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Relevance of radiative transfer processes on Nd^{3+} doped phosphate glasses for temperature sensing by means of the fluorescence intensity ratio technique

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ABSTRACT

We analyze the suitability of Nd^{3+} doped phosphate glasses as optical temperature sensors based on the response of their luminescence bands to temperature. At room temperature, laser excitation of the sample at 532 nm results in an emission spectrum with an intense band centered at 880 nm and an adjacent weak broad band centered at 810 nm, corresponding to the Nd^{3+} ion transitions: $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{5/2} \rightarrow {}^4I_{9/2}$ respectively. Because of thermalization effects between the next $^4F_{3/2}$ and $^4F_{5/2}$ energy levels ($\Delta E \approx 908\,cm^{-1}$), a detectable change on the relative intensities of these emission bands occurs when temperature is increased, affording the experimental calibration of the fluorescence intensity ratio with temperature in the range 300–850 K. It has been shown that the radiative transfer processes favored by the content of Nd^{3+} ions are also responsible for changes to the spectra shapes and so play an important role in the fluorescence intensity ratio. A reliable thermal sensing operation was obtained in a 0.1 mol% doped Nd^{3+} phosphate glass with relative sensitivity values ranging from $153 \times 10^{-4}\,K^{-1}$ at 300 K to $22 \times 10^{-4}\,K^{-1}$ for 850 K, demonstrating good prospects for optical temperature measurements compared to other reported results. However, the reabsorption measurements seen in the samples with a higher Nd^{3+} content reveal that the reliability of the sensing performance is compromised with the doping concentration and the experimental conditions of the measurement.

1. Introduction

Of note among the various optical methods for developing temperature sensors are those based on luminescence properties [1,2]. These sensors analyze the thermally 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 temperature information with these sensors. These kinds 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 for 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 Rare Earth (RE) elements have been one the most reported luminescence centers in the literature. Several fluorescence emissions from RE^{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_2O_2S [7], or the thermal induced evolution of the Ce^{3+} emission decays in YAG nanocrystals [8].

Uniquely, the RE^{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

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that suggest its study for sensing applications. The band shape change is caused by a 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 lower common 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 the 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 by 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 RE^{3+} luminescence features. In general terms, the key factors are the properties of the host, the choice of RE^{3+} ions, the concentration in which they are found and the transitions considered.

Our aim in this work is to fully characterize the luminescence of Nd^{3+} doped phosphate bulk 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 provided in Wade's conscientious thesis [6], since it provides a favorable environment for the intense emission of the Nd^{3+} doping ions [14,15]. As demonstrated in this work, they have a wide thermal operating range between 300–850 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 a few reports in the early 2000' [6,22]. However, since very recently it has started to attract attention and this use of the ion 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 $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (890 nm) and $^4F_{5/2} \rightarrow {}^4I_{9/2}$ (810 nm) yield a sensitivity value in FIR that is higher compared to those terminating at the $^4F_{11/2}$ or $^4F_{13/2}$ 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 relaxations $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{5/2} \rightarrow {}^4I_{9/2}$, and hence these are the transitions studied in this work in keeping with the example in most of the available FIR reports involving Nd^{3+}. In addition, the energy level distribution of the Nd^{3+} ion permits employing an indirect pumping at 532 nm to populate the $^4F_{3/2}$ 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, and is suggested since it simplifies the detection of fluorescence. We note here that the prototype shown in reference [6] exemplifies temperature measurement without the need for either spectrographs or optical spectrum analyzers. It uses a simple scheme consisting mainly of an Nd^{3+} doped silica fiber as sensing material coupled by 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 for each of the aforementioned transitions. The output of the silicon detectors is just 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 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 the pumping laser should be 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 cause the FIR response to 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. A. Stoita et al. proposed in [25] 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 the reabsorption and total internal reflection effects can significantly affect the result of the lifetime measurements if certain experimental conditions are not established. Taking these results into account we have researched the correlation between the FIR response and the concentration of Nd^{3+} in phosphate glasses.

2. Experimental methods

This section describes the experimental procedure, from sample preparation to optical measurements, followed to obtain the information presented in this paper.

2.1. Glass preparation

A conventional melt-quenching method was used to fabricate the phosphate glasses doped with Nd^{3+}. The glasses presented in this study have the following chemical compositions: $(59-x/2)$ P_2O_5, 17.45 K_2O, 14.55 BaO, 9 Al_2O_3 and xNd_2O_3 with $x = 0.1$, 2 or 4. They are labeled 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