CHAPTER 7

Characterization of Nd$^{3+}$-doped phosphate glasses for temperature sensor applications
7.1. INTRODUCTION

Among the various optical methods used for developing temperature sensors are those based on luminescence properties are found to be very prominent [1, 2]. These sensors analyze the thermal induced changes in the spectral features of the light emitted by ions such as intensity, phase, polarization, wavelength, lifetime and band shape. Therefore, spectral analysis is required to obtain the temperature information with these sensors. These kind of systems demonstrate advantages over their electrical counterparts as they are free from electromagnetic interference, are electrically isolated, show a wide dynamic range and can sense the emission remotely through a transparent medium without the need of wires or coupling devices [3]. Regarding their construction and the region measured, these systems are designed to be small sized [4, 5] or distributed [3]. As with several other sensing devices, temperature optical sensors are widely proposed in the form of optical fibers since, apart from their inherent light guiding of the luminescence, this construction also confers light weight, small size and low cost [6]. Linked with the optical fibers the trivalent lanthanide (Ln$^{3+}$) ions have been one the most reported luminescence centers in the literature. Several fluorescence emissions from Ln$^{3+}$ in adequate hosts have exhibited spectral changes associated with a temperature variation. Some remarkable examples are the variations in the intensity of the emission lines from Eu$^{3+}$ in La$_2$O$_2$S [7], or the thermal induced evolution of the Ce$^{3+}$ emission decays on YAG nanocrystals [8].

Uniquely the Ln$^{3+}$ luminescence emitters - Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Ho$^{3+}$, Er$^{3+}$, Dy$^{3+}$, Er$^{3+}$ and Yb$^{3+}$ - undergo modifications in the band shapes of specific emissions due to the effect of the temperature that suggest its study for sensing applications. The band shape change is caused by thermally induced population redistribution between two adjacent energy levels of the emitting center. In the aforementioned ions there is a high probability of non-radiative transitions between the two energy levels that causes them to be thermally coupled states, additionally, each level is optically coupled to a common lower level [9]. Hence, the intensities associated with the relaxations from the thermalized pairs are temperature dependent, as is the ratio between these intensities, which would be the measurable output of the sensor. The advantages of this measurement, known as Fluorescence Intensity Ratio (FIR)
method, are that it reduces the influences of different factors such as measuring conditions, resolution and time exposures [10]. The relative intensities of the luminescence bands should depend only on temperature and not on the local concentration of the emitting center.

However, these luminescence systems may present some difficulties caused by the superposition of different effects that influence the unambiguous interpretation of the signals. One example is the Eu$^{3+}$ ion, in which the thermal response of its FIR varies almost an order of magnitude when the temperature is increased only a few tens of degrees. This behavior points to a potential emitter with an excellent sensitivity, unfortunately the FIR method as applied to Eu$^{3+}$ is not reliable because this hyperthermal sensitivity has been shown to rely on the strong thermal dependence of its energy transfer rate [11–13] and not on the thermal coupling of the levels. This fact exemplifies that several aspects related to the origin of the luminescence at the microscopic level must be considered in order to obtain an optimized optical temperature sensor based on the Ln$^{3+}$ luminescence features. In general terms, the key factors are the properties of the host, the choice of Ln$^{3+}$ ions and the concentration in which they are found and the transitions considered.

