temperature rates below 0.5 °C/s were not tested and for rates above 5 °C/s, it is necessary to obtain a new set of PID parameters. For TL spectroscopy, elevated heating rates are not desirable, since as the heating rate is increased, the TL emission is shifted to higher temperatures and hence trap depths are not determined accurately. TL spectrometers reported in literature presented range of heating rates from 0.1 °C/s up to 10 °C/s and 20 °C/s [28,29]. Therefore, the range of heating rates of the developed instrument, 0.5 °C/s up to 5 °C/s is an acceptable range and also satisfies our needs.

Besides temperature ramps generation, the software can be used for generating temperature plateaus and hence annealing procedures may be carried out. The annealing is necessary when one desires to repeat readings with TL materials or

Table 4.1: *Fitting parameters of ramps generated by the temperature control software. The standard deviations for intercepts and slopes were smaller than 0.12% and 0.018%, respectively. In these results we are not taking into account the inaccuracies from thermometer, thermocouple and electronics.*

Control parameter	Fitting parameters					
Rate (Gy/s)	Intercept (°C)	Slope (°C/s)	Residual Sum of Squares	Pearson's r	R-square	Adj. R-Square
0.5	49.4	0.50	133	1	1	1
	46.3	0.50	131	1	1	1
	44.6	0.50	226	1	1	1
1	34.4	1.00	289	1	0.99999	0.99999
	41.8	1.00	323	1	0.99999	0.99999
	45.8	1.00	106	1	1	1
3	30.5	3.00	90	1	0.99999	0.99999
	34.9	3.00	69	1	1	1
	35.7	3.00	71	1	1	1
5	44.5	4.99	205	0.99999	0.99998	0.99998
	43.4	5.00	54	1	0.99999	0.99999
	40.9	4.99	248	0.99999	0.99998	0.99998

Figure 4.8: Temperature plateau at 500°C. After 5 seconds from overshoot, the temperature stabilized with a maximum variation of 0.5°C

when they need to be quenched. A new set of PID parameters had to be chosen for the generation of temperature plateaus.

Three plateaus at 500°C followed by ramps using 5°C/s heating rate were recorded. Figure 4.8 depicts an example of a generation of temperature plateau followed by ramp. The whole acquisitions were carried out over 400 seconds for demonstrating the stability over the plateaus. Notice that there is an overshoot following a stabilization after 5 seconds. During the stabilization, the temperature variations along the plateau did not exceed 0.5°C. The Table 4.2 shows the results we obtained for the three plateaus. The stabilization time is the time after the

Table 4.2: Averages and standard deviations of the temperature plateaus at 500°C.

	Mean temperature (°C)	Standard deviation (°C)	Overshoot- ing temperature(°C)	Stabilization time (s)
Test 1	500.0	0.23 (0.05%)	502.7	5.2
Test 2	500.0	0.26 (0.05%)	502.9	4.9
Test 3	500.0	0.30 (0.06%)	503.1	8.0

overshoot in which the temperature stabilizes at about the specified temperature. The standard deviation of the temperature was calculated with dataset points after the stabilization time.

RESULTS AND DISCUSSIONS II: FEASIBILITY OF RL AND TL SPECTRA

In this chapter we report the feasibility of RL and TL spectra. A test for verifying the reliability on wavelength readings of *USB2000* was performed, following a calibration and correction. Furthermore, a measurement of the spectral resolution had to be carried out, since the slit of spectrometer was altered. As in RL spectra the dose rate is an important parameter and the TL emission is dependent on the dose delivered, calibration of the X-ray source was performed. At last, the RL and TL spectra tests were carried out. For RL spectra tests, four different materials, namely, carbon-doped aluminium oxide $\text{Al}_2\text{O}_3\text{:C}$, terbium-doped gadolinium oxysulphide $\text{Gd}_2\text{O}_2\text{S:Tb}$, europium-doped yttrium oxide $\text{Y}_2\text{O}_3\text{:Eu}$ and dysprosium-doped calcium borate $\text{CaB}_6\text{O}_{10}\text{:Dy}$ were used. The luminescence of these materials or due to their activators (dopants used) is well known and comparison with literature is presented. For TL spectra tests, $\text{Al}_2\text{O}_3\text{:C}$ was used and as for RL spectra tests, comparison with literature is reported.

