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Optical Fiber Sensors: An Overview

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1. Introduction

Fiber optic sensor technology has been under development for the past 40 years and has resulted in the production of various devices, including fiber optic gyroscopes; sensors of temperature, pressure, and vibration; and chemical probes. Fiber optic sensors offer a number of advantages, such as increased sensitivity compared to existing techniques and geometric versatility, which permits configuration into arbitrary shapes. Because fiber optic sensors are dielectric devices, they can be used in high voltage, high temperature, or corrosive environments. In addition, these sensors are compatible with communications systems and have the capacity to carry out remote sensing. Recently, investigation in the field has focused on the development of new materials with non-linear optical properties for important potential applications in photonics. Examples of these materials are the conjugated semiconducting polymers that combine optical properties with the electronic properties of semiconductors. In addition, these conducting polymers have photoluminescent and electroluminescent properties, making them attractive for applications in optoelectronics.

This chapter presents an overview of fiber optic sensors and their applications. It also describes new optical materials that are being investigated for the development of chemical optical sensors. The chapter is organized into five sections (including conclusions) to provide a clear and logical sequence of topics. The first section briefly reviews optical fiber fundamentals, including basic concepts, optical fiber structure, and their general characteristics. The propagation of light in optical fibers, which involves Snell's law, the critical angle, and the total internal reflection, is also discussed. The second section offers an extensive introduction to fiber optic sensors, including their characteristics, functional classification, modulation methods, and principal applications. The third section discusses fluorescent optical sensors that employ rare-earth-doped fibers, such as erbium (Er^{3+}), neodymium (Nd^{3+}), ytterbium (Yb^{3+}), praseodymium (Pr^{3+}), samarium (Sm^{3+}), europium (Eu^{3+}), holmium (Ho^{3+}), and erbium/ytterbium (Er/Yb). A review of the performance of rare-earth-doped fiber sensors and their applications in remote temperature measurement is also presented, taking into account the sensing material, the temperature range, and its temperature sensitivity. The next section provides an overview of new materials with optical properties and evaluates their potential as optical fiber sensors. Conducting polymers, such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh), and their derivatives, are discussed as potential optical

sensors because of their interesting electrical, chemical, and optical properties. The final section provides the conclusions of the chapter.

The chapter ends with a bibliography on the topic that offers the reader an extensive selection of scientific references on optical fiber sensors.

2. Optical fiber basics

The optical fiber has represented a revolution in the world of telecommunications mainly because of its capacity to transmit large quantities of information, including video and data. Erbium-doped fibers can be used as optical amplifiers to extend the distance of transmission. The investigations in this field have permitted the expansion of the spectrum of applications of optical fibers, leading to the development of new devices, such as fiber lasers and optical fiber sensors, which are the subject of this chapter.

An optical fiber is an optical waveguide in the shape of a filament and is generally made of glass (although it can also be made of plastic materials). An optical fiber is composed of three parts: the core, the cladding, and the coating or buffer. Fibers can be produced in a range of sizes; a common cladding diameter is 125 μm, whereas the core typically ranges from 10 to 50 μm. The basic structure of an optical fiber is shown in Figure 1.

The core is a cylindrical rod of dielectric material and is generally made of glass. Light propagates mainly along the core of the fiber. The cladding layer is made of a dielectric material with an index of refraction, n_2, that is less than that of the core material, n_1. The cladding is generally made of glass or plastic. The cladding decreases the loss of light from the core into the surrounding air, decreases scattering loss at the surface of the core, protects the fiber from absorbing surface contaminants, and adds mechanical strength. The coating or buffer is a layer of plastic used to protect the optical fiber from physical damage. The core and the cladding provide the conditions necessary to permit an optical signal to be guided along the optical fiber.

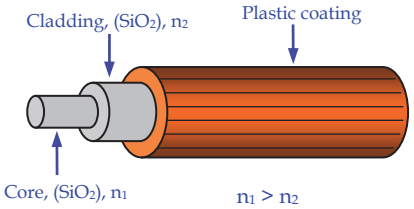

Fig. 1. Schematic of a single fiber optic structure.

The principle of transmission of light along optical fibers is based on *total internal reflection*, which is related to a light beam incident on the boundary between two materials with different refractive indices, as illustrated in Figure 2. When light is incident from a medium with a high index (n_1) to one with a lower index (n_2), the transmitted beam always emerges at an angle, ϕ_2, that is greater than the incident angle, ϕ_1 (see Fig. 2a). If we increase the measure of ϕ_1, there will come a point where ϕ_2 is 90º; at this point, the value of the angle of incidence is known as the critical angle, ϕ_c (see Fig. 2b). If the angle of incidence is greater

than ϕ_c, there is no refraction of the light, and all of the rays (radiation) become *totally internally reflected* toward the material with the refractive index n_1 (see Fig. 2c).