Our aim in this work is to characterize the luminescence of Nd$^{3+}$-doped phosphate glasses with different doping concentrations so as to gain an insight into its application to thermometry. The phosphate matrix possesses the suitable qualities for optical sensors [6], such as providing favorable environment for the intense emission of the Nd$^{3+}$ doping ions [14, 15]. As demonstrated in this work, phosphate glasses have a wide thermal operating range between 300-800 K and can be manufactured in the form of optical fibers with good mechanical properties [16]. They also have a low manufacturing cost [17]. Contrary to the continuous attention aroused by Er$^{3+}$-doped materials [5, 18–21], the FIR thermal response of Nd$^{3+}$ was the object of only few reports [6, 22]. However, since very recently it has started to attract attention and has been reported in a variety of forms: bulk, microspheres and nanoparticles [4, 10, 23]. There are several reasons that support this interest. First, for thermal sensing purposes, the Nd$^{3+}$ ion exhibits several luminescence transitions from the thermally coupled energy levels, $^4F_{5/2}$ and $^4F_{3/2}$, that are attainable under excitation with low-cost diode-pumped solid-state lasers. Among these possible transitions, the
relaxations through $^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$ (890 nm) and $^{4}F_{5/2} \rightarrow ^{4}I_{9/2}$ (810 nm) channels yield a sensitivity value in FIR that is higher compared to those terminating at the $^{4}F_{11/2} \rightarrow ^{4}I_{13/2}$ levels [6]. The spectral shape of the former transitions shows well separated bands without overlaps, which is critical to reducing errors when determining the fluorescence intensity ratio. Moreover, the 800 and 890 nm emissions lying in the operating range of inexpensive CCD detectors is a feature that enables its industrial production. For these reasons, we can conclude that the promising results of the Nd$^{3+}$ fluorescence intensity ratio response are associated with the $^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$ and $^{4}F_{5/2} \rightarrow ^{4}I_{9/2}$ transitions. In addition, the energy level distribution of the Nd$^{3+}$ ion permits employing an indirect pumping at 532 nm to populate the $^{4}F_{3/2}$ level that is well separated from the spectral emissions being analyzed. This strategy is used here in order to avoid the errors caused by detecting the laser overlapped with the emission bands. The prototype shown in Ref. [6] exemplifies temperature measurement without the need for either spectrophotographs or optical spectrum analyzers. It uses a simple scheme consisting mainly of an Nd$^{3+}$-doped silica fiber as sensing material coupled to a fiber coupler arrangement to low-cost excitation and detection branches, consisting respectively of an 808 nm laser diode and two silicon detectors with proper band pass filters. The output of the silicon detectors is measured with voltmeters, and the proper ratio of these measurements is proportional to FIR and related to the temperature of the doped fiber surroundings. The fact that FIR thermal sensing is not constrained to bulk shapes and makes it possible to apply this method to biomedicine. U. Rocha et al. [23] propose a scheme in which a solution of Nd$^{3+}$-doped LaF$_3$ nanoparticles can sense temperature variations in the biological range for human tissues, and indicate its potential use as tool for early disease detection and control of thermal treatments.

These sensor applications require high fluorescence intensities to yield a good signal to noise ratio when using low-cost detectors. Since the power of pumping laser should be as low to avoid optically heating the glass, the dopant concentration is the parameter to optimize in order to obtain a bright emission.

Recent results [24] show that certain concentrations of Er$^{3+}$ in fluorotellurite bulk glasses make the FIR response be dependent on the zone in the sample where the spectra are measured due to reabsorption effects. Reabsorption, due to the overlap
between the absorption and emission spectra, is for most luminescence applications an important loss factor to be avoided. Regarding the FIR application, this effect can be a source of disagreement with the theory according to reference [24]. To investigate the relevance of this effect in the Nd$^{3+}$-doped phosphate glass under study, we tested the FIR in a set of samples with different concentrations of dopants. Stoita et al. [25] proposed an experimental arrangement useful for determining the reabsorption effects on the luminescence lifetimes and that is used extensively here for measuring emission spectra. The work by Stoita et al. reveals that reabsorption together with total internal reflection effects that can significantly affect the result of the lifetime measurements if certain experimental conditions are not established. Taking these results into account, the correlation between the FIR response and the concentration of Nd$^{3+}$ in phosphate glasses have been investigated and the results are presented in this chapter.

7.2. EXPERIMENTAL METHODS

This section describes the experimental procedure, from sample preparation to optical measurements, are presented in this chapter.

7.2.1. Glass preparation

A conventional melt-quenching method was used to synthesize the phosphate glasses doped with Nd$^{3+}$. The glasses presented in this study have the following chemical compositions: (59-x/2) P$_2$O$_5$ - 17.45 K$_2$O - 14.55BaO - 9 Al$_2$O$_3$ - xNd$_2$O$_3$ with x = 0.1, 2 or 4 and they are labeled as PKBANx. To ensure a very smooth surface the glass samples were carefully polished with a carbide abrasive paper and then with a FIS polishing film. Their resulting thickness was 0.8 mm. Specimens in the shape of 1 cm squares were extracted from the preliminary samples by means of a diamond point cutter. A refractive index of 1.525 was measured on an Abbe refractometer at sodium wavelength (589.3 nm) with 1-bromonapthalene as the contact liquid.

