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Luminescent Thermometry

Applications and Uses

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Contents

Introduction to Luminescence Thermometry

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Abstract In this chapter, the fundamentals of luminescence thermometry are reviewed, concerning the different mechanisms on which luminescence thermometry relies, and the main performance parameters that should be given for a particular luminescent thermometer so that it can be compared with others. Finally, the different families of materials on which luminescent thermometers have been developed are reviewed, giving key examples of how each class of materials can be adapted to work as temperature sensors.

Keywords Luminescence · Luminescence thermometry · Temperature sensors · Methods · Performance · Figures of merit · Materials

1 What is Luminescence Thermometry?

The finality of luminescence thermometry is to measure temperature. So, what is temperature? As a simple definition, the temperature is the measure of the hotness or coldness of a body expressed in any temperature scale (Fahrenheit, Celsius, Kelvins) [12]. In physics, the temperature is a physical quantity that measures the average kinetic energy of the atoms or molecules in the system [8]. So, in other words, the temperature is the external manifestation of the thermal energy existing in any system. The lowest theoretical temperature is the absolute zero. At this temperature, labelled as 0 K, there is no thermal energy in the matter. Besides, by measuring the temperature difference between two media, one can know in which direction the heat (energy) will spontaneously flow, always from the area at which a higher temperature is detected to the area in which a lower temperature is present [8]. From these definitions, one can deduce the importance of temperature in several fields

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such as biology, chemistry, metallurgy, climate… a long list that does not need to be discussed here.

As mentioned above, thermometry has the aim of measuring temperature. As it is known, using the terminology of the metrology field, a measurement is the determination of the magnitude of something [48]. This measurement needs a comparison of the unknown quantity with some standard quantity of equal nature, known as measurement unit. Then, a physical measurement is defined by the act of obtaining quantitative information about this physical magnitude in a body by the comparison with the standard [48].

When defining a physical measurement, it is important to identify and understand the principle of measurement: which is the physical phenomenon in which the measurement is based. In luminescence thermometry the principle of measurement will be the change of any parameter of the luminescence generated by a material affected by the temperature at which this material is exposed.

On the one hand, it is worth to define here the meaning of the error of the measurement, which will be related to the accuracy and reproducibility of the instrument used for measuring. However, the error is related to the measurement of the magnitude itself, and not to the instrument used for measuring it. In mathematics, the error of a measurement can be defined as the difference between the observed value of a variable and the true, but unobserved, value of that variable. Furthermore, when discussing about the instrument used for the measurement (here in this book the luminescent thermometer) it is important to determine, as in all measurement instruments: (i) the resolution (related to the accuracy); (ii) the uncertainty; and (iii) the operational range. In the NIST handbook [*NIST/SEMATECH e-Handbook of Statistical Methods*, http://www.itl.nist.gov/div898/handbook], we can find a list of helpful definitions when dealing with measurements; here some of them, which terms will be used repeatedly along the book:

- Resolution is the ability of the measurement system to detect and faithfully indicate small changes in the characteristic of the measurement result. The resolution of the instrument is δ if there is an equal probability that the indicated value of any artefact, which differs from a reference standard by less than δ, will be the same as the indicated value of the reference.
- Uncertainty is a measure of the 'goodness' of a result. Without such a measure, it is impossible to judge the fitness of the value as a basis for making decisions.
- Operation range (also measurement range, measuring interval, working interval) Set of values of quantities of the same kind that can be measured by a given measuring instrument or measuring system with specified instrumental uncertainty, under defined conditions.

The measurement of the temperature in our case is done through the instrument called thermometer. Thermometers are calibrated in various temperature scales. The most known scales are the Celsius scale, also called in the past centigrade scale, in which the unit of temperature is the centigrade degree (°C), and based on defining the 0 °C for the freezing point of water and 100 °C for the boiling point of water and dividing this interval between the defined points in 100-degree steps. From another

side, one can also encounter the Fahrenheit scale, in which the unit of temperature is the Fahrenheit degree (°F), and based, originally, on defining the 0 °F for the freezing temperature of a brine solution composed by a mixture of water, ice and ammonium chloride that forms a eutectic system which stabilizes its temperature automatically to a single value. The other limit established is the estimate of the average human body temperature at 96 °F. During the twentieth century, the Fahrenheit scale was defined by two fixed points with a 180 °F separation. The first one, as in the case of the Celsius scale, is the temperature at which water freezes at sea level under standard atmospheric pressure, and located at 32 °F, and the second one corresponds to the boiling point of water, defined to be 212 °F, with a separation between these two points of 180 °F. Finally, it is also important to mention here the Kelvin scale of temperatures, also designated as the absolute thermodynamic temperature scale, in which the unit of temperature is the kelvin (K), that is by convention the international system unit for temperature. One kelvin corresponds to the change in the thermo-dynamic temperature that results in a change of thermal energy kT by 1.380649×10^{-23} J, corresponding to the value of the Boltzmann constant k.

In 1953, Bradley [11] studied the use of thermographic phosphors mixed with binders and ceramic materials to measure surface temperature in aerodynamics. A thin layer of temperature-sensitive phosphor particles deposited on the surface of a flat plate showed the distribution of temperature on this surface when exposed to the conditions of a supersonic flow. The calibration of the phosphor was described in that case using a photograph in which the brighter parts show surface parts that were cooler by about 2 K than the darker parts of the image (see Fig. 1.1). It was also possible to show that the temperature of the surface of the flat plane was about 5 K colder by the action of the supersonic flow. By the use of a photomultiplier tube, Bradley was also able to determine the temporal response of the temperature evolution. This study may be considered the first applicative study of the, new at that time, luminescence thermometry method.

Fig. 1.1 Photograph of the half-wedge of a wing model surface covered with temperature sensitive ZnCdS phosphor after 2 s of being introduced in a wind tunnel under the conditions of a supersonic flow. Adapted with permission from Ref. [15] after Ref. [11]
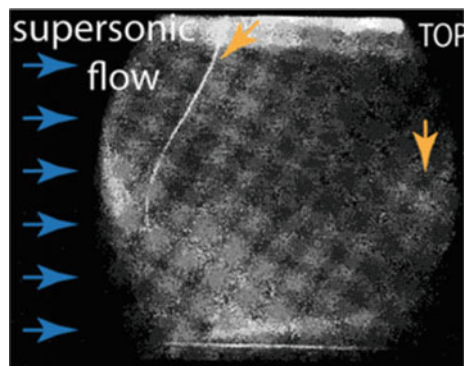
2 Luminescence

Luminescence is the spontaneous emission of light by a substance that is not the result of its heating process; this is why it is also called "cold light". Luminescence should not be confused with incandescence, which is the process of light emission by a substance as a result of overheating.

The process of emission of luminescence occurs after a suitable material has absorbed energy. Depending on the source of excitation used or the type of energy absorbed, the different types of luminescence are classified. For example, if an optical radiation was used as the excitation source, then this phenomenon would be called photoluminescence. This energy absorbed makes the material to pass to an excited state by elevating its electrons to a higher energetic state. Then, as an excited state is an unstable form of energetic state, the material undergoes another transition relaxing its electrons to the ground energy state, and some of the absorbed energy is released in the form of light, hence generating photons. The physical characteristics of these photons depend on the properties of the electronic states involved in their emission.

Luminescence can be found in multiple applications and devices in our daily lives, such as neon and fluorescent lamps, television screens, radars and X-ray fluoroscopes, in organic substances such as the luminol highly used in forensic applications, or in luciferins that are responsibles for the generation of light in bright worms, in certain pigments used in outdoor advertising, and also in natural electrical phenomena such as lightning and the northern lights. The term "luminescence" was introduced in 1888 by Lum [64].

As mentioned above, depending on the source of excitation of the material and the type of energy that it absorbs, we can find different types of luminescence. In this book the one about which we will be talking fundamentally is photoluminescence. Photoluminescence is the result of the absorption of photons by the material. It can be divided in fluorescence that is the photoluminescence resulting of the electronic relaxation of singlet–singlet electronic transitions. In that case, the lifetime of a typical emitting excited state is of the orders of nanoseconds. Another form of photoluminescence is the phosphorescence that is the photoluminescence resulting either of a triplet–triplet electronic relaxation or the persistent luminescence. In that case the average lifetime of the emitting excited state goes from microseconds to hours.