For a ray to be effectively "*trapped*" within the fiber core, it must strike the core/cladding interface at an angle, ϕ, that is greater than the critical angle, ϕ_c. This critical angle is related to the refractive indices of the core n_1 and the cladding n_2 by Snell's law ($n_1 \sin \phi_1 = n_2 \sin \phi_2$) and can be calculated as $\phi_c = \arcsin (n_2/n_1)$. This requirement means that any ray entering the fiber with an incidence angle, ϕ_0, between 0 and $\pm\ \theta$ will be internally reflected along the fiber core. This angle θ is known as the acceptance angle and is related to the numerical aperture (NA) of an optical fiber as follows: $NA = n_0 \sin \theta = (n_1^2 - n_2^2)^{1/2}$, where n_0 is the refractive index of the medium surrounding the optical fiber.

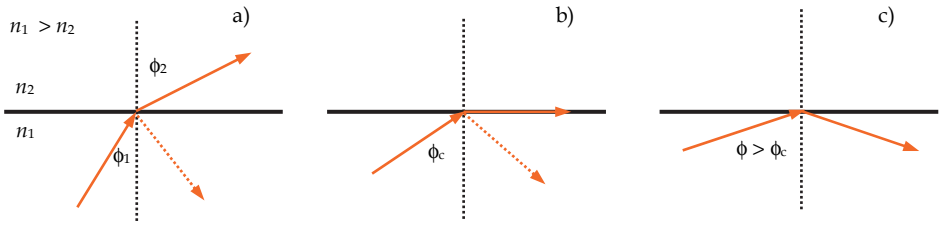

Fig. 2. Representation of the *critical angle* and *total internal reflection (TIR)* between two different materials.

Two types of fibers are commonly used: *step-index fibers* and *graded-index fibers*. In the first case, the refractive index of the core is uniform throughout and undergoes an abrupt change (or step) at the cladding boundary. In the second case, the core refractive index is made to vary as a function of the radial distance from the center of the fiber. Both types of fibers can be further divided intro *single-mode* and *multimode fibers*. A single-mode fiber sustains only one mode of propagation, whereas multimode fibers contain many hundreds of modes.

One of the principal characteristics of an optical fiber is its attenuation as a function of wavelength. The systems of optical communications operate in the band centered at 1550 nm because, in this region, the optical signal travelling by an optical fiber suffers from the lowest attenuation. This region is the named the third window of communications. Currently, new materials are being investigated for the production of optical fibers that further diminish the attenuation of the signal for applications in communications.

The main advantages of optical fiber technology are low attenuation, wide bandwidth, reduced weight and size, and immunity to electromagnetic interference (EMI). A more extensive description of the characteristics and properties of optical fibers can be found in the following references (Ghatak & Thyagarajan, 2000; Keiser, 1991).

Today, the investigation and development of optical-fiber devices encompasses optical amplifiers (Erbium Doped Fiber Amplifiers, EDFAs), fiber lasers, and optical fiber sensors.

3. Optical fiber sensors

Currently, the research and development of fiber-optic sensor devices has extended their applications to diverse technological fields, including the medical, chemical, and

telecommunications industries. Optical fiber sensors have been developed to measure a wide variety of physical properties, such as chemical changes, strain, electric and magnetic fields, temperature, pressure, rotation, displacement (position), radiation, flow, liquid level, vibrations, light intensity, and color. Fiber-optic sensors are devices that can performance in harsh environments where conventional electrical and electronic sensors have difficulties.

In comparison with the other types of sensors, optical fiber sensors exhibit a number of advantages; they

- Are non-electrical devices
- Require small cable sizes and weights
- Enable small sensor sizes
- Allow access into normally inaccessible areas
- Often do not require contact
- Permit remote sensing
- Offer immunity to radio frequency interference (RFI) and electromagnetic interference (EMI)
- Do not contaminate their surroundings and are not subject to corrosion
- Provide high sensitivity, resolution and dynamic range
- Offer sensitivity to multiple environmental parameters
- Can be interfaced with data communication systems

Optical fiber sensors are dielectric devices that are generally chemically inert. They do not require electric cables for their performance and are technically ideal for working in hostile media or corrosive environments for applications in remote sensing.

The basic components of an optical fiber sensor are an optical source, a transducer, and a receiver, as is observed in the schema of Figure 3. Lasers, diodes, and/or LEDs are often used as the optical source in these sensing devices. An optical fiber (single or multimode), doped fibers, and/or bulk materials are employed as the transducer (sensor heart). At the output of the sensor system, a photodetector is used to detect the variation in the optical signal that is caused by the physical perturbation of the system. In the optical fiber sensors systems, the optical parameters that can be modulated are the amplitude, phase, color (spectral signal), and state of polarization. The optical modulation methods of the sensors involve the following:

The **amplitude change** is related to the transmission, absorption, reflection, or scattering of the optical signal. Currently, Fiber Bragg Gratings (FBG) and Long Period Fiber Gratings (LPFG) are employed as the sensor heads in optical fiber sensors systems. The optical parameters that can be modulated for these sensors are the wavelength, transmission, reflection, and refraction index, which are associated with the perturbation environment.

The **phase change** is associated with the optical frequency and wavelength variation.

The **change in color** is proportional to the changes in the absorption, transmission, reflection, or luminescence of the optical signal, whereas the polarization is related to the strain birefringence.