7.2.2. Absorption spectra

The optical absorption spectra of the glass samples in the range from 700 to 950 nm were measured with a Perkin Elmer Lambda 9 spectrophotometer at room temperature.
7.2.3. Thermal spectra response

For the luminescence temperature dependence study, each sample was placed inside a horizontal tubular furnace in which a heating rate of 1K/min was applied. The excitation and luminescence detection branches were aligned along the axis of the furnace as shown in the diagram in Fig 7.1. On one side of the furnace a 532 nm Nd-YAG laser was focused by a lens on the bulk sample, while on the other side a system of two lenses collimated and focused the emission at the tip of an optical fiber.

![Diagram of experimental set-up](image)

**Fig. 7.1.** Experimental set-ups employed for the (a) measurement of dependence of temperature emission spectra. The correspondence between the acronym labels and the elements in the set-ups is as follows: Diode Laser (DL), Lens (L), Tubular Furnace (TF), Sample (S), Filter (F), Optical Fiber (OF), Thermocouple (TC), Digital Multimeter (DM) and Spectrophotometer (SM). (Note that the furnace has been depicted with transparency in order to enable the appreciation of the elements).

A high pass filter was placed in the path of the emission collection branch in order to filter away the excitation beam. The luminescence spectra were recorded using a CCD Spectrophotometer (Ocean Optics HR4000, resolution 1 nm) coupled to the optical fiber (ThorlabsM25L02, spectral range: 400 to 2400 nm, core diameter 200 μm, NA 0.22). The temperature was monitored with a K-type thermocouple connected to a digital multimeter and situated very close to the sample without touching it. The temperature range analysed was from the room temperature to 850 K. Both sides of the furnace were thermally isolated from the outside, the excitation side by a mullite cover with a small hole in the center that allowed the excitation beam to
pass, while the detection side was nearly completely covered by the collimating lens. The power of the excitation laser was checked to be low enough in order to avoid laser heating of the sample. This experimental setup is commonly employed to measure the thermal dependences of spectra, as described in the Refs. [3, 10, 26, 27]. Because of the placement of the sample inside the tubular furnace, no special care could be taken on choosing the bulk sample region from which the collected light spectra were measured.

7.2.4. Reabsorption measurements

These measurements were performed in order to study the influence in the spectral shape by increasing the emission optical path through the glass. The set-up was configured so as to have a 90° angle between the excitation and detection axes with the sample placed in a translation stage that allowed it to be moved along the axis of the detection branch. A diagram of this set-up is given in Fig 7.2, where a blue arrow is used to show the direction and orientation of the sample translation. The sample was oriented with the narrower side facing the detector and the wider side facing the excitation. A 20× microscope objective lens (Mitutoyo, M-Plan NIR, NA = 0.4) was employed to focus the 532 nm excitation beam at points located on the

![Fig. 7.2. Determination of the reabsorption inside the sample. The correspondence between the acronym labels and the elements in the set-ups is as follows: Microscope Objective (MO), XYZ translation stage.](image)
wider face of the sample as the translation stage was moved. The detection branch consists of a 60 mm convergent lens that focused the emission on the tip of an optical fiber (ThorlabsM25L02, spectral range: 400 to 2400 nm, core diameter 200 μm, NA 0.22) coupled to an Andor CCD Spectrophotometer with a 0.3 nm spectral resolution. To compare the spectra measured with two different sets of detection equipment, both data were corrected from instrumental response.

7.3. **THEORETICAL BACKGROUND**

7.3.1. **Fluorescence intensity ratio technique**

Fluorescence intensity ratio is a kind of temperature determination technique based on the change in the band shape luminescence, generally from a Ln\(^{3+}\)-doped material. The technique studies the relative intensities of two radiative transitions, one from the electronic energy level \(E_2\) to \(E_1\) and the other from the upper energy level \(E_3\) to \(E_1\), as shown in the left labels of the energy levels in Fig. 7.3. The proximity

![Diagram of energy levels](insert_diagram)