There are other types of luminescence that we want to mention, although they are not directly involved in the concepts treated in this book, but still, they are important in the context of materials science. For instance, when considering aspects related to the electrical properties of the material, we encounter the electroluminescence, that is the result of the pass of an electrical current through a material. We can also find the cathodoluminescence, in which the excitation energy comes from the impact of a beam of electrons on the material. When considering aspects related to the mechanical properties of the material, we can talk about mechanoluminescence, that is the result of a mechanical action on a solid; triboluminescence, generated when the bonds of the atoms in a material are broken when it is scratched, crushed, or

rubbed; or piezoluminescence, produced by the action of the application of pressure or a strength on the material. There are other types of luminescence, more specific ones, and related with the composition of the material. For instance, we can talk about radioluminescence, that is the result of the bombardment of the material with ionizing radiation. We can also find the thermoluminescence that is the re-emission of the energy absorbed when a substance is heated, or the cryoluminescence, that is the emission of light when a material cools down. Finally, a special mention should also be made to the crystalloluminescence, in which the initial energy comes from the crystallization process, and that is a special case of triboluminescence due to a chemical process, in that case the recombination of ions to form a non-dissociated salt.

Thus, the most used type of luminescence in luminescence thermometry is photoluminescence. Photoluminescence is a process that, in general, proceeds in two different steps. The first one is the excitation of the emitter, i.e., the absorption of one or more photons of the excitation source by the material. This causes the electrons of the luminescent material (either molecule or ion) to jump to higher electronic states. From here, the second step takes place, when the electrons of the luminescent material relax, returning back to the ground energetic state or to an intermediate electronic state, this extra energy will be emitted in the form of light (if a radiative process takes place) or dissipated in the form of heat (if a non-radiative process is occurring) [94]. The Jablonski energy level diagram shown in Fig. 1.2 illustrates this luminescence process, including the absorption of energy by the electrons of the luminescent material, the internal energy conversion processes, and the luminescence phenomena that might occur.

The properties of the light emitted through these processes depend on the properties of the electronic levels involved, which are influenced, among other parameters, by the local temperature of the system. When a change in temperature is produced, many of the parameters describing the light emitted are modified, including the intensity of the luminescent bands emitted, the shape of the emission spectra, or the luminescence decay time, among others. Many of these parameters can be exploited to determine the temperature of a particular event if the physical mechanism that produces the change in the considered parameter is known. Thus, we can define that luminescence thermometry consists of correlating the changes in these parameters of the light emitted with the variation of temperature produced.

3 Methods Used in Luminescence Thermometry

Methods used in luminescence thermometry can be classified in two big groups: (i) time-integrated methods; and (ii) time-resolved methods.

For time-integrated methods, luminescent materials should be illuminated with a constant intensity of light during the period of detection of the luminescence generated, and then, the signal integration, or the spectral changes of the emission spectra generated, can be analyzed.
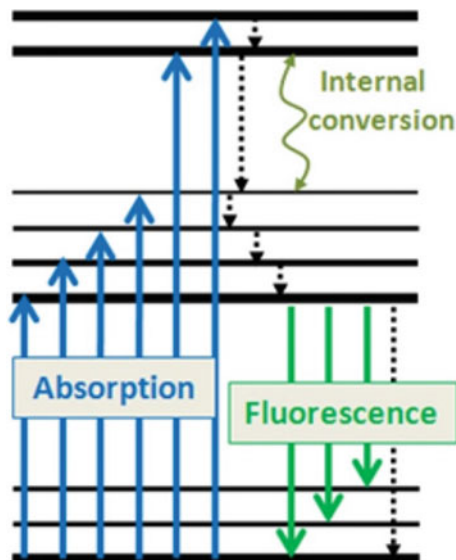
Fig. 1.2 Schematic representation of the luminescence process through a Jablonski energy level diagram. The arrows looking up represent the absorption of energy that might occur through the absorption of light. The straight arrows looking down represent the emission of light. The twisted and discontinuous arrows represent the internal conversion processes and the non-radiative processes (including vibrational relaxation and quenching processes) which hamper the emission of light, including vibration relaxation mechanisms

For time-resolved methods, a pulsed illumination source should be used, while the observation of the emission takes place during the period in between pulses, allowing analyze the temporal changes of the emission spectra. These time-resolved methods can also be developed by modulating periodically the illumination intensity while the signal analysis is produced in the frequency domain.

In general, it has been observed when comparing their performances, that time-integrated methods provide higher thermal sensitivity values than time-resolved methods [15]. Also, it has been observed that time-resolved approaches are more precise and reliable than time-integrated methods for determination of temperature in biological samples [76]. Recent investigations seem to indicate that accurate determination of temperature in biological systems using time-integrated approaches is nontrivial, as the optical transmission of biological tissues changes with temperature, distorting the emitted luminescence spectral shape before reaching to the detector [117]. To solve this problem, time-resolved methods should be used.

However, the most used time-integrated techniques require monitoring two different emissions to achieve self-referencing techniques, while measurements on time-resolved methods require only the observation of one emission band. Also, we must consider that measuring temporal emission changes can be done with much more accuracy than emission intensity measurements. Nevertheless, reduced uncertainties compensate for lower sensitivities, and therefore time-integrated methods

show this better performance. Also, regarding the complexity and the cost of the equipment used in time-resolved methods, time-integrated approaches are more favorable, since they require simpler measurement set-ups and cheaper equipment.

Here we present both methods, since they have been used to determine temperature by analyzing different parameters in luminescence thermometry.

3.1   Time-Integrated Methods

There are three main parameters that define the emission bands in the luminescence spectrum generated by a substance that can be used in the time-integrated methods:

- The **band position**: it represents the wavelength at which the maximum intensity for the emission is encountered.
- The **bandwidth**: it represents the energy or wavelength interval for which the intensity of the emission takes half of its maximum value.
- The **intensity**: it is the variation of the recorded signal as a function of the wavelength or energy.

These three parameters might change with temperature due to different processes, including:

- Population redistribution over the different electronic levels of the active ion or molecule according to the Boltzmann statistics: changes in temperature would activate the population redistribution among the different energy states.
- Quenching mechanisms activated by temperature: an increase of temperature would activate mechanisms of cross-relaxation between electronic levels, while luminescence quenching centers would reduce the luminescence intensity until eliminating it completely.
- Non-radiative relaxations or deactivations: through these mechanisms, electrons relax from the excited states towards the ground or intermediate states dissipating the energy in the form of heat instead of emission of light at a different wavelength.
- Auger conversion processes assisted by phonons: as temperature increases processes of Auger electrons ejection would be activated, that influence the parameters of the corresponding spectra.
- Dilatation or contraction of the crystal lattice: due to temperature changes, the crystal lattice in which the active ions or molecules (emitters) are embedded will expand or contract. That might produce changes in the position of their electronic levels, and consequently, changes in the luminescent properties of the material.
- Changes in the refractive index of the media in which the emitters are located: again, due to the expansion or contraction of the material as the temperature changes, or to changes in its polarizability that are also a consequence of the temperature changes, the luminescent parameters might change with temperature.

Based on the three main parameters that define the emission bands in the luminescence spectrum generated by a substance (band position, bandwidth and intensity),

we can define five different methods of operation in the time-integrated approaches for luminescence thermometry:

i.   intensity-based luminesce thermometry: here the variation of the intensity from a single emission band as a function of the temperature is measured;
ii. intensity ratio (or band shape) thermometry: in this technique the variation of the intensity ratio between two emission bands as the temperature changes, that also affects their band shape, is quantified;
iii. spectral bandwidth luminescence thermometry: for this approach the variation of the bandwidth of an emission band when the temperature change is determined;
iv. spectral position luminescence thermometry: in that case the spectral shift of a particular emission band as a function of the temperature is considered;
v.   spectral polarization luminescence thermometry: in this particular technique the variation of the polarization of a particular emission band as the temperature changes is analyzed.