5.1 Wavelength calibration and spectral resolution

A test to verify the reliability on the wavelengths reading and an eventual calibration of the *USB2000* spectrometer. A reference lamp, mercury-argon calibration source, *HG-1, Ocean Optics*, was used for performing the test. Figure 5.1 shows an example of the calibration source used. This source exhibits well defined spectral lines in the UV-Vis and shortwave near-infrared regions (253 nm up to 922 nm). For performing the test, the light source was connected to the spectrometer by the opti-

Figure 5.1: Mercury-Argon calibration source HG-1 Ocean Optics. Model used in the wavelength calibration

cal fiber. However, the saturation of the large intensities of spectral lines could not be avoided even using the least integration time available (3 ms). The optical fiber hence was removed and the calibration source was placed *ca.*15 cm from the *USB2000* spectrometer in such a way that the source pointed to the slit spectrometer.

The tests were carried out using different integration times, since the spectral lines exhibit different relative intensities. Five spectral lines were selected ranging from 230 nm and 570 nm. Figure 5.2 depicts the spectral lines obtained. The first line was obtained using a 3 ms integration time and for the other ones the integration time was increased to 8 ms for better visualization of the spectral lines. The wavelength for each line was recorded and compared with the expected values from *HG-1* calibration source. The *HG-1* wavelengths, the recorded wavelengths and FWHM for each line are summarized in Table 5.1. The recorded wavelengths showed to be shifted to higher wavelengths and the wavelength shifts ranged from 5.25 nm to 6.83 nm.

A plot showing the correlation between the HG-1 and recorded wavelengths is depicted in Figure 5.3a. The error bars represent the FWHM of the recorded emission lines. The intercept of the curve suggests that a calibration must be performed and the slope of data fit indicates that correction on wavelengths reading must be linear and wavelengths above 550 nm can be corrected as well, since data

Figure 5.2: Spectral lines from HG-1 calibration source. The first line was obtained using a 3 ms integration time. The others lines were obtained using a 8 ms integration time. These lines were obtained for wavelength calibration of the USB2000 spectrometer.

extrapolation can be fairly carried out. Thus, to correct the wavelengths reading, the wavelength shifts were averaged. Figure 5.3b depicts the wavelength shifts for the five emission lines recorded, including the average and the standard deviation of the wavelength shifts. Thus, a factor of 5.83 ± 0.65 nm must be subtracted from the wavelengths reading.

As reported in the previous chapter, the slit of the spectrometer was enlarged and hence its spectral resolution altered. The spectral resolution before the spectrometer be modified was ~ 1.4 nm (FWHM). As a direct measurement of the spectral resolution, the full width at half maximum for each line of HG-1 calibra-

Table 5.1: HG-1 emission lines with the corresponding recorded ones and the FWHM for each line.

HG-1 emission lines (nm)	253.65	365.01	404.66	435.83	546.07
Recorded emission lines (nm)	258.90	370.68	410.76	441.16	552.90
FWHM(nm)	7.6	7.1	6.6	7.1	6.9

(a)

(b)

Figure 5.3: (a) Correlation between HG-1 and recorded wavelengths. Intercept suggests a calibration on wavelengths reading and the slope suggests that calibration must be linear and can be extended to wavelengths above 550 nm. (b) Plot showing the wavelength shifts for the five lines recorded. The solid red line represents the average of the wavelength shifts and the dotted lines represent the standard deviation.

tion source was measured. As shown in Table 5.1, the FWHM values ranged from 6.6 nm to 7.6 nm. Therefore, considering the real spectral resolution as the least value obtained, we can consider the new spectral resolution of the spectrometer as 6.6 nm. The increase in spectral resolution from 1.4 nm to 6.6 nm can be justified, since we intend to investigate materials with relatively large emission bands.