**Fig 7.3.** Partial Energy levels diagram of the Nd\(^{3+}\) ions showing the 532 nm pumping and the transitions resulting in the 880 nm and the 810 nm emissions.
between the electronic levels $E_2$ and $E_3$ allows the upper level to be populated from the $E_2$ population by thermal redistribution. Thus, the intensities ratios of these transitions depend on the temperature, but they are independent of the source power intensity. Under low pump power excitation the relative population between the two emitting levels, $R$, follows a Boltzmann-type population distribution given by [3]:

$$R = \frac{I_{31}}{I_{21}} = \frac{c_1(v)\beta_{31}A_3g_3h\nu_3}{c_2(v)\beta_{21}A_2g_2h\nu_2} \exp\left(-\frac{E_{32}}{K_B T}\right) = B \exp\left(-\frac{E_{32}}{K_B T}\right)$$  \hspace{1cm} (7.1)

with $B = \frac{c_2(v)\beta_{21}A_2g_2h\nu_2}{c_2(v)\beta_{21}A_2g_2h\nu_2}$

where $K_B$ is the Boltzmann constant, $E_{32}$ is the energy gap between the two excited levels $E_3$ and $E_2$, $h\nu_i$ is the average photon energy of each band, $g_i$ is the degeneracy $(2J_i + 1)$ of the $i$th level, $A_3$ and $A_2$ are the spontaneous radiative rates of the $E_3$ and $E_2$ levels, respectively, $\beta_{31}$ and $\beta_{21}$ represent the branching ratio of the transitions with respect to ground state and $T$ is the absolute temperature. The $c_i(v)$ in this equation has to do with the instrument response. Since the emission spectra have been corrected from the instrument response, this coefficient can be assumed to be unity. The $I_{31}$ and $I_{21}$ correspond to the intensity of the luminescence associated with the transitions to $E_1$ from states $E_3$ and $E_2$, respectively. In this work these emission intensities have been determined by integrating each transition band over the proper wavelength range, with the limits defined by the shape of the band. These limits correspond to 780-845 nm for the transition band associated with $^4F_{5/2} \rightarrow ^4I_{9/2}$ and 845-925 nm for the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition. These ranges determine the Boltzmann fitting and therefore establish the application of the temperature calibration. The energy levels of the Nd$^{3+}$ emitters in the phosphate glass samples studied are shown partially in Fig 7.3. In this ion the FIR involves the levels $E_3$: $^4F_{5/2}$, $E_2$: $^4F_{3/2}$ and $E_1$: $^4I_{9/2}$, with the corresponding transitions being $^4F_{5/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{9/2}$.

All the pre-exponential factors can be grouped together in the $B$ factor, which is determined using the Judd-Ofelt theory to calculate the rates $A_3$, $A_2$ and the branching ratios $\beta_{31}$ and $\beta_{21}$. The Judd-Ofelt parameters of the Nd$^{3+}$-doped PKBAN glass samples were determined in the Ref. [14] and are given by $\Omega_2 = 9.23 \times$
10^{20} \text{ cm}^2, \quad \Omega_4 = 7 \times 10^{20} \text{ cm}^2 \quad \text{and} \quad \Omega_6 = 8.74 \times 10^{20} \text{ cm}^2. \quad \text{Using the value of } E_{32} = 908 \text{ cm}^{-1} \quad \text{from the absorption spectrum, the theoretical FIR dependence } R_{th} \text{ yields:}

\[ R_{th} = 5.36 \exp\left(\frac{908}{K_B T}\right) \quad (7.2) \]

**7.3.2. Sensitivity**

A key descriptive parameter of a sensor is its sensitivity \( S \), which gives an estimate as how the sensor output reacts when the value of the measured quantity changes. For a fluorescence intensity ratio based sensor, the sensitivity is the rate of change of the intensity ratio with the temperature \( (S = \left| \frac{dR}{dT} \right|) \). However, in order to analyze the sensing performance of various host materials, a relative sensitivity \( S_R \) is often reported, defined as [3]:

\[ S_R = \frac{S_R}{S} = \frac{1}{R} \left| \frac{dR}{dT} \right| = \frac{E_{32}}{K_B T^2} \quad (7.3) \]

From this Eq. (7.3) it would seem that larger energy gaps for the \( E_{32} \) transition confer greater sensitivities. In practice, the separation between the energy levels must allow for significant thermalization, resulting in the upper level being sufficiently populated so as to obtain a detectable transition. Moreover, the levels need to be sufficiently far to avoid overlap of the two fluorescence wavelengths, meaning the eligible range for the energy gaps between 200-2000 \text{ cm}^{-1}.