Figure 1.3 presents, schematically, how can we observe the changes of these parameters induced by the change in temperature in an electromagnetic spectrum. These different methods of operation in the time-integrated approaches for luminescence thermometry are described in detail in the following sections.
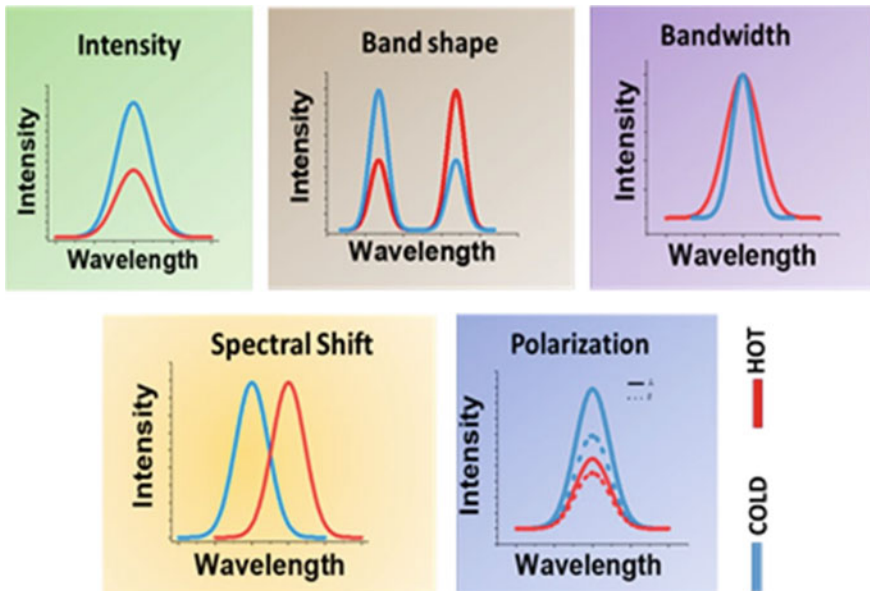
Fig. 1.3 Time-integrated possible effects caused by an increase of the local temperature on the properties of the luminescence emission spectrum of a given emitter
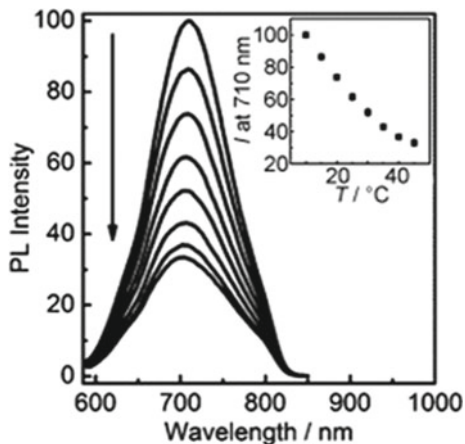
Intensity-based luminescence thermometry

It has been observed that, in general, the intensity of the emission of any material is reduced when the temperature increases until it is totally quenched. This decrease of intensity, especially in the dominant band of a spectrum, can be easily observed, even visually. For this reason, this became one of the first mechanisms used to sense temperature through luminescence thermometry [11], even in the application of this thermometric technique to biomedical sciences [55].

Intensity-based luminescence thermometry has been analyzed in different systems, including quantum dots [39, 105], organic dyes [63, 83], lanthanide-doped systems [32, 115], polymers [97], and gold nanoclusters [92].

However, luminescent thermometers based on following the evolution of the intensity of a single emission band as the temperature changes are substantially influenced by the measurement conditions, since the emission intensity depends also on other parameters. Among them, it is important to mention power fluctuations or illumination oscillations of the excitation source, the signal-to-noise ratio and instabilities in the detection set-up system, the absorption and scatter cross-sections of the emitters, the variation of the concentration of emitters in the sample where the temperature wants to be measured, or the inhomogeneity on the distribution of the emitters in the luminescent thermal probes. Thus, it requires recursive calibration procedures that are not compatible with friendly end-user applications.

As an example of application of this class of luminescent thermometers, it can be described the use of fluorescence gold nanoclusters as intensity-based luminescent thermometers. For that, lipoic acid protected fluorescent gold nanoclusters, with ultrasmall sizes (1.6 ± 0.3 nm in diameter), with excellent colloidal stability in biological media, and good biocompatibility, were used as luminescent thermometers operating under the intensity-based technique [92]. These properties are crucial for the potential application of these luminescent probes in biological media especially. The emission intensity of these gold nanoclusters, which changed considerably over the physiological range of temperatures [288 K (15 °C)–318 K (45 °C)] was used as the thermometric parameter under the intensity-based luminescence thermometry technique. These gold nanoclusters emitted bright fluorescence in the near-infrared region as a single peak centered at ~700 nm, in the so called first biological window where the optical transparency and scattering of light of biological tissues is reduced, as it is described more in depth in Chap. 6, after being excited at 580 nm with an excitation power density of 2.8 kW cm^{-2}. Figure 1.4 shows the pronounced temperature dependence of the steady-state fluorescence emission spectra of the gold nanoclusters suspended in phosphate-buffered saline (PBS). In the figure it can be seen how the intensity of the emission of the gold nanoclusters decreased substantially from the lowest temperature at which the spectrum was recorded (283 K, 10 °C), in the upper part of the figure, to the highest temperature analyzed (318 K, 45 °C) in the lower part of the graph. This decrease in intensity represented a 67% of reduction upon raising the temperature. The inset in the figure shows how the maximum intensity of the emission band decreased as the temperature increased.

Fig. 1.4 Dependence with
temperature of the
fluorescence emission
intensity of lipoic
acid-capped gold
nanoclusters dispersed in
PBS, after excitation at
580 nm. Adapted with
permission from Ref. [92]

This graph indicates that an intensity change of 0.5% K^{-1} is required to resolve a temperature difference of 0.1–0.3 K.

Intensity ratio or band shape luminescence thermometry

The intensity ratio luminescence thermometry (also called band shape thermometry in some sources since it is depicted in fact by a change on the shape of the spectra) can be used when the luminescence spectrum of a given system consists of several emission bands or lines, and the intensity of at least one of them changes significantly as the temperature increases to respect the intensity of the others. So that, it exploits the relative change in the intensity ratio between two electronic transitions. At present, this is, by large, the most used method in luminescence thermometry, since it constitutes a self-referencing method. This means that the second emission serves as an internal standard to calibrate the response of the luminescent probe.

The intensity ratio luminescence thermometry technique has demonstrated that it can provide a high thermal sensitivity and has been used for imaging with better thermal resolution than the intensity-based luminescence thermometry technique. It also mitigates most of the problems that have been identified for the intensity-based luminescence thermometry technique, especially those referring to changes in the measurement conditions affecting the signal obtained. This is because the intensity ratio luminescence thermometry technique determines the ratio between two absolute intensities.

In the intensity ratio luminescence thermometry technique, we have to distinguish between two different cases for which even different theories to model the defined intensity ratio between two different emission lines must be used:

- Single-center thermometers: this situation can be considered when the emission bands/lines used to build the luminescent thermometer are generated by a single luminescent center. Here, the changes in the band shape of the spectrum are caused by the redistribution of the electronic population among the different energy levels

of the emitting center caused by changes in temperature. Although simpler conceptually that the following case, even here different situations must be considered, depending on whether the emissions used to calculate the intensity ratio are generated from thermally coupled levels (known as TCL) or not, as we will discuss in the following section.

- Dual-center thermometers: this situation can be considered when the emission bands/lines used to build the luminescent thermometer are generated by two different emitting centers. Here, the changes in the band shape of the spectrum are induced by the different thermal quenching ratios of each luminescent center, or by changes in the energy transfer rates between the two emitting centers, caused in all cases by changes in temperature, as we will see more in detail later.