The *transmission concept* is normally associated with the interruption of a light beam that is travelling via the optical fiber. The sensors that are based on *reflection* employ two bundles

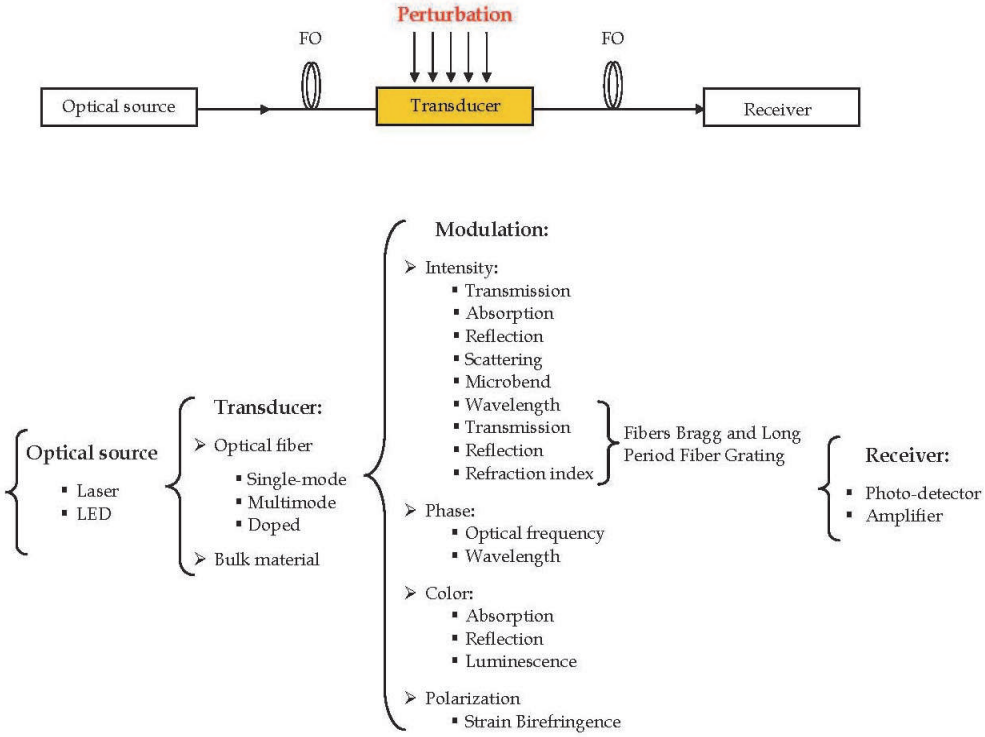

Fig. 3. Basic components of an optical fiber sensor.

of fibers or a pair of single fibers. One bundle of fibers transmits light to a reflecting target; the other bundle traps reflected light and transmits it to a detector. The variation in the intensity detected with a photodetector is directly proportional to the perturbation environment. In a sensor that is based on *microbending*, small amounts of light are lost through the wall of the fiber if the fiber is bent. If the fiber is bent due to a physical perturbation (e.g., pressure), then the amount of received light is related to the value of the physical parameter.

In addition, the optical fiber can be doped in the core with a chemical. Then the *absorption concept* is related to the absorbance spectrum of the chemical (dopant) incorporated in the fiber. According to the characteristics of the dopant, some peaks or bands of the absorption are dependent on some physical parameters, such as temperature. A similar approach can be considered for *scattering*.

Similar to the absorption concept, *luminescence* can be achieved by doping the fiber or some glass material with a chemical. In this kind of sensor, a light source can be used to stimulate a fluorescence signal, which is affected by some external physical parameter. In the same way, the fiber can be stimulated by outside radiation, and the fluorescence signal can be detected as a measure of the level of incident radiation. Similarly, a change in the *luminescence wavelength* can be transduced in a change of *color* as a function of a perturbing environment. *Refractive index changes* in the core of an optical fiber (e.g., fiber grating) due to

a perturbing environment can change the optical frequency and, consequently, the amount of received light (transmitted or reflected) on the photodetector. The combination of some of these concepts can be used with some of the mechanisms of modulation to improve or to complement the sensor required for covering a specific need.

Optical fiber sensors can be divided into two basic categories: intensity-modulated sensors and phase-modulated sensors.

Intensity-modulated sensors: This class of sensors detects the variation of the light intensity that is proportional to the perturbing environment. The concepts associated with intensity modulation include transmission, reflection, and microbending. For this, a reflective or transmissive target can be incorporated in the fiber. Other mechanisms that can be used independently or in conjunction with the three primary concepts include absorption, scattering, fluorescence, and polarization. Intensity-modulated sensors normally require more light to function than phase-modulated sensors; as a result, they employ large core multimode fibers or bundles of fibers.

Phase-modulated sensors: This type of sensor compares the phase of the light in a sensing fiber to a reference fiber in a device known as an interferometer. Generally, these sensors employ a coherent laser light source and two single-mode fibers. The light is split and injected into the reference and sensing fibers. If the light in the sensing fiber is exposed to the perturbing environment, a phase shift occurs between them. The phase shift is detected by the interferometer. There are four interferometric configurations used in optical sensors: the Mach-Zehnder, Michelson, Fabry-Perot, and Sagnac. The Mach-Zehnder interferometer configuration is the most widely used for acoustic sensing. Phase-modulated sensors are much more accurate than intensity-modulated sensors.