5.2 X-ray tube calibration

The X-ray tube calibration was performed, since the RL emission is proportional to the dose rate in which the material is exposed. Moreover, the TL emission of any material is proportional to the dose delivered. The X-ray tube calibration was performed by an ionizing chamber, mod. 10X5-6, *Radcal Corporation*. For 50 kV of energy the uncertainty of the chamber is of 1.5% in a 95% confidence interval, according to Guide to the expression of Uncertainty in Measurement - ISO GUM. The tube was positioned in an external arrangement with position markers in order to measure dose rate on several distances from the source spot. The calibration was

Figure 5.4: Calibration of X-ray source, Moxtek, with 50 kV and 0.2 mA. The dotted lines are shown for indicating the dose rate that corresponds to the distance between sample and source spot (3.8 cm).

carried out for nine different positions, ranging from 3 cm to 50 cm. Figure 5.4 depicts the dose rates obtained for each distance. By exponential fitting we estimated the dose rate on sample position on the TL-RL spectrometer as 5.5 Gy/min, considering the distance between sample and source spot to be 3.8 cm¹. The dotted lines are shown for indicating the dose rate that corresponds to the distance between sample and source spot (3.8 cm).

5.3 Radioluminescence tests

Since the spectrometer tests were performed and the X-ray calibration as well, the radioluminescence tests could be carried out. For performing that, four different materials were used. The first test of RL spectra acquisition was performed using a carbon-doped aluminium oxide dosimeter Al₂O₃:C, *Landauer Inc., USA*, in pellet shape with 4.5 mm in diameter (rounded shape in Figure 5.5). This material is well known by the scientific community due to its luminescent and dosimetric properties [30–32]. For acquiring the RL spectrum, an average of three scans was recorded using *SpectraSuite* software, *Ocean Optics*, with an integration time of 5 s and a smoothing boxcar width of three pixels. Figure 5.6 depicts the RL spectrum obtained. The spectrum exhibits a main peak at ~411 nm and a second peak at ~693 nm.

Figure 5.5: Al₂O₃:C dosimeters in pellet (rounded) and film shapes used in RL measurements as well as TL spectra acquisition. The pellet shape dosimeter has 4.5 mm in diameter and the film shape dosimeters have dimensions of 6 mm X 6 mm.

¹The reason for the range between 3 cm to 50 cm in the calibration is that the X-ray tube was used with others purposes before the TL-RL spectrometer development.

Figure 5.6: Radioluminescence spectrum of the Al₂O₃:C dosimeter. The main peak exhibited maximum amplitude at 411 nm and the second peak at 693 nm. Acquisition parameters: 3 scans, integration time of 5 s and a smoothing boxcar width of 3 pixels.

Erfurt *et al.* reported RL measurements with Al₂O₃:C dosimeters and found a main emission at 420 nm and two other emissions at 700 nm and 790 nm obtained through a gaussian fitting (least square approximation) [33]. Morono *et al.* and Poolton *et al.* also reported RL measurements using Al₂O₃:C and found the main emission at 410 nm and 416 nm, respectively [34, 35]. Moreover, the official website of the manufacturer of the dosimeter we used, *Landauer*, informs that the Al₂O₃:C exhibits the main emission at 410 - 420 nm [36]. Therefore, the main peak at ~411 nm shows a good agreement with literature. The peak at 693 nm may be the peak at 700 nm reported by Erfurt *et al.* since this emission was attributed indirectly through a gaussian fitting [33].