The intensity ratio luminescence thermometry technique has been reported in a wide variety of luminescent systems, such as quantum dots [44, 103], organic dyes [28, 77], and especially in lanthanide-doped systems [88, 89, 102].

However, the intensity ratio luminescence thermometry technique suffers from an important drawback when it is applied to biological systems, as will be detailed later in Chap. 8. In fact, the optical transmission of biological tissues is temperature-dependent and varies from one type to another (it is not the same the optical transmission of muscle tissue than that of the epithelial tissue, for instance). This makes the shape of the emitted luminescent spectra to be distorted by the biological tissue before being recorded by the detector. Thus, important precautions must be taken into consideration when using this technique to measure temperature in biological system, despite it is widely extended in the literature, or alternatively time-resolved techniques should be used.

Single-center luminescent thermometers. Regarding the use of single-center luminescent thermometers, the ratiometric approach that constitutes the intensity ratio luminescence thermometry technique, usually exploits the ratio between the intensity of two emissions originated from two different excited states, closely separated in energy, that are considered to be in thermal equilibrium. For instance, in lanthanide-doped systems it can be considered that two different electronic energy levels are in thermal equilibrium when the energy difference between them is in the range 200–2000 cm^{-1} [104]. This relatively small energy difference allows the promotion of electrons from the low energy level to the high energy level using only thermal energy [81].

This situation constitutes a particular case when analyzing single-center luminescent thermometers that is referred to as the fluorescence or luminescence (depending on the bibliographic source) intensity ratio (FIR or LIR, respectively). In these systems we can apply Boltzmann's statistics to describe the distribution of electronic population between the two electronic levels involved in this process. The electronic population of these two electronic levels is regulated according to the Boltzmann's distribution law as:

$$N_2 = \frac{g_2}{g_1} N_1 \cdot \exp\left(\frac{-\Delta E}{k_B T}\right) \tag{1.1}$$

where N_2 and N_1 are the number of electrons in the higher and lower energy levels, respectively; ΔE is the difference of energy between the two electronic levels involved in the process, defined as the energy gap between the barycenters' of the $1 \rightarrow 0$ and $2 \rightarrow 0$ emission bands; k_B is the Boltzmann's constant; g_i are the degeneracies of the two energy levels; and T is the absolute temperature.

According to that, FIR or LIR is defined using the emission intensities corresponding to the $2 \rightarrow 0$ and $1 \rightarrow 0$ transitions, where 0 denotes the ground state or an electronic level with lower energy than 2 and 1 [104]:

$$FIR(LIR) = \frac{I_2}{I_1} = \frac{A_{02}h\vartheta_{02}N_2}{A_{01}h\vartheta_{01}N_1} = \frac{g_2 A_{02}h\vartheta_{02}}{g_1 A_{01}h\vartheta_{01}} \cdot \exp\left(\frac{-\Delta E}{k_B T}\right) = B \cdot \exp\left(\frac{-\Delta E}{k_b T}\right) \tag{1.2}$$

where A_{0i} are the total spontaneous emission rates from the high energy levels to the ground or lower energy state, $\upsilon 0i$ are the frequencies corresponding to the $1 \rightarrow 0$ and $2 \rightarrow 0$ transitions; and h is the Plank's constant.

To determine the values of B and $\Delta E / k_B$ the natural logarithm of Eq. 1.2 can be used, since it will show a linear dependence with the inverse of temperature, and then, can be calculated from the line-slope and the intercept with the y-axis, respectively, of the function obtained.

For instance, different emission lines can be used to calculate the FIR of different Er^{3+}, Yb^{3+}-doped materials that constitute the broad emission band observed at around 1500 nm, associated to the radiative transition between the $^4I_{13/2}$ first excited state and the $^4I_{15/2}$ ground state of Er^{3+} ($^4I_{13/2} \rightarrow {}^4I_{15/2}$). Figure 1.5a shows the emission spectra of Er^{3+} at around 1500 nm when doped in different materials, including simple oxides, complex oxides, fluorides and oxyfluorides, always accompanied by Yb^{3+}, at room temperature and at 333 K [88, 89]. In this figure, it can be clearly seen how the shape of the spectra changes as the temperature increases. Spectra were recorded at different temperatures in this interval, and by comparing the absolute intensity of two lines in the different spectra for each material as they change when the temperature increases (in that case the emission lines located at 1534–1535 nm and at 1553–1555 nm were considered), the intensity ratio between these two lines could be calculated. Figure 1.5b shows the trend of these intensity ratios as the temperature increases, in which different slopes can be observed depending on the type of material considered. The higher the slope of the trend of the intensity ratio with the temperature, the more sensitive the luminescent thermometer is. In that case, oxyfluoride materials exhibited the highest change of the intensity ratio with temperature, and thus constitute the most sensitive luminescent thermometer of the range of materials selected, despite the emitting ion is the same in all cases (Er^{3+}) and the excitation conditions were kept the same for all the materials analyzed. This indicates the importance of a correct selection of the host in which a particular lanthanide ion is embedded to optimize the sensitivity of the luminescent thermometer.

From the FIR graph (Fig. 1.5b), the B parameter can be calculated, fitting in a graphic representation software the different lines plotted for the different materials with Eq. 1.2.
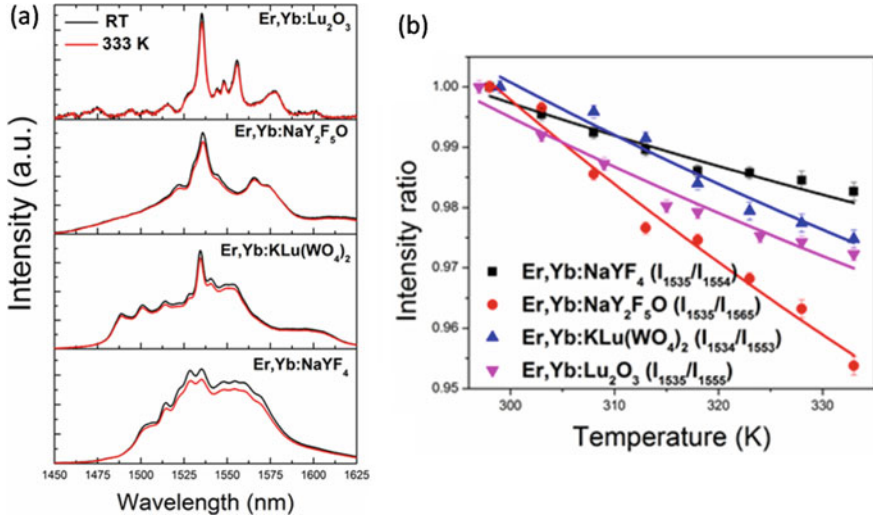
Fig. 1.5 **a** Representation of the Er^{3+} emission at around 1500 nm in different Er^{3+}, Yb^{3+} co-doped nanoparticles for different materials (single oxides, complex oxides, fluorides and oxyfluorides) taken at room temperature and at 333 K to show the different shape of the spectra as the temperature increases. **b** FIR between the emission lines located at 1535 and 1555 nm of Er^{3+} in the different materials at different temperatures, showing the trend evolution of the intensity ratio with temperature. The highest the slope, the more sensitive the luminescent thermometer is. Adapted with permission from Ref. [88, 89]

There is still another way of determining the B parameter using the Judd–Ofelt theory [49, 72]. For this, the integrated coefficient of spontaneous emission of the $J \rightarrow J'$ transition must be considered:

$$A_{JJ'} = \frac{64\pi^4 e^2 n_i^3}{3hc^3}\left[\frac{n(n^2+2)^2}{9}S_{ed} + n^3 S_{md}\right] \tag{1.3}$$

where e is the electronic charge, n is the refractive index of the medium, and S_{ed} and $S_{md} W_\lambda$ are the electric and magnetic dipole strengths, respectively, given by:

$$S_{ed} = \frac{1}{(2J+1)}\sum_{\lambda=2,4,6} W_\lambda |\langle J' \| U^{(\lambda)} \| J^2 \rangle|^2 \tag{1.4}$$

$$S_{md} = \frac{h^2}{16\pi^2 mc^2}|\langle 0 \| L+2S \| i \rangle|^2 \tag{1.5}$$

where W_λ with $\lambda = 2, 4,$ and 6 are the Judd–Ofelt intensity parameters, and m is the electron mass. $U^{(\lambda)}$ and $L + 2S$. are reduced matrix elements tabulated by Carnall and Crosswhite [17], where the L and S angular operators are in units of h. The $W_{2,4,6}$ parameters in Eq. 1.4 can be obtained from the absorption spectra

of the corresponding lanthanide ion [36], or if Eu^{3+} is used, and only in this case from its emission spectra [16]. This allows calculating the coefficient of spontaneous emission, and thus, the B parameter.