Generally, fiber optic sensors can be conveniently classified according to the manner in which the optical fiber is used. These sensors can then be functionally classified into intrinsic and extrinsic sensors.

Intrinsic fiber-optic sensor: These sensors directly employ an optical fiber as the sensitive material (sensor head) and also as the medium to transport the optical signal with information of the perturbation environment to be measured. They operate through the direct modulation of the light guided into the optical fiber. The light does not leave the fiber, except at the detection end (the output) of the sensor. In intrinsic sensors, the variable of interest (physical perturbation) must modify the characteristics of the optical fiber to modify the properties of the light carried by the fiber (see Fig. 4a). These sensors can use interferometric configurations, Fiber Bragg Grating (FBG), Long Period Fiber Grating (LPFG), or special fibers (doped fibers) designed to be sensitive to specific perturbations.

Extrinsic or hybrid fiber-optic sensor: In an extrinsic sensor, the optical fiber is simply used to guide the light to and from a location at which an optical sensor head is located. The sensor head is external to the optical fiber and is usually based on miniature optical components, which are designed to modulate the properties of light in response to changes in the environment with respect to physical perturbations of interest. Thus, in this configuration, one fiber transmits optical energy to the sensor head. Then this light is appropriately modulated and is coupled back via a second fiber, which guides it to the optical detector. This is the principle of an intensity-based optical transmission sensor.

Alternatively, the modulated light may be coupled back into the same fiber by reflection or scattering and then guided back to the detection system (see Fig. 4b).

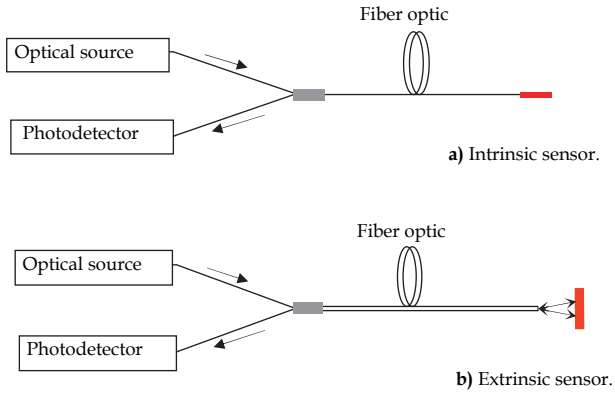

Fig. 4. Arrangements of an optical fiber sensor: a) intrinsic and b) extrinsic sensor.

Optical fiber sensors, whether intrinsic or extrinsic, operate by the modulation of one (or more) of the following characteristics of the guided light: the intensity, wavelength or frequency, state of polarization, and phase.

Today, fiber optic sensors have become essential devices for process control in measurement systems, finding countless applications in, for example, factory automation, the automotive industry, telecommunications, computers and robotics, environmental monitoring, health care, and agriculture. An extensive review of fiber optic sensors and their applications can be found in the following bibliography (Culshaw, 2004; Krohn, 1999; Lopez-Higuera, 2002; Othonos & Kalli, 1999; Rai, 2007; Udd, 1991; Yu et al., 2008).

New challenges in diverse technological fields requiring the monitoring, control, and security of processes are continuously arising. New optical sensor systems, for example, have been implemented for the monitoring of corrosion processes as an alternative to electrochemical sensor systems. The corrosion in metallic structures is a serious problem that involves security, maintenance or replacement costs, and the occasional interruption of the machine, which affects diverse processes in the industry.

Typically, the corrosion rate in a metallic sample is evaluated through measuring its weight-loss or by electrochemical techniques. Alternatively, one of the most well known optical techniques employed for corrosion monitoring is based on holographic interferometry (Habib, 1993, 1995). The main constraint of these techniques arises when measurements need to be taken *in situ* under different laboratory-controlled conditions. Therefore, it is important to investigate new alternatives for measurements. Recently, optical sensor systems based on the change in intensity have been proposed for the measurement of corrosion (Castrellon-Uribe et al., 2008; Dong S, 2005a, 2005b). The main advantages of this optical technique include its insensitivity to the intensity variations of the optical source signal, which helps to avoid errors in measurements; the simple detection system of the signal with the corrosion information; and the possibility of developing a fiber optic sensor to carry out measurements of corrosion *in situ*.

4. Rare-earth-doped optical fiber sensors

A rare-earth-doped optical fiber (laser fiber) undergoes the processes of absorption and spontaneous and stimulated emission of radiation when it is excited with photons of a particular energy. An investigation of these processes was conducted to improve the development of an erbium-doped fiber amplifier (EDFA) with the goal of extending the distance of transmission in optical communication systems (Desurvire, 1994; Digonnet, 2001). The investigation of nonlinear processes in laser fibers has allowed for the development of new optical fiber lasers by up-conversion (Mejia et al., 2002; Talavera & Mejia, 2005). In addition, laser fibers have been investigated to develop new temperature sensors because their properties of emission and absorption are dependent on temperature (Berthou & Jorgensen, 1990; Farries et al., 1986; Krug et al., 1991).