**7.4. RESULTS AND DISCUSSION**

**7.4.1. Absorption and luminescence spectra of Nd^{3+}-doped PKBAN samples**

Absorption and luminescence spectra of the 0.1 mol % of Nd^{3+}-doped PKBAN glass samples are shown in the graph in Fig. 7.4. The absorption spectrum plotted in blue in the Fig. 7.4 shows three bands centered at 750 nm, 800 nm and 870 nm with their corresponding transitions from the ground state: \( ^4I_{9/2} \rightarrow ^4F_{7/2} \), \( ^4I_{9/2} \rightarrow ^4F_{5/2} \) and \( ^4I_{9/2} \rightarrow ^4F_{3/2} \). The energy gap between the \( ^4F_{5/2} \) and \( ^4F_{3/2} \) is determined by the distance between the centroids of the last two absorption transition bands yielding a value of 908 \text{ cm}^{-1}.

In Fig. 7.4 the luminescence resulting from laser excitation at 532 nm on the PKBAN01 sample at 310 K is plotted with a solid line, while that measured at 693 K is shown with a dashed black line. The mechanisms that give this luminescence can be followed with the aid of the energy level diagram in Fig. 7.3. The pump at 532 nm
excites the Nd$^{3+}$ ions from the $^4I_{9/2}$ ground state to the $^4G_{7/2}$ levels, as represented with a green up arrow in the diagram. As a consequence of the small energy gaps between the adjacent lower levels, there are successive non-radiative deexcitations to the $^4F_{3/2}$ level, depicted with a dashed down arrow. The energy distance between the $^4F_{3/2}$ level and the next lower $^4I_{15/2}$ level is large enough to ensure absence of non-radiative deexcitations. Instead, radiative transitions predominate, like the relaxation to the ground state $^4F_{3/2} \rightarrow ^4I_{9/2}$ associated with the intense emission band centered at 880 nm, shown on the diagram with a solid down arrow. Additionally, at 693 K the emission spectrum shows a strong emission band related to the $^4F_{5/2} \rightarrow ^4I_{9/2}$ transition centered at 810 nm. This band exists at this temperature because an induced thermal redistribution of the $^4F_{3/2}$ population increments the population of $^4F_{5/2}$ one and triggers the transition of the $^4F_{5/2}$ level to the ground state. Moreover, the next higher $^4F_{7/2}$ level can also be populated through thermalization from the $^4F_{5/2}$ and a weaker band associated with the $^4F_{7/2} \rightarrow ^4I_{9/2}$ transition is evident in the spectrum at 740 nm. Thermal induced redistributions are depicted by curved red arrows in Fig. 7.3.
Note the overlap shown in Fig. 7.4 that exists between the luminescence and the absorption bands related to the same transitions. It can be also observed that the main absorption response relays on the blue region of the emission bands associated with the $^{4}F_{5/2} \rightarrow ^{4}I_{9/2}$ and $^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$ transitions, while the absorption completely covers the $^{4}F_{7/2} \rightarrow ^{4}I_{9/2}$ transition band. These facts may be indicative of the potential relevance of the absorption by the material of its own emission, an occurrence that is expected to gain importance as the concentration of Nd$^{3+}$ content increases.

### 7.4.2. Temperature dependence of emission spectra

Fig. 7.5 shows the emission spectra obtained at room temperature and at 840 K for all the samples. Notice that how at high temperatures the thermalized emission bands coming from the $^{4}F_{5/2}$ and $^{4}F_{7/2}$ levels are clearly discernible. However, the ratio of intensities between the bands at 810 nm and 880 nm is different for all the samples. As will be shown later, radiative transfer processes, which depend on the concentration of the samples, can explain these differences.

![Normalized spectra of PKBAN01, PKBAN2 and PKBAN4 doped glasses measured at two different temperatures: 300 K (black lines) and at 840 K (red lines).](image)

**Fig. 7.5.** Normalized spectra of PKBAN01, PKBAN2 and PKBAN4 doped glasses measured at two different temperatures: 300 K (black lines) and at 840 K (red lines).
Fig. 7.6(a) shows the dependence of fluorescence intensity ratio on each sample’s temperature in the measured range of 300-850 K. The data fitted to Eq. (7.1) are also plotted with the parameters given in Table 7.1. As can be seen, these fittings properly reproduce the experimental data. Also, the theoretical dependence given in Eq. (7.2) is included in this figure. The varying behavior on the FIR response among the different samples with different concentrations is clearly evident. The dependence obtained for the PKBAN01 is close to the theoretical value, with slight lower intensity ratios. Increasing the concentration favors some kind of interaction between Nd$^{3+}$ centers that affects the emissions associated with the $^4F_{5/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{9/2}$ transitions that produces change in the FIR dependence.