The second material used for the RL tests is the terbium-doped gadolinium oxysulphide Gd₂O₂S:Tb in film shape with 14 mm in diameter. This is a X-ray phosphor used in the manufacture of intensifying screens for medical diagnosis since it exhibits bright green luminescence with high efficiency under X-ray excitation [37]. For acquiring the RL spectrum of Gd₂O₂S:Tb, a single scan with a 0.5 s

Figure 5.7: *RL spectrum of $\text{Gd}_2\text{O}_2\text{S:Tb}$ acquired using a 0.5 s integration time. The spectrum exhibits four lines well defined at 486, 541, 583 and 616 nm.*

integration time was used and without spectrum smoothing, since it was unnecessary. Figure 5.7 depicts the spectrum recorded. Clearly, the spectrum exhibited four well defined lines at 486, 541, 583 and 616 nm. Popovici *et al.* reported the emission of $\text{Gd}_2\text{O}_2\text{S:Tb}$ in photoluminescence studies² and the phosphor exhibited four main emission bands 489, 544, 586 and 619 nm that are attributed to activating terbium ions. Therefore, the $\text{Gd}_2\text{O}_2\text{S:Tb}$ RL spectrum exhibited a small shift of 3 nm for each emission band, i.e., a negligible error of $\sim 0.6\%$.

For the third RL test, europium-doped yttrium oxide $\text{Y}_2\text{O}_3\text{:Eu}$ in powder form was used. This material was synthesized by solution combustion synthesis (SCS) as described by Yukihiro *et al.* [38]. For collecting the $\text{Y}_2\text{O}_3\text{:Eu}$ RL spectrum, a single one scan using a 1 s integration time was used, without spectrum smoothing as for $\text{Gd}_2\text{O}_2\text{S:Tb}$ RL spectrum acquisition. Figure 5.8 depicts the spectrum recorded. The small green emission at ~ 537 nm and the strong red emissions

²Photoluminescence is the luminescence emitted by a material when excited by ultraviolet light.

Figure 5.8: *RL spectrum of $\text{Y}_2\text{O}_3:\text{Eu}$ acquired using a 1 s integration time. The spectrum exhibits two strong emission bands at $\sim 594\text{ nm}$ and $\sim 613\text{ nm}$ and two others bands at $\sim 537\text{ nm}$ and $\sim 710\text{ nm}$.*

at 594 nm and 613 nm due to activating europium ions are in perfect agreement with the literature. Srinivasan *et al.* reported photoluminescence studies of $\text{Y}_2\text{O}_3:\text{Eu}$ and presented these three emission bands at $\sim 540\text{ nm}$ and the strong red emissions at 595 nm and 612 nm [39]. The band emission at $\sim 710\text{ nm}$ was not found in literature.

At last, dysprosium-doped calcium borate $\text{CaB}_6\text{O}_{10}:\text{Dy}$ in powder form was used. The material was synthesized by solid state reaction as described in [40], only changing the dopant used. The RL spectrum was acquired using a single scan with a 30 s integration time. Figure 5.9 depicts the spectrum recorded. Clearly, the spectrum exhibited two strong emission bands at $\sim 478\text{ nm}$ and $\sim 571\text{ nm}$. The pure calcium borate does not exhibit any emission and hence those lines are attributed to dysprosium activating ions. This is in agreement with the literature, since the dysprosium-doped calcium sulfate $\text{CaSO}_4:\text{Dy}$ dosimeter exhibits the same emission bands and the dysprosium ions are the luminescent activators [41].

Figure 5.9: *RL spectrum of $\text{CaB}_6\text{O}_{10}:\text{Dy}$ acquired using a 30 s integration time. The spectrum exhibits two strong emission bands at $\sim 478\text{ nm}$ and $\sim 571\text{ nm}$.*

5.3.1 Radioluminescence versus integration time

The radioluminescence of a material can be enhanced through the increasing of integration time on spectrum acquisition and the spectrum shape can be better defined. Furthermore, some spectral bands may be visualized by enhancing the integration time and the material may be more deeply investigated.