In general, radiative methods of temperature measurement are highly advantageous because they do not require physical contact or temperature equilibrium between different objects with distinct thermal masses. Frequently, the temperature can only be measured indirectly at a distance from the object to be measured. Fiber optic sensors have proven to be very efficient due to their small thermal mass, their ability to transmit light efficiently, and their mechanical flexibility, which allows for access to small remote volumes.

A number of optical fiber-based temperature sensors have been developed using approaches based on fluorescence. The techniques most commonly used are based on the fluorescence lifetime (FL) and the fluorescence intensity ratio (FIR). These techniques generally use rare-earth-doped optical fibers as the sensing medium. In these materials, the fluorescence signal is induced by widely available light sources (CW or pulsed) in a variety of wavelengths. A simple photodetector can be used to measure the variation in the intensity of the fluorescence signal as a function of temperature.

The fluorescence intensity generated from two closely spaced energy levels of an ensemble of ions doped in a host material depends on a number of parameters, including the host material, the particular energy level of interest, the dimensions of the material doped with the ion, the concentration level (doping), and the excitation method employed. The separation of the energy levels should be of the order of the thermal energy (a few kT, where kT is ~200 cm^{-1} at room temperature). There are a number of materials that have pairs of energy levels that are separated by energy differences such that they may be considered to be thermally coupled; hence, they could potentially be used in conjunction with the FIR method for temperature sensing. In particular, rare-earth-doped materials have been extensively investigated in the development of new fluorescent sensors of temperature.

The **fluorescence lifetime (FL)** of an energy level of a material is a measure of the rate of reduction in the intensity of fluorescence after the source of excitation has been removed. This rate of decay has been shown to depend strongly on temperature for the energy levels of many materials; therefore, it can be used as a measure of temperature. This technique has been investigated using a relatively large number of sensing materials in a variety of forms, including phosphors, bulk samples, and doped optical fibers. (Grattan & Zhang, 1995; Rai & S.B. Rai, 2007)

The **fluorescence intensity ratio (FIR)** technique involves utilizing the fluorescence intensities from two closely spaced energy levels for monitoring the temperature. In this technique, the fluorescence intensities from these levels to a common final (lower) level are

monitored at the desired wavelength. The temperature dependent ratio of these intensities is independent of the source intensity because the emitted intensities are proportional to the population of each energy level involved. Therefore, the fluorescence intensity ratio, R, from two thermally coupled energy levels may be given as (Maurice et al., 1995)

$$R = \frac{N_2}{N_1} = \frac{I_2}{I_1} = B \exp\left[-\frac{\Delta E}{k T} \right] \tag{1}$$

An extensive review of rare-earth doped optical fiber sensors based on the fluorescence-intensity ratio technique is given in the references at the end of the chapter (Castrellon-Uribe, 1999, 2002a, 2002b, 2005, 2010; Dos Santos et al., 1999; Imai & Hokazono, 1997; Maurice, 1994, 1995a, 1995b, 1997a, 1997b; Wade 1997, 1998, 1999a, 1999b).

There are several advantages of using thermally coupled levels over using two non-coupled levels when the fluorescence intensity ratio method is utilized:

- The theory of the relative changes in the fluorescence intensity originating from thermally coupled levels is reasonably well understood, and thus, their behavior can be easily predicted.
- The population of the individual thermally coupled levels is directly proportional to the total population. Therefore, any changes in the total population due to changes in excitation power, for example, will affect the individual levels to the same extent. This helps to reduce the dependence of the measurement technique on the excitation power, which avoids errors in the measurements.
- For relatively closely spaced energy levels, the fluorescence wavelengths will be relatively close, which helps to reduce any wavelength-dependent effects caused by the fiber bends.

In the sensor systems, it is important to know the rate at which the fluorescence intensity ratio changes as a result of a change in temperature. This parameter is known as the sensitivity, *S(R)*, which is given by

$$S(R) = \frac{1}{R}\frac{dR}{dT} = \frac{\Delta E}{kT^2} \tag{2}$$

From Equation 2, it is clear that when using a pair of energy levels with a larger energy difference, the sensitivity of the fluorescence intensity ratio is increased. It is important to notice that the largest energy difference is limited by the occurrence of thermalization. As the energy difference becomes larger, the population and hence the fluorescence intensity from the upper of the two thermalizing levels will decrease, which may introduce problems when measuring very low light levels.

Additionally, there are other factors that limit the feasibility of using a material as a sensor. These factors include costs and availability, the temperature range for which the material can be used, and the fluorescence yield of the particular level of interest. The materials that have been found to meet the above requirements are the triply ionized rare-earth ions.