**Fig. 7.6.** (a) Experimental fluorescence intensity ratio obtained from the $^4F_{5/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{9/2}$ transitions versus temperature for the PKBAN glasses doped with 0.1, 2 and 4 mol % of Nd$^{3+}$. The theoretical FIR (black solid line) was calculated in the framework of the Judd-Ofelt theory (see Eq. (7.2)). Dashed lines are the corresponding fittings to Eq (7.1). (b) Relative sensitivity of the PKBAN samples and theoretical relative sensitivity calculated from Eq (7.3).
Figure 7.6(b) plots the relative sensitivity values for the different doped samples in the temperature range considered. The dependence of $S_R$ in all the samples shows a decrease when the temperature increases. Also, based on the energy gap values that resulted from the fittings of the FIR temperatures responses (see Table 7.1), one can see that increasing the content of Nd$^{3+}$ gives rise to greater relative sensitivity values, even greater than the values obtained in the matrices reported in Refs. [6, 10]. This result suggests that more sensitive results are obtained from the phosphate glass doped with 4 mol % of Nd$^{3+}$. Nevertheless, the results shown in Figs. 7.6(a)-(b) indicate that there is a discrepancy between the theoretical and the experimental results that is more noticeable when the doping concentration increases. This reveals that certain factors become more important as the Nd$^{3+}$ doping concentration is increased, factors that are not included in the Boltzmann model. A detailed analysis is needed in order to determine how well the sensor performs in these systems.

Table 7.1. Data obtained in this work and in other Nd$^{3+}$-doped samples reported in the literature. The parameters for the FIR equation given by the Boltzmann theory as well as the absorption coefficients obtained from the absorption spectra ($\alpha_A$) and from the Lambert-Beer equation fittings of the reabsorption measurements ($\alpha$) are shown.
7.4.3. Energy transfer processes

There are two main processes that could produce a decrease in the population of an emitting level: namely multiphonon relaxation and energy transfer. In multiphonon relaxation, its rate decreases with an increase of the energy gap of the emitting level with respect to its lower level. But due to the gap for the $^4\text{F}_{3/2}$ emitting level and the energy phonons in the phosphate glasses, this rate can be considered negligible [15]. As for the energy transfer processes, Ref. [14] states that there is a slight chance for non-radiative transfer processes to OH$^-$ ions, which act as traps for the energy. Moreover, the cross-relaxation processes between pairs of Nd$^{3+}$ ions dominated by dipole-dipole interaction, which is favored when the concentration increases could also be relevant. However, even though these effects imply a loss on the radiative decays, they do not change the band shapes, as was observed in the experimental spectra that result as a consequence of the different FIR values obtained for the doping concentrations (see Fig. 7.6 (a)). However, radiative transfer processes between Nd$^{3+}$ ions can affect the shape of the emission bands. These processes are due to the reabsorption of the emitted radiation by the Nd$^{3+}$ ions. As can be seen in Fig. 7.4, this process could probably be due to the overlap among the emission and absorption bands. Therefore, in order to analyze these radiative transfer processes, we used the set-up described in the experimental section to obtain the emission spectra as a function of the path of the emission and of the Nd$^{3+}$ concentration.

Fig. 7.7 shows the spectra of each sample corresponding to the luminescence collected at the edge and at 25 mm from the edge (referred to as “inner” in the sample). The bands in each spectrum centered at 810 nm were multiplied by a factor 2 for the purpose of highlighting in the graph, the differences between the surface and the collected luminescence through the thickness at this wavelength. In order to be able to compare the relative intensities of the bands centered at 810 nm, all the spectra were normalized to the intensity value of the sub-band centered at 905 nm. At this wavelength the absorption processes can be neglected (see Fig. 7.4). An arrow in the Fig. 7.7 depicts the normalized value for each sample. In general terms, for the entire range of wavelengths in the spectra, there are more differences between the inner and surface spectra when concentration of the sample increases. The differences between the inner and surface spectra in the 0.1 mol % doped Nd$^{3+}$ sample are small with
respect to the PKBAN2 and PKBAN4 samples. These results are in agreement with the fact that reabsorption effects on the spectra are more pronounced when the concentration increases.