In this experiment, six $\text{Al}_2\text{O}_3:\text{C}$ dosimeters in film shape (Figure 5.5) were used. The dosimeters were exposed over different integration times from 1 s to 30 s. The acquisition of each spectrum was done using one single scan and a boxcar width of three pixels. Figure 5.10 depicts the radioluminescence spectra for the six dosimeters acquired in different integration times. Changing the integration time from 1 s to 30 s increased the luminescence more than 50 times. The inset graph shows that using an integration time of 5 s a band around 690 nm arises and grows for higher integration times. This measurement was carried out three times and before each measurement, the dosimeters were exposed to blue LEDs over 8 h in order to quench the dose remnant still present due to radiation exposure in others measurements.

Figure 5.10: Radioluminescence spectra of $\text{Al}_2\text{O}_3:\text{C}$ dosimeters for different integration times. The inset depicts the growth of a band around 690 nm as the integration time is increased.

Figure 5.11a shows the change of the RL amplitudes of the main emission for different integration times. Each point represents the average of three measurements. Clearly the curve exhibits a superlinear behaviour and that can be justified as it follows. The ionizing radiation induces in the material a dual process, trapping the charge carriers in the defects of the material and the prompt recombination of radiation-induced electron-hole pairs that generates the radioluminescence. As time goes by, the radioluminescence becomes more relevant since the material has a finite number of defects. Therefore, for materials that exhibit radioluminescent properties as well as contain defects in which radiation may induce the charge carriers trapping, the radioluminescence process takes part more intensely for longer integration times. This behaviour can be seen in Figure 5.11b. This plot depicts the acquisition of radioluminescence of a $\text{Al}_2\text{O}_3:\text{C}$ dosimeter over 32 s of acquisition time. Each point represents the RL amplitude for the $\text{Al}_2\text{O}_3:\text{C}$ main emission collected over 1 s of integration time. This result is in agreement with the analytical model for RL of $\text{Al}_2\text{O}_3:\text{C}$, proposed by Pagonis *et al.*, in which asserts that for a constant dose rate,

(a)

(b)

Figure 5.11: (a) Radioluminescence spectra amplitudes of $\text{Al}_2\text{O}_3:\text{C}$ dosimeters for different integration times. Clearly the dosimeter exhibited a superlinear behaviour. (b) RL spectra amplitudes of a $\text{Al}_2\text{O}_3:\text{C}$ dosimeter over 30s of acquisition time. The RL grows abruptly as the X-ray is turned on and increase the intensity by $\sim 50\%$ at the end of the spectra acquisition.

the RL intensity increases linearly with time [21]. As the X-ray is turned on, the RL grows abruptly and increase the intensity by $\sim 50\%$ at the end of the spectra acquisition. This abrupt transition is due to the thermal stabilization of the X-ray tube. Once the steady state is achieved the x-rays fluence becomes constant. Some x-rays sources have a diaphragm that opens the source after a time to avoid this transition. In our case we need to use a longer acquisition time to avoid this transition.

5.4 Implementations on λ -TL software

For acquiring and saving wavelength-resolved thermoluminescence (λ -TL) spectra properly, a series of implementations was necessary. Firstly, synchronization between temperature and spectra acquisitions was performed since each spectrum must be related to a certain temperature. In view of that, the heating control and spectrometer softwares were built in two parallel loops so that they are triggered at the same time.

Another important step in the λ -TL software is the automatic correction on spectrum baseline before λ -TL spectra acquisitions. Spectrum baseline is the spectrum of the environment background including the spectrometer electronic effects on spectrum collection. For the correction of the baseline, the software was adapted in such a way that the first acquired spectrum is stored and subtracted from the spectra of interest. In addition, a smoothing filter in spectra acquisitions was created, enabling the user to select the intensity of spectra smoothing.