As an example, and for the particular case of Er^{3+} and its emissions in the green arising from the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ induced electric-dipole transitions, the B parameter can be calculated as follows [57]:

$$
\begin{aligned}
B &= \frac{n_2^4}{n_1^4} \frac{\beta_2}{\beta_1} \frac{\sum_{\lambda=2,4,6} W_\lambda \langle I \| U^{(\lambda)} \| H \rangle^2}{W_6 \langle I \| U^{(6)} \| S \rangle^2} \\
&\approx \frac{n_2^4}{n_1^4} \frac{\beta_2}{\beta_1} \frac{0.7158 W_2 + 0.4138 W_4 + 0.0927 W_6}{0.2225 W_6}
\end{aligned}
\tag{1.6}
$$

where I stand for the $^4I_{15/2}$, H for the $^2H_{11/2}$, and S for the $^4S_{3/2}$ electronic levels.

Apart from FIR (LIR), for which the electronic levels from which the emission bands arise need to be in thermal equilibrium, i.e., thermally coupled, we can also determine an intensity ratio between two emission lines arising from a single-centre luminescent thermometer whenever their intensities change at different rates when the temperature changes. This is the case, for instance of Tm^{3+} ions sensitized by Yb^{3+}, in which, after pumping at 980 nm, the energy absorbed by Yb^{3+} ions is transferred to Tm^{3+} ions that generate emissions in the blue and the deep red spectral regions of the electromagnetic spectrum, arising from the $^1G_4 \rightarrow {}^3H_6$ and $^3F_3 \rightarrow {}^3H_6$ transitions, respectively [87]. It can be seen in Fig. 1.6, how the relative intensity of these transitions changes when the temperature increases in the case of Yb, Tm: $GdVO_4@SiO_2$ core–shell nanoparticles. At room temperature the blue emission, located at 475 nm, is dominant, while at 473 K (200 °C) the deep-red emission, located at 700 nm, reaches an intensity comparable to that of the blue emission, and becomes clearly dominant at 673 K (400 °C). Thus, a luminescent thermometer can be built based on the changes induced thermally in the intensity ratio of deep red and blue UC emissions, derived from the different temperature dependence of radiative and non-radiative relaxation rates of the $^1G_4$ and $^3F_3$ emitting levels, as well as of the temperature dependent energy transfer rate between them, providing an internally calibrated signal for the thermometer [45, 104]. The mechanism proposed for this luminescent thermometer can also be seen in Fig. 1.6, in which at room temperature, the population of the blue emitting $^1G_4$ electronic level can be explained by the sequential absorption of three photons from an energy transfer process from excited Yb^{3+}. In a first step, the excited Yb^{3+} $^2F_{5/2}$ level transfers part of its energy to the $^3H_5$ electronic level of Tm^{3+}, from which electrons relax in a very fast way towards the $^3F_4$ electronic level of Tm^{3+}. Here, a second energy transfer process from Yb^{3+} takes place, promoting the Tm^{3+} electrons to the $^3F_2$ energy level, which relaxes at its time, populating the $^3F_3$ and $^3H_4$ levels. Finally, the third energy transfer process occurs, promoting Tm^{3+} electrons in the $^3H_4$ level to the $^1G_4$ level. It is from here that the blue emission centred at 475 nm is generated, arising from the $^1G_4 \rightarrow {}^3H_6$ radiative transition. The progressive quenching of the blue emission

as the temperature increases, and the simultaneous development of the deep-red emission arising from the $^3F_3$ level point towards the existence of some efficient cross-relaxation processes, labelled as CR1 in Fig. 1.6, from which both $^1G_4$ depopulation and $^3F_3$ population take place. Additionally, the enhanced population of the $^3F_4$ level of Tm^{3+} can also contribute to feed the $^3F_3$ level via energy transfer from Yb^{3+} to Tm^{3+}, labelled as CR2 and CR3 in Fig. 1.6. Furthermore, the $^3F_3$ level is only separated by $\Delta E = 900$ cm^{-1} from the $^3H_4$ level [59], so that it can also be populated by this last level when the temperature increases [68, 111], indicated in Fig. 1.6 with orange circular arrows. These processes are evident for high Tm^{3+} concentrations.

When we plot the intensity ratio between these two emission bands as a function of temperature (see Fig. 1.6), it can be seen that it is strongly temperature dependent, and that the plot follows an increasing exponential function that can be fitted to the
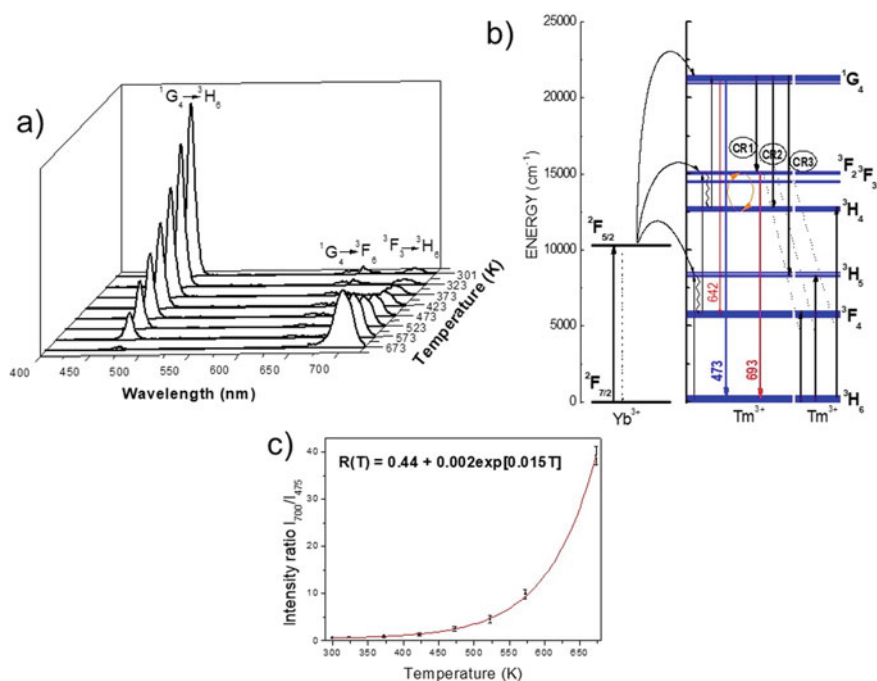
Fig. 1.6 Example of an intensity ratio based single-center luminescent thermometer involving two emission lines generated by two electronic levels that are not thermally coupled: **a** Evolution from room temperature up to 673 K (400 °C) of the up-conversion spectra under 980 nm excitation recorded for 1% Tm^{3+}, 15% Yb^{3+}:GdVO$_4$@SiO$_2$ core–shell nanoparticles. **b** Schematic representation of the Yb^{3+} and Tm^{3+} electronic energy levels and proposed mechanisms responsible for populating Tm^{3+} levels generating the blue and deep red emissions involved in the luminescent thermometer proposed. **c** Calibration curve of the intensity ratio [R(T)]$^®$ between the emission peaks located at 475 and 700 nm (I_{700}/I_{475}) as a function of temperature. Error bars reflect the reproducibility of the calibration curve after the analysis of several spectra for each measured temperature. Adapted with permission from Ref. [87]

following equation:

$$R(T) = \frac{I_{700}}{I_{475}} = A + B \cdot \exp(CT) \tag{1.7}$$

where A, B and C are fitting parameters and $R(T)$ defines the intensity ratio, indicated with a different symbol than FIR (LIR) since the emissions do not arise from two thermally coupled levels.