In the implementation of temperature sensors, the energy levels do not only have to be thermally coupled, but they should also meet other requirements that depend largely on the

host matrix into which the active ions are doped. When considering a silica-based glass host, for example, the energy levels should meet the following requirements:

- The first condition is that the pair of energy levels should be thermally coupled, and as a result, Equation 1 can be applied. The energy level separation should be smaller than 2000 cm^{-1} (the separation should not be too large); otherwise, the upper level would have a very small population for the temperature range of interest.
- The separation between the energy levels must be more than 200 cm^{-1} to avoid substantial overlap of the two fluorescence wavelengths.
- To obtain sufficient fluorescence intensity from the pair of upper levels, the radiative transitions must dominate the non-radiative transitions. The non-radiative transition rate decreases with the increase of the energy gap to the next lower energy level. Therefore, it is preferable that the two thermalizing levels lie at least 3000 cm^{-1} above the next lowest energy level.
- For commonly available detectors (such as silica photodiodes) to be utilized in the sensor system, the energy levels should have radiative transitions (fluorescence) with energies between 6000 and 25000 cm^{-1} corresponding to wavelengths of 1.66 μm and 0.4 μm, respectively.
- For practical sensors, the fluorescence signal must be excited by commercially available light sources, such as laser diodes (LD) or light-emitting diodes (LEDs).

A review of the literature shows that there are only a few rare-earth ions with a pair of energy levels that meet all of these above requirements. Therefore, the rare-earth ions that can be used as sensing materials for temperature measurements are praseodymium (Pr^{3+}), neodymium (Nd^{3+}), samarium (Sm^{3+}), europium (Eu^{3+}), holmium (Ho^{3+}), erbium (Er^{3+}), and ytterbium (Yb^{3+}), which can be doped into a wide variety of glass or crystal hosts. The energy levels of the rare-earth ions, as well as their fluorescence transitions of particular interest, can be found in the literature for a variety of host materials. The performance characteristics of rare-earth-doped fibers used as temperature sensors that employ the fluorescence-intensity ratio technique are provided in Table 1.

There are a number of experimental arrangements employed in the fluorescence intensity ratio technique (FIR) for sensing temperature; the basic elements used in the technique are described as follows. To investigate the photo-thermal properties of these rare earth ions in different hosts, the samples can be excited by a pump source (a laser or pig-tailed diode) that excites the fluorescence from a pair of energy levels of interest. Then the samples can be cooled and/or heated, and their temperature can be detected independently using a thermocouple or a similar device in close proximity to the sample. Next, an optical spectrum analyzer (OSA) can be used for recording the fluorescence spectrum and calculating the intensity ratio as a function of the temperature of the sample from the data obtained. A photodetector and bandpass filters also can be used to measure the fluorescence intensity changes as a function of temperature in the sample.

In most practical cases, compact optical fiber sensors with a high signal-to-noise ratio (SNR) and sensitivity are desirable. To evaluate these parameters, an erbium-doped fiber was analyzed as a temperature sensor in terms of the standard radiometric figures of merit to evaluate its ability to detect thermally generated radiation (Castrellon-Uribe, 1999, 2002). Afterward, the performance of the erbium-doped fiber as a temperature sensor was shown

Sensing material	Transition	Energy gap[1]	λpump	Fluorescence Intensity Ratio Technique (FIR)	Temperature Range	Sensitivity at 20°C	Ref.
Er^{3+}: silica fiber	$(^2H_{11/2}\,;\,^4S_{3/2}) \rightarrow {}^4I_{15/2}$	~800 cm^{-1}	800 nm	530 nm/555nm	23 – 600°C	1.3 %/°C	a
Er^{3+}: silica fiber	$(^2H_{11/2}\,;\,^4S_{3/2}) \rightarrow {}^4I_{11/2}$	~800 cm^{-1}	800 nm	1.13 nm/1.24nm (lines)	25 - 600°C	0.8 %/°C	b
Er^{3+} and Er/Yb: chalcogenide glasses	$(^2H_{11/2}\,;\,^4S_{3/2}) \rightarrow {}^4I_{15/2}$	~800 cm^{-1}	1.540 μm and 1.064 μm	530 nm/555 nm	20 - 220°C	1.02 %/°C, 0.52 %/°C at 220°C	c
Nd^{3+}: silica fiber	$(^3F_{3/2}\,;\,^4F_{5/2}) \rightarrow {}^4I_{9/2}$	~1000 cm^{-1}	802 nm	[820-840 nm]/[895-915 nm]	-50 – 500°C	1.68%/°C	d
Pr^{3+}: silica fiber	$[(^3P_1 + {}^1I_6)\,;\,{}^3P_0] \rightarrow {}^1G_4$	~580 cm^{-1}	488 nm	[820 - 850 nm]/[890 – 900 nm]	22 – 250 °C	0.39 %/°C	e
Pr^{3+}: aluminosilica fiber	$[(^3P_1 + {}^1I_6)\,;\,{}^3P_0] \rightarrow {}^1G_4$	~580 cm^{-1}	488 nm	[820 - 850 nm]/[890 – 900 nm]	-185 – 257 °C	0.14 %/°C	f
Pr^{3+}: ZBLAN glass	$[(^3P_1 + {}^1I_6)\,;\,{}^3P_0] \rightarrow {}^1G_4$	~580 cm^{-1}	450 nm (LED)	877 nm/906 nm	-45 – 255°C	0.48%/°C	g
Yb^{3+}: silica fiber	$^2F_{5/2} \rightarrow {}^2F_{7/2}$	Stark sublevels	810 nm	910 nm/1030 nm	20 - 600 °C	0.95 %/°C	h
Er^{3+} doped fiber	$^4I_{13/2} \rightarrow {}^4I_{15/2}$	Stark sublevels	1.48 μm	1552 nm/1530 nm	-50 – 90°C	0.7 %/°C	i
Sm^{3+}: silica fiber	$(^4F_{3/2}\,;\,^4G_{5/2}) \rightarrow {}^6H_{5/2}$	~1000 cm^{-1}	476.5 nm	[520-535 nm]/[564-574 nm]	~22 – 475 °C	1.85 %/°C	j
Eu^{3+}: silica fiber	$(^5D_1\,;\,^5D_0) \rightarrow {}^7F_2$	~1750 cm^{-1}	465 nm	[552-560 nm]/[607-630 nm]	-172 – 400 °C	0.178 %/°C	k
Dy^{3+}: silica fiber	$(^4I_{15/2}\,;\,^4F_{9/2}) \rightarrow {}^6H_{13/2}$	~1000 cm^{-1}	477 nm	[530-542.5 nm]/[560–590 nm]	21.5 – 250 °C	1.05 %/°C	l
Er^{3+}: silica fiber	$(^2H_{11/2}\,;\,^4S_{3/2}) \rightarrow {}^4I_{15/2}$	~800 cm^{-1}	975 nm	[525–535 nm]/[555–565 nm]	20 – 200°C	3.5 %/°C	m