For starting λ -TL spectra acquisitions, the users have in the software interface some parameters to choose, namely, final temperature (not surpassing 500°C), heating rate (from 0.5°C/s to 5°C/s) and integration time of spectra acquisitions (from 3ms to 65s). Figure 5.12 depicts the software interface for collecting λ -TL spectra. The software was implemented so that the spectra acquisition finishes when the final temperature is achieved. For saving spectra data, the software was implemented in such a way that a table containing the temperatures of each spectrum, wavelengths and the corresponding intensities is generated. Figure 5.13 shows an example of how λ -TL spectra data is saved, in the case of a 2°C/s heating rate and

Figure 5.12: Interface of the software implemented in Labview for collecting λ -TL spectra. It shows an instant print of $\text{Al}_2\text{O}_3\text{:C}$ λ -TL spectra acquisition.

	A	B	C	D	E	F	G	H
1								
2	$\lambda(\text{nm})$	$T(^{\circ}\text{C}) \rightarrow$	27,65	29,65	31,65	33,65	35,65	37,65
3	$\downarrow$	0	0	0	0	0	0	0
4	200,092	0	0,62582	-0,34704	-0,02429	0,37744	-0,18247	-0,65533
5	200,469	0	0,46702	-0,50001	-0,12373	0,28015	-0,31465	-0,80265
6	200,846	0	0,29472	-0,64619	-0,23779	0,18015	-0,44248	-0,92522
7	201,222	0	0,13896	-0,79904	-0,3588	0,05399	-0,57568	-1,02892
8	201,599	0	-0,00432	-0,96975	-0,47302	-0,11036	-0,68972	-1,12618
9	201,975	0	-0,15318	-1,14208	-0,57266	-0,29344	-0,76071	-1,22388
10	202,352	0	-0,27196	-1,24808	-0,62967	-0,43883	-0,76205	-1,30244
11	202,729	0	-0,33487	-1,24268	-0,62119	-0,49987	-0,70142	-1,33847
12	203,105	0	-0,3682	-1,18756	-0,59061	-0,51475	-0,63688	-1,36373
13	203,482	0	-0,39801	-1,1387	-0,57094	-0,53787	-0,60622	-1,4122
14	203,858	0	-0,44255	-1,07406	-0,54982	-0,5784	-0,60798	-1,47578

Figure 5.13: Table showing how λ -TL spectra data is saved. The zeros are delimitators for better organizing data.

1 s in integration time. As can be seen, the temperatures are attributed in evenly spaced steps. This was necessary since spectra acquisition and temperature acquisition comes from different parallel loops and saving data in a single file was not possible. The evenly spaced temperatures can be justified by the good performance of ramps.

In the choice of integration time, the user has to take into account the time latency on spectra acquisition, i.e., the time spent for storing a spectrum after the acquisition and this is an intrinsic feature of the optical spectrometer. This is important since a series of spectra is supposed to be collected and each spectrum must be attributed to a certain temperature. If the time latency is neglected, an error in the temperature attribution for each spectrum is continuously propagated so that the last spectra are the most affected. For clarifying this, if a spectrometer has a 50 ms of time latency and 100 spectra are supposed to be collected using 1 s in integration time, i.e., one spectrum per second, the last spectrum will be collected 105 s after the acquisition start, i.e., 100 s of acquisitions plus 5 s due to the time latency (50 ms times 100).

For determining the time latency of the *USB2000* optical spectrometer, a series of experiments was carried out. No sample was used and the emission of the blackbody radiation due to heating planchet was the parameter used for attributing the final temperature to the highest emission spectrum. The software was config-

ured to generate temperature ramps in a $5^\circ\text{C}/\text{s}$ heating rate up to 500°C . Several spectra were collected using different integration times, starting from 1000 ms following lower integration times. For the test using 1000 ms in integration time, the last spectrum did not correspond to the highest blackbody emission but it was associated to a temperature when the system was cooling down, after achieving the final temperature. Thus, lower integration times were used until finding an integration time so that the last spectrum would match the final temperature. Using a 985 ms the final temperature matched the highest blackbody emission. Therefore, the time latency of the *USB2000* optical spectrometer is ~ 15 ms and hence in λ -TL spectra acquisitions, 15 ms must be subtracted from the integration time to be chosen. To confirm this result, a video camera recorded the λ -TL spectra of $\text{Al}_2\text{O}_3:\text{C}$ and by comparison with saved data, the different acquisition forms successfully matched.