In that case, however, no equation of state governs the intensity ratio, and thus, it is not possible to develop a primary thermometer with this approach, as can be seen in Chap. 3.

Dual-center luminescent thermometers Dual-center luminescent thermometers are those in which the emissions arise from two different luminescent centers. Different schemes have been proposed for this kind of luminescent thermometers:

- The same particle or molecule contains the two luminescent centers that can be excited with a single wavelength.
- The same particle or molecule contains the two luminescent centers, but they must be excited at two different wavelengths simultaneously.
- The two luminescent centers are distributed in two different particles or molecules, but they can be excited at the same time with the same wavelength.
- The two luminescent centers are distributed in two different particles or molecules, and they must be excited at two different wavelengths simultaneously.

In all these cases a phenomenological equation describing the dependence of the luminescence with temperature is established, and thus, an equation of state cannot be established, and thus, primary luminescent thermometers, as those described in Chap. 3 cannot be developed using dual-center luminescent thermometers.

### Spectral position luminescence thermometry

This method is based on the analysis of the position of the emission lines in the spectrum. The position of the lines depends on the energy separation between the electronic levels involved in their generation. Such differences in energy between the electronic levels are a function of several temperature dependent parameters, such as the refractive index of the material and the inter-atomic distances among emitting centers due to the expansion of the crystal lattice as the temperature increases, for instance [67]. Thus, a correlation between temperature and the spectral positions of the different emission bands or lines of the spectra can be established to use them as luminescent thermometers, provided that these spectral shifts are sufficiently large to allow for accurate measurements.

The main advantage of using this method to determine temperature is that the measurements are not affected by luminescence intensity fluctuations due to changes in the concentration of the emitting centers, or fluctuations of the power of the excitation source, neither by the shadowing effects or the movement of the sample in which the temperature is being determined.

Spectral position luminescence thermometry has been developed principally using quantum dots (QD), where spectral shifts with temperature are relevant [65, 67]. Nevertheless, other materials, like lanthanide-doped nanoparticles have also been explored for this kind of luminescence thermometry [82]. However, the shift position observed in the spectra for the different emission lines was much smaller than the one observed in the case of QDs, of the order of 0.1 cm^{-1} K^{-1}. From another side, the fact that the FWHM of the emission bands of lanthanide ions is substantially narrower than that observed in QDs, makes easier the determination of the position of these emission bands.

As an example, Maestro et al. [65] used CdSe quantum dots for spectral position luminescence thermometry, since the peak emission wavelength of these QDs is temperature sensitive. Figure 1.7 shows the variation of the emission peak position for these CdSe QDs as the temperature increases under one-photon (excitation in the blue at 488 nm with a continuous laser) and two-photon excitation (excitation in the near-infrared, 800 nm, with a femtosecond pulsed laser) conditions. The two-photon excitation conditions lead to a higher confinement of the luminescence generated by these nanoparticles, interesting for achieving higher spatial resolutions, even below the wavelength of excitation. Figure 1.7a, b show how the position of the luminescence band and the emitted intensity depend on the temperature. Thus, an increase in temperature results in a shift of the emission band towards longer wavelengths (red shift), while the emitted intensity is also reduced due to a reduction in the optical conversion efficiency. This latter phenomenon is more evident in the case of the two-photon excitation since near-infrared (NIR) light is used to generate visible light, a less efficient mechanism than pumping above the emission wavelength of these nanoparticles, as it happens with the one-photon excitation mechanism. Figure 1.7c the spectral shift and the variation of the emitted intensity as a function of temperature for these CdSe QDs that can be used for an accurate calibration of the spectral parameters to be used later as luminescent thermometers.

A different way of using spectral position luminescence thermometry, in that case reported for lanthanide-doped materials, is through the comparison of their excitation spectra. Excitation spectra provides an alternative way of determining the position and the strength of absorption features in a material. This kind of spectra are obtained by measuring the intensity of an emission band while the excitation wavelength changes [3]. These spectra are formed normally by two different structures: (i) a strong and broad absorption band called charge transfer (CT) band, due to electron transfer processes between the host material and the doping ion [25], whose position in largely influenced by temperature; and (ii) several narrow bands due to the electronic transitions within f electrons in the doping lanthanide ions, whose position is almost temperature independent. Thus, the position of this CT band can be used as a thermal sensor. Figure 1.8 shows the change in the position of the CT band in the excitation spectra of $Eu:Y_2O_3$ particles as the temperature increases from 114.5 to 350.0 °C. In the same spectra, it can be seen how the position of the small bands attributed to the f-f transition of Eu^{3+} ions are almost insensitive to temperature, while the broad and highly intense CT band changes substantially its position to longer wavelengths as the temperature increases, at a rate of 0.6 nm/°C.
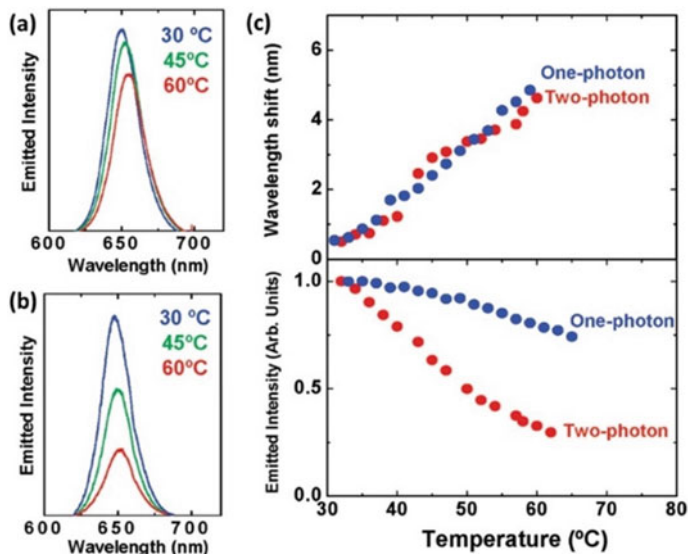
Fig. 1.7 Emission spectra of CdSe QDs dispersed in a phosphorus buffered saline (PBS) solution at three different temperatures showing the displacement of the position of the emission band and the decrease in intensity under **a** one-photon and **b** two-photon excitation conditions. **c** Temperature variation of the position of the emission band (top) and integrated emission intensity (bottom) recorded for the dispersion of the CdSe QDs in PBS. Adapted with permission from Ref. [65]
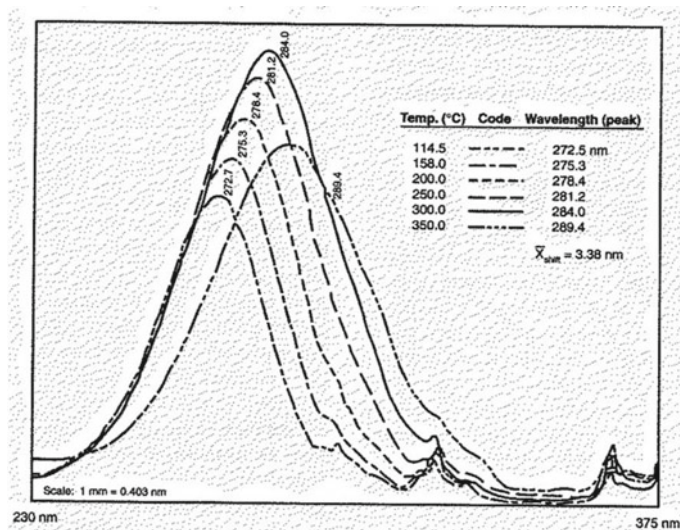
Fig. 1.8 Temperature dependence of the excitation spectra of $Eu:Y_2O_3$, in which it can be clearly seen how the charge transfer band, very broad, with a high intensity and located at shorter wavelengths changes substantially its position, while the position of the low intensity bands attributed to the f-f transitions of Eu^{3+} are almost insensitive to the changes in temperature