[1] Energy gap of thermally-coupled energy levels.

a (Maurice et al., 1995); b (Maurice et al., 1995); c (Dos Santos et al., 1999); d (Wade et al., 1999); e, f, j (Wade, 1999); g (Maurice et al., 1997); h (Maurice et al., 1997); i (Imai & Hokazono, 1997); k (Wade et al., 1998); l (Wade et al., 1997); m (Castrellon-Uribe & Garcia-Torales, 2010).

Table 1. Summary of the performance of rare-earth-doped fibers and materials as temperature-sensing elements based on the fluorescence intensity ratio technique.

experimentally. In the fluorescent sensor, a detection system was incorporated to interpret the temperature information encoded in the measured fluorescence spectrum. The detection system incorporated two optic channels to select the fluorescence spectral bands emitted from levels $^2H_{11/2}$ and $^4S_{3/2}$ of the erbium-doped fiber (Castrellon-Uribe, 2002, 2005).

Recently, this new method based on the analysis of radiometric figures of merit, such as the SNR, the noise equivalent power (NEP), sensitivity, and the temperature resolution (ΔT_{min}), was applied to evaluate the performance of rare-earth-doped fiber sensors (Castrellon-Uribe & Garcia-Torales, 2010). To select the optimum sensor for the monitoring of temperature *in situ*, this radiometric analysis allowed the selection of the limits of detection for these fluorescent sensors. In that work, the performance of an erbium-doped fiber as a remote temperature sensor employing the fluorescence intensity-ratio technique was analyzed. In this case, the green fluorescence signal was generated by up-conversion processes in the erbium-doped fiber pumped by a pigtail laser diode at 975 nm. A summary of the main results obtained in this investigation are presented as follows.

When an erbium-doped fiber was pumped with a photon energy of 2.028×10^{-19} J (λ=980 nm), the $^4I_{11/2}$ erbium level was excited through ground state absorption (GSA), and the $^4I_{13/2}$ metastable level was quasi-instantaneously populated due to non-radiative transitions. At the $^4I_{13/2}$ level, an emission to the ground state was observed around 1530 nm (near-IR). The $^4I_{11/2}$ level absorbed the pump photons and excited the $^4F_{7/2}$ level through excited state

absorption (ESA). The latter process populated the $^2H_{11/2}$ and $^4S_{3/2}$ levels, which were responsible for emissions around 530 nm and 545 nm, respectively (see Fig. 5). The latter levels were said to be in quasi-thermal equilibrium because of the small energy gap between them (about 800 cm^{-1} = 1.59x10^{-20} J) in contrast to the relatively large energy difference between them and the next lowest level (about 3000 cm^{-1} = 5.9636x10^{-20} J). In silica, a fast thermal coupling between these two levels has been studied theoretically and observed experimentally (Berthou & Jorgensen, 1990; Krug et al., 1991; Maurice, 1994, 1995).

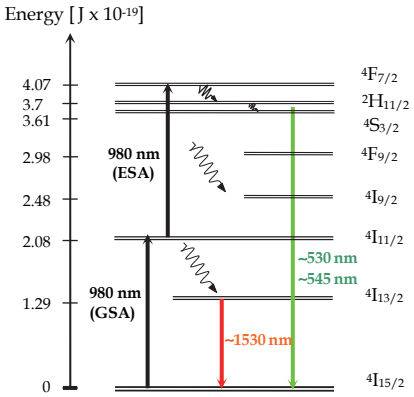

Fig. 5. Erbium energy levels diagram illustrating the excited state absorption (ESA) and the up-conversion fluorescence process. (Castrellon-Uribe & Garcia-Torales, 2010).