5.5 λ -TL spectra test

Since the temperature ramps showed a good performance, the optical spectrometer tests, namely, wavelength reading correction and spectral resolution were performed and data is acquired and saved in a satisfactory form, λ -TL spectra test could be carried out. For that, a carbon-doped aluminium oxide $\text{Al}_2\text{O}_3:\text{C}$ dosimeter was utilized. A picture of this dosimeter is the rounded sample in Figure 5.5. No annealing procedure was performed, since the test concerns about the verification of the temperatures and wavelengths associated to the $\text{Al}_2\text{O}_3:\text{C}$ emission. The dosimeter was exposed to the X-ray source of the TL-RL spectrometer over 20 min^3 and temperatures ranged from RT up to 400°C using a $2^\circ\text{C}/\text{s}$ heating rate. In spectra acquisition, 1 s integration time was chosen and hence spectra are saved in a 2°C step.

The $\text{Al}_2\text{O}_3:\text{C}$ exhibited a single TL emission. According to the acquired data, the highest TL emission was seen at $\sim 182^\circ\text{C}$, i.e., the dosimetric peak of $\text{Al}_2\text{O}_3:\text{C}$. The single λ -TL spectrum at 182°C is depicted in Figure 5.14. As can be seen, this spectrum exhibits a maximum amplitude at $\sim 414\text{ nm}$. Summers *et al.* reported

³According to the X-ray calibration, this exposure time corresponds to $\sim 100\text{ Gy}$ in air as calibrated by the ionizing chamber described in the previous chapter.

Figure 5.14: Single spectrum of $\text{Al}_2\text{O}_3\text{:C}$ λ -TL spectra corresponding to the highest TL emission (182°C). The band emission exhibited maximum amplitude at $\sim 414\text{ nm}$.

that $\text{Al}_2\text{O}_3\text{:C}$ presents a TL emission at 410 nm and attributed this emission to the radiative decay of F centers, i.e., luminescence generated by the detrapping of electrons captured in a F^+ center (electron trap) [42]. Akselrod *et. al* confirmed this when reported some optical properties of $\text{Al}_2\text{O}_3\text{:C}$ and found the spectrum emission with the maximum intensity at 420 nm [43]. Thus, the emission band at 414 nm is in agreement with literature, since this value lies between the two band emissions reported in the works cited previously.

The highest emission at 182°C can be justified as it follows. The position of TL glow curves depends on the heating rate used to generate the ramps. As the heating rate is increased, the TL glow curve emission is shifted to higher temperatures. That is expected by TL theory as discussed in the section 2.4 and Yüksel *et al.* reported quantitative measurements of this effect [44]. Akselrod *et al* reported $\text{Al}_2\text{O}_3\text{:C}$ TL glow curve peak at $\sim 187^\circ\text{C}$ using a 4.3°C/s . Yoshizumi *et al.* reported $\text{Al}_2\text{O}_3\text{:C}$ λ -TL spectra with TL maximum intensity at $\sim 210^\circ\text{C}$ using a 10°C/s heating rate [28]. These discrepancies on temperatures of $\text{Al}_2\text{O}_3\text{:C}$ TL peak can be justified by the TL peak position dependence on heating rates. In addition,

different synthesis may generate samples with slightly different crystal structures, i.e., crystals with variations on trap depths. Even a same synthesis does not ensure that samples will exhibit the same TL peak positions. Furthermore, the performance of ramps for different heating systems can highly contribute to different TL peak positions.