![Normalized spectra collected exciting on the surface (blue lines) and in the inner (red lines) of the samples.](image)

**Fig. 7.7.** Normalized spectra collected exciting on the surface (blue lines) and in the inner (red lines) of the samples.

More specifically, the decrease of the $^4F_{5/2} \rightarrow ^4I_{9/2}$ and the $^4F_{3/2} \rightarrow ^4I_{9/2}$ emission bands can be explained by the overlapping with the respective absorption bands, as can be observed in Fig. 7.4. This further indicates that the emission from the directly excited Nd$^{3+}$ ions interacts with other centers by means of radiative reabsorption, a critical component being the increment in the number of doping ions in the optical emission path.

It is worth noting that in the two most concentrated samples the spectra detected at its surface show profiles similar to that for the sample doped at 0.1 mol %. This is because on the surface of the most doped samples, the emission from excited Nd$^{3+}$ ions does not pass regions with optically active ions that could reabsorb it as it travels towards the detection system.
A detailed analysis of the dependence of the intensity obtained at 810 nm, normalized as mentioned above, on the increasing path length through the sample is shown for each sample in Fig. 7.8, which was obtained using the experimental setup shown in Fig. 7.2. The experimental data were fitted to the known Lambert Beer Law

\[ I(x) = I_0 e^{-\alpha x} \]  

which relates how fast light intensity decays in a material by means of its absorption coefficient at this wavelength as follows:

![Fig. 7.8. Intensity obtained at 810 nm as a function of the distance between the excitation zone to the border of the sample (dots) and fitting to a Lambert-Beer dependence (solid lines).](image)

where \( I_0 \) is the measured emission intensity at the edge of the sample and \( \alpha \) is the absorption coefficient. As can be seen in Fig. 7.8, the most concentrated samples result in the largest drops in emission intensity. A comparison of the absorption coefficients obtained from the fittings \( \alpha \), with their values obtained from absorption spectra (\( \alpha_A \)) is shown in Table 7.2. Note the relatively good concordance between both absorption coefficients, with more discrepancies for the sample with lowest concentration due to the small effect of the reabsorption in this sample. This result lead us to conclude that the reabsorption of the emission from the directly excited ions by the other Nd\(^{3+}\) centers is the main cause for the changes in the profiles of emission spectra, and therefore the differences in the FIR response between the differently doped Nd\(^{3+}\):PKBAN samples.
From an applied point of view, it can be concluded that the FIR technique for measuring the temperature of luminescence in bulk samples can exhibit ambiguity if the excitation and emission regions do not coincide. This drawback is less relevant in lightly doped samples, as demonstrated in the results reported for PKBAN01. This fact implies a need to compromise between the higher intensity emissions than can be obtained in most doped samples and the reliability of the temperature determination. However, it would be beneficial, when implementing an optical sensor design that takes into account the power excitation constraint, to be able to detect luminescence easily, and thus to have a high doping content. In this sense it could be interesting to use point sources for FIR temperature determination in order to limit the radiative transfer processes that would lead to spurious temperature determinations. Such point sources for thermal sensing are the object of current research and span everything from glass microspheres [4] to a sort of Ln$^{3+}$-doped nanoparticles in solution [23].

7.5. CONCLUSIONS

The luminescence of Nd$^{3+}$-doped phosphate glasses has been investigated for their application as Fluorescence Intensity Ratio based sensors. After pumping at 532 nm, the PKBAN doped Nd$^{3+}$ show a luminescence spectrum due to transitions from the thermally coupled levels: $^4F_{3/2}$ and $^4F_{5/2}$, that exhibit a band shape dependent on temperature. By employing a set-up with aligned excitation and detection devices, the band shapes were also found to be dependent on the Nd$^{3+}$ concentration. A specific optical set-up was used in order to analyze the radiative transfer processes among Nd$^{3+}$ ions. Considering the importance of the influence of the radiative transfer on the shape of the spectral bands in the samples, we conclude that the 0.1 mol % Nd$^{3+}$-doped PKBAN glass, which is less prone to radiative transfer, shows good prospects for reliable thermal sensing. Phosphate glasses with higher content of Nd$^{3+}$ optically active ions also show potential as temperature sensor, but the reabsorption processes must first be reduced by employing small volumes, such as through the use of glass microspheres or colloidal nanoparticles.
Chapter 7
Nd\textsuperscript{3+}: glasses for temperature sensor applications

REFERENCES