Spectral bandwidth luminescence thermometry

Whenever temperature increases above 0 K, higher energy phonon levels are populated in a material, generating the intrinsic vibrations of the structural lattice. The population of these higher energy phonon levels leads to a broadening of the absorption and the emission bands. This is due to the fact that the excited electronic sublevels can also be populated, and they contribute to the absorption and emission processes. This phenomenon is known as the homogeneous broadening of the absorption or emission bands. From another side, the presence of different optical centers, as well as the presence of defects in the host, might generate also a broadening of the absorption and emission lines, known as inhomogeneous broadening. Since these broadening effects of the absorption and emission bands depend on temperature, they can be used to generate a luminescent thermometer. The homogeneous broadening effect is very sensitive to temperature changes, while the inhomogeneous broadening effect is less sensitive to temperature variations. The change in the broadening of the absorption or emission band can be quantified as [42]:

$$\omega(T) = \omega_0 \sqrt{\coth\left(\frac{hW}{2k_BT}\right)} \tag{1.8}$$

where ω_0 is the FWHM of the absorption or emission band at 0 K and hW is the energy of the vibration of the structural lattice or the energy of the phonon or phonons interacting with the electronic transition. Thus, as the temperature increases, the width of the absorption or the emission band becomes wider, due to the contribution of thermal vibrations to the luminescence processes, but also due to the contribution of thermal vibrations arising from the neighboring atoms and/or molecules.

However, this luminescence thermometric technique has a major disadvantage, and it is that the broadening change is small, and it can only be observed in systems that present narrow absorption and emission bands such as those found in lanthanide ions [6]. Figure 1.9 shows the broadening of the emission bands of Nd^{3+} in YAG corresponding to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition and the evolution of the FWHM as the temperature increases, as well as with changing the excitation power, that results in an increase of temperature.

Nevertheless, this luminescence thermometry technique has also been implemented when using QDs as luminescent thermometers [75]. This change in the width of the absorption and emission bands can be made more evident by generating electron–phonon coupling effects through the careful selection of emitting centers and hosting materials, as it has been demonstrated for instance in Tm^{3+} doped TiO_2 particles [116] or when embedding Eu^{3+} in a coordination compound containing ketoprofen [54]. Despite this disadvantage, it seems that spectral bandwidth luminescence thermometry offers a higher thermal sensitivity and a lower thermal resolution than the most commonly used FIR (LIR) technique [43]. In spite of this, since discriminating the changes in the bandwidth of absorption and emission bands is a time-consuming procedure, this luminescence thermometric technique has

Fig. 1.9 a Emission spectra of Nd:YAG at around 940 nm obtained at two different pumping powers of the excitation source emitting at 800 nm, resulting in two different temperatures (the higher the pumping power, the higher the temperature). **b** Full width at half maximum (FWHM) of one of the emission lines corresponding to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition of Nd^{3+} in YAG as a function of temperature. Reproduced with permission from Ref. [6]
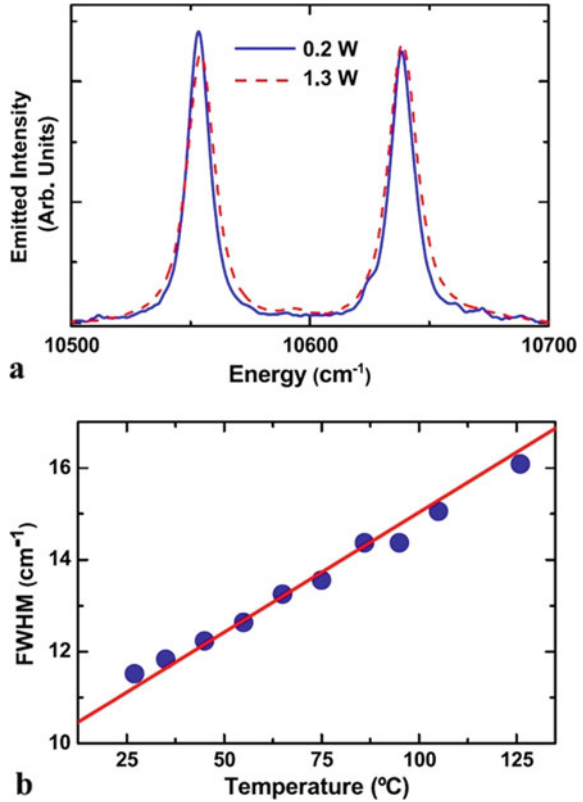
been reported as a possibility for the determination of temperature, but not practical application has been reported for it up to now.

Spectral polarization luminescence thermometry

Spectral polarization luminescence thermometry is based on the changes in the polarization of the luminescence generated by the material using the property of the anisotropy of the polarization depending on the direction of observation. Thus, this luminescence thermometric technique can only be used in anisotropic materials. The degree of anisotropy in these materials depends on the temperature, as an increase in temperature accelerates the Brownian rotational motion of the emitting entities. This higher rotation speed of the emitting entities when the temperature increases causes that a higher number of photons loose the memory of the incident light polarization during their luminescence lifetime. Thus, the degree of anisotropy of the luminescence changes as the temperature changes [23].

In practice, when a group of emitting centers embedded in different bodies is illuminated with linearly polarized light, their emission will be partially polarized due to the random orientation of the different bodies. This partial polarization is due to the polarization anisotropy of the light generated, and can be expressed as:

$$r = \frac{I_{parallel} - I_{perpendicular}}{I_{parallel} - 2I_{perpendicular}} \tag{1.9}$$

where $I_{parallel}$ is the intensity of the emission band polarized parallel to the polarization of the incident illumination light, and $I_{perpendicular}$ is the intensity of the emission band polarized perpendicularly to the polarization of the incident light. Since this polarization anisotropy is due to the rotational diffusion induced by the molecular Brownian dynamics, that at its time depends on temperature, this correlation can be estimated by the Deby-Stokes–Einstein equation:

$$\tau_R = \frac{V\mu(T)}{k_B T} \tag{1.10}$$

where τ_R is the rotational lifetime; $\mu(T)$ is the viscosity, that depends also on temperature; and V is the hydrodynamic volume of the emitting entity. By using Perrin's equation, and considering Eqs. 1.9 and 1.10, the polarization anisotropy ban be correlated with the rotational lifetime [24]:

$$\frac{1}{r} = \frac{1}{r_0}\left(1 + \frac{\tau_L}{\tau_R}\right) \tag{1.11}$$

where τ_L is the luminescence lifetime and r_0 is the polarization anisotropy in the absence of any molecular motion.

In general, as explained above, when the temperature increases the emitted photons will lose the memory of polarization of the incident light, since the Brownian rotational motion of the emitting particles is accelerated. Thus, the higher the temperature, the faster the Brownian rotational motion of the particles and thus, the larger the number of emitted photons that will lose the memory of the polarization of the pumping light. This is why an increase of temperature leads to a decrease of the degree of polarization of the emission band, and thus, to the polarization anisotropy.