λ -TL full spectra for $\text{Al}_2\text{O}_3\text{:C}$ was plotted in a 3D contour map form, showing the spectra wavelengths, the emission intensities and the temperatures corresponding to each spectrum. The 3D contour map is depicted in Figure 5.15. The emission after 600 nm at high temperatures is due to the blackbody radiation from the heating planchet. A measurement was performed to account for the effect of blackbody

Figure 5.15: λ -TL $\text{Al}_2\text{O}_3\text{:C}$ expressed as a 3D contour map. The map shows the TL emission centered at ~ 414 nm and the temperature for the highest emission at $\sim 182^\circ\text{C}$.

radiation at high temperatures. A temperature ramp was generated from RT up to 500 °C using a heating rate of 3 °C. The spectra were collected using 1 s in integration time. Figure 5.16 depicts the blackbody emission recorded. Clearly, after 360 °C, emission at wavelengths higher than 800 nm becomes a point of concern. Moreover, the blackbody emission enlarges to lower wavelengths as the temperature is increased. Thus, if the emission of a certain material lies on blackbody emission region, correction procedures must be carried out.

Figure 5.16: *Contour plot showing the emission spectra of blackbody radiation from heating planchet. The temperature was raised using a 3 °C/s heating rate.*

CONCLUSIONS AND FUTURE PERSPECTIVES

The heating system exhibited a good performance on generation of temperature ramps, as well as, temperature plateaus. Temperature ramps were raised from RT up to 500 °C on different heating rates between 0.5 °C/s and 5 °C/s, with maximum temperature deviations of 2 °C. Furthermore, the temperature plateaus to be used in annealing procedures showed a good stability, exhibiting a maximum deviation of 0.5 °C at 500 °C over ~300 s.

As expected, the alteration on slit of the optical spectrometer lead a loss on its spectral resolution but did not compromise its usage, as verified in RL spectra tests. These tests were carried out using materials which emission spectra are well known and showed a quite good agreement with the literature. The implemented software to perform TL spectra measurements showed to be straightforward for running tests, as well as, for data acquisition and recording. The TL spectrum test was carried out using carbon-doped aluminium oxide $\text{Al}_2\text{O}_3\text{:C}$ and also exhibited agreement with the literature. Therefore, the instrument arrangement enabled us to carry out RL and TL spectra measurements with a good performance.

6.1 Further steps

In a further stage, the developed instrument will be used to investigate materials, i.e., to better understand the radioluminescent and thermoluminescent properties using materials which luminescent and dosimetric properties are well known. Moreover, new materials will be synthesized in order to find new phosphors and dosimeters

with promising properties.

The instrument developed is able to perform another type of measurement, i.e, radioluminescence in high temperatures. This technique has been used to study thermal quenching of radioluminescence processes [34, 45, 46]. Besides thermal quenching of RL, this technique will be explored to investigate possible connections between radioluminescent and thermoluminescent properties still unknown currently.

To enhance sensitivity, as well as, spectral resolution, a new optical spectrometer will be developed. This spectrometer consists mainly by two devices, a photomultiplier and a linear variable bandpass filter, 400-700 nm range, *Edmund Optics*. Figure 6.1 shows an example of the optical filter. The modelling of the new spectrometer has already been done. Figure 6.2 depicts the first modelling of the new spectrometer. The black box represents the photomultiplier. Under the photomultiplier, the white drawer represents a holder in which the optical filter must slide in a fast speed. The filter must slide in all its range during each spectrum acquisition. The slit at the bottom of drawer is the entrance aperture in which the light from the sample should pass through. The yellow-conical shape component represents the X-ray source. At the bottom, the heating planchet is shown.

Figure 6.1: *Example of linear variable bandpass filter, 400-700 nm range, that will be used in the development of the new optical spectrometer*

Figure 6.2: (a) *Modelling of the new optical spectrometer. The black box represents the photomultiplier. Under the photomultiplier, the white drawer represents a holder in which the optical filter must slide in a fast speed. The slit at the bottom of drawer is the entrance aperture in which the light from the sample should pass through. The yellow-conical shape component represents the X-ray source. At the bottom, the heating planchet is shown.* (b) *Modelling seen from another angle.*

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