This luminescence thermometry method has the advantages that is insensitive to fluctuations in the intensity of the light emitted produced by photobleaching effects, or fluctuations of the illumination intensity, as well as changes in the concentration of the emitting centers, since it is based on a ratio of intensities. Thus, it constitutes again a self-referenced method, and after the appropriate calibration process, it gives the temperature of the medium in which the temperature probe is embedded. However, this method suffers from some severe drawbacks for practical applications. The first one is that it requires a complex measurement set-up, especially for thermal imaging purposes, since it requires the use of a polarization beam splitter, and that the luminescence is recorded simultaneously on two avalanche photodiodes. The second one is that, since the rotation Brownian motion is very fast, viscous systems, like mixtures of glycerol and water must be used to allow the measurement of the polarization degree. It is also possible to measure this parameter by increasing the hydrodynamic volume of the emitting molecule, using for instance proteins. This luminescence thermometry method has been used to map the internal temperature
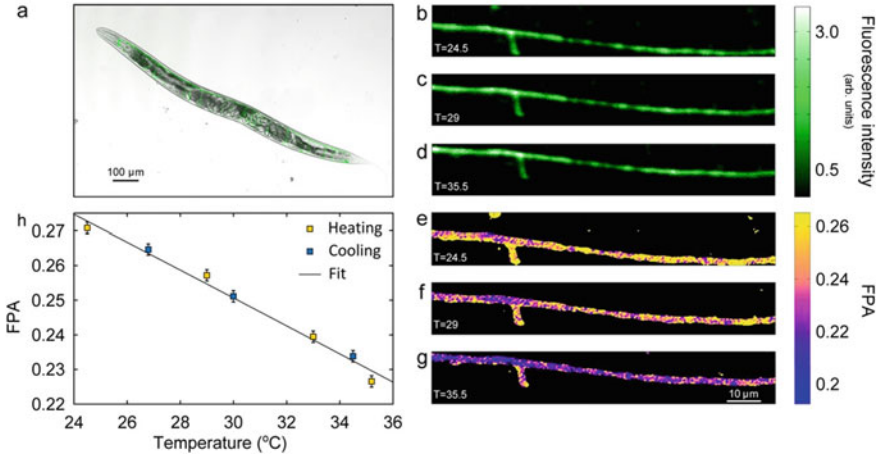
Fig. 1.10 Fluorescence polarization anisotropy (FPA) measured in a living C. elegans to determine the temperature. **a** Bright-field image of the living organism overlapped with the fluorescence intensity arising from the green fluorescent protein (GFP) located in the neurons of the C. elegans. **b–d** GFP luminescence intensity recorded at three different temperatures (24.5 °C, 29 °C and 35.5 °C). **e–g** Mapping of the FPA at these three temperatures. **h** Calibration performed for the luminescence thermometer developed by using the spectral polarization luminescence thermometry technique, in heating and cooling cycles. Reproduced with permission from Ref. [24]

of HeLa cells when heated externally [23] and map the internal temperature of a living *Caenorhabditis elegans* (*C. elegans*) modified genetically to express the green fluorescent protein (GFP) [24]. This, together with the fact that a low acquisition speed is required (it takes between 0.5 and 2 min to map the distribution temperature of the *C. elegans*), questions if the temperatures mapped can be considered as real-time temperatures. Figure 1.10 shows this kind of measurements taken on a living C. elegans.

3.2   Time-Resolved Methods

Time-resolved methods, or lifetime luminescence thermometry, as it is commonly reported in the literature, estimates the temperature of the thermal probe from the temporal dependence of its emission. Three different moments or periods can be distinguished in general in this temporal evolution of an emission, as can be seen in Fig. 1.11. In the first instant, the emission lifetime follows the time dependence of the pulse train used for excitation. Then, a rise in the emission intensity is observed, due to the accumulation of electrons in the excited level. Finally, in the third period, the intensity of the emission decreases due to interactions with phonons and internal conversion and non-radiative processes. This last period is longer than the two

Fig. 1.11 General shape of the temporal evolution of the luminescence emission intensity generated by a thermal probe. Reproduced with permission from Ref. [27]
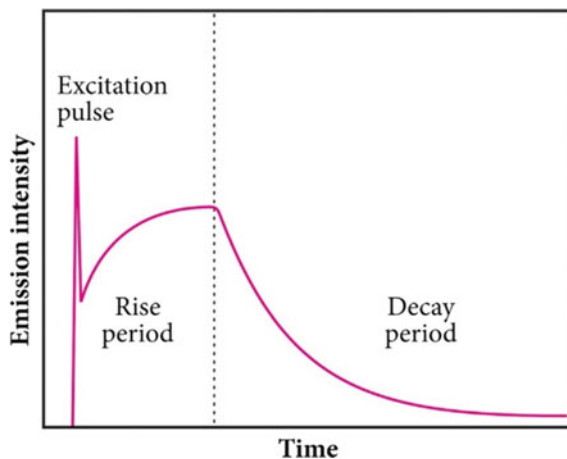
previous ones, and it is the one used normally to determine temperature in lifetime luminescence thermometry.

Decay time luminescence thermometry

Decay probabilities from electronic levels depend on many parameters, some of which are temperature dependent, including phonon-assisted energy transfer processes and multiphononic decay processes.

In general, lifetime luminescence thermometry has an important advantage when compared to intensity-based luminescence thermometry: it does not depend on the local concentration of luminescent probes. Thus, this solves problems related to non-controllable spatial fluctuations of the fluorescence intensity due to an uneven distribution or concentration of the thermal probes on the sample to be thermally analyzed. Also, problems associated with the uncontrolled motion of the thermal probes (by themselves or because they are being carried in a fluid, for instance) are also avoided. Finally, the distribution and shading of the light generated by the sample, that might also mask some characteristics of the recorded spectra can be minimized. Consequently, decay time luminescence thermometry is a self-referencing and robust method. It also allows for very fast time resolutions of the order of picoseconds to milliseconds, depending on the thermal probe used. With this technique, temperature can be determined at the time interval of the luminescence lifetime that is independent on light scattering, reflection, and intensity fluctuations of the excitation source. Also, this luminescence thermometry method has been used for high temperature measurements, avoiding the undesired contribution of the blackbody radiation [40]. An additional advantage is that this technique does not require recording the complete luminescence spectrum, saving time during temperature measurements. This is especially important when low signal levels from the thermal probes are generated, in cases, for example, where high spatial resolution is required, or when living organisms are being analyzed, allowing also for thermal imaging in real time.

These hypothetical short measuring times would avoid, or at least minimize, problems related with local heating of the system under investigation by long lasting illumination with the pumping source. Normally in decay time luminescence thermometry time domain techniques are used to measure the emission decay times. These techniques require using a pulsed excitation source, together with long illumination and acquisition times, which at the end limit the use of this method, although the recent technological advances simplified its use and reduced the costs of this kind of excitation sources. Nevertheless, the use of these techniques has been widely used in lifetime luminescence thermometry.

Figure 1.12 shows the luminescence decay curves of the green emission of Er^{3+} in $NaYF_4$ and NaY_2F_5O particles, always co-doped with Yb^{3+}, at two different temperatures. It can be easily seen that the lifetime of this luminescence emission is more sensitive to temperature changes for NaY_2F_5O than for $NaYF_4$ particles, due to the activation of phonon-assisted processes and of multiphonon decay processes as the temperature increases. The reason for these changes is the higher phonon energy exhibited by the oxofluoride compound when compared to the fluoride one, as can be seen in the Raman dispersion spectra shown in Fig. 1.12e. This results in a more sensitive decay time luminescent thermometer when using $Er,Yb:NaY_2F_5O$ particles.

Rise time luminescence thermometry

As indicated above, a rise of the intensity of the emission is observed shortly after the thermal probe is illuminated with an excitation pulse. This is due to an accumulation of electrons in the excited level of the thermal probe because of fast non-radiative transitions ending to this level and generated from higher energy levels. Also, energy migration processes from nearby excited ions must be considered. All these processes are much faster than the radiative transition of the thermal probe to the ground state or to a lower energy state [27]. This technique, however, has been much less used for luminescence thermometry than the decay time technique.

For the particular case of lanthanide ions, the number of electrons in the emitting level as a function of time can be approximated to [73]:

$$N(t) = N_0 + N_1 \cdot \left[1 - \exp\left(\frac{-t}{\tau_r} \right) \right] \tag{1.12}$$

where N_0 is the number of electrons directly excited within the ion, N_1 is the number of electrons accumulated by energy migration from nearby excited ions, t is time and τ_r is the rise time. Thus, the general temporal dependence of the emission intensity, considering it proportional to the number of electrons in the excited level, might be expressed as:

$$I(t) = \left\{ A + B \cdot \left[1 - \exp\left(\frac{-t}{\tau_r} \right) \right] \right\} \cdot \exp\left(\frac{-t}{\tau_d} \right) \tag{1.13}$$

where τ_d is the decay time and A and B are fitting parameters.