The ratio, R, of the intensities, I, radiating from two respective levels ($^2H_{11/2}$ and $^4S_{3/2}$) was proportional to their frequency ratio (ν), their emission cross-section ratio (σ), and the population distribution:

$$R = \frac{I(\Delta\lambda, T; {}^2H_{11/2})}{I(\Delta\lambda, T; {}^4S_{3/2})} = \frac{\nu({}^2H_{11/2})}{\nu({}^4S_{3/2})} \times \frac{\sigma({}^2H_{11/2})}{\sigma({}^4S_{3/2})} \exp\left[-\frac{\Delta E}{k \times T}\right] \quad (3)$$

Figure 6 shows the experimental setup that was used to evaluate the performance of the erbium-doped silica fiber sensor for remote temperature measurements. A pigtail laser diode with an emission at 975 nm (near-IR) was employed to excite the fluorescence of an erbium-doped (960-ppm) fiber with a length of 20 cm and a core diameter of 3.2 μm, which was located inside an enclosure whose temperature, T, was additionally monitored with a thermocouple. The green fluorescence power measured was 50 μW at 20°C for 60 mW of pump power when considering a pump power coupling efficiency to the fiber core of about 30%. A dichroic mirror transmitted the pumping infrared laser radiation and reflected the green fluorescence radiation. In the detection system, a dichroic mirror and wavelength division multiplexing (WDM) was used to separate the different spectral lines of the fluorescence-spectrum toward the two optical channels of the sensor. Interference filters with a 10-nm transmission spectral width centered on the maximum peak of transmission were employed to isolate the fluorescence spectral bands of the beam in each channel. A transducer was placed in each channel to interpret the temperature information encoded in

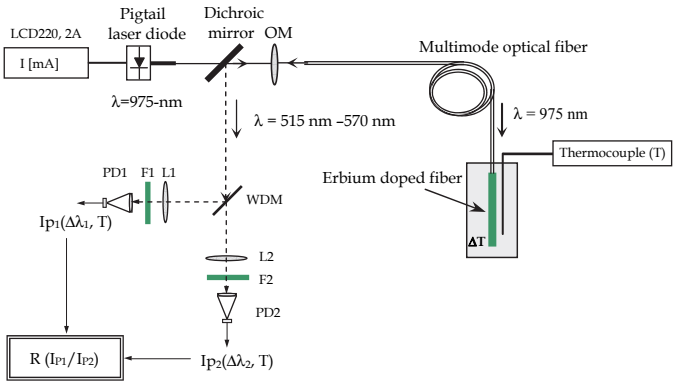

Fig. 6. Experimental setup of the erbium-doped silica fiber sensor for remote temperature measurements, employing the up-conversion fluorescence intensity ratio technique. (Castrellon-Uribe & Garcia-Torales, 2010).

the optical signal. Finally, the integrated radiation over the different wavelength intervals was detected and divided to give the spectral band power ratio. The detection system converted the measured fluorescence spectrum of the two thermally coupled energy levels ($^2H_{11/2}$ and $^4S_{3/2}$) of the erbium-doped fiber into temperature information.

Figure 7a shows the normalized fluorescence spectrum of the erbium-doped silica fiber as a function of the wavelength in the temperature interval from 20ºC to 200ºC. The power of the fluorescence spectrum centered at 530 nm ($^2H_{11/2}$ transition) increased with temperature, while the fluorescence spectrum centered at 545 nm ($^4S_{3/2}$ transition) decreased over the same temperature interval (see Fig. 7a). Figure 7b shows the measured power ratio (photocurrent-ratio measured in the detection system) as a function of temperature for the different fluorescence spectral bands integrated over the 10-nm width determined by the interference filters. The power ratios for a number of possible different fluorescence spectral bands considered for use in the erbium-doped fiber as remote temperature sensors were analyzed. The power ratio varied roughly linearly with the temperature in the interval from 20ºC to 200ºC with different slopes and a nearly linear increase in the y-intercepts (see Fig. 7b).

Afterward, the sensitivity of the sensor, *S(R)*, was evaluated as the ratio of the change in intensity integrated over the spectral bands, $\Delta R(I_1/I_2)$, to an increase in its temperature signal input, ΔT_{fiber}. The expression used to evaluate the sensitivity of the sensor was as follows:

$$S(R) = \frac{\Delta R\left[\dfrac{I_{p1}(\Delta\lambda_1, T)}{I_{p2}(\Delta\lambda_2, T)}\right]}{\Delta T_{fiber}} \qquad [1/^oC] \tag{4}$$

where $I_{p1}(\Delta\lambda_1, T)$ is the photocurrent of the channel 1 ($^2H_{11/2}$ transition) for the different spectral bands as a function of the temperature, and $I_{p2}(\Delta\lambda_2, T)$ is the photocurrent of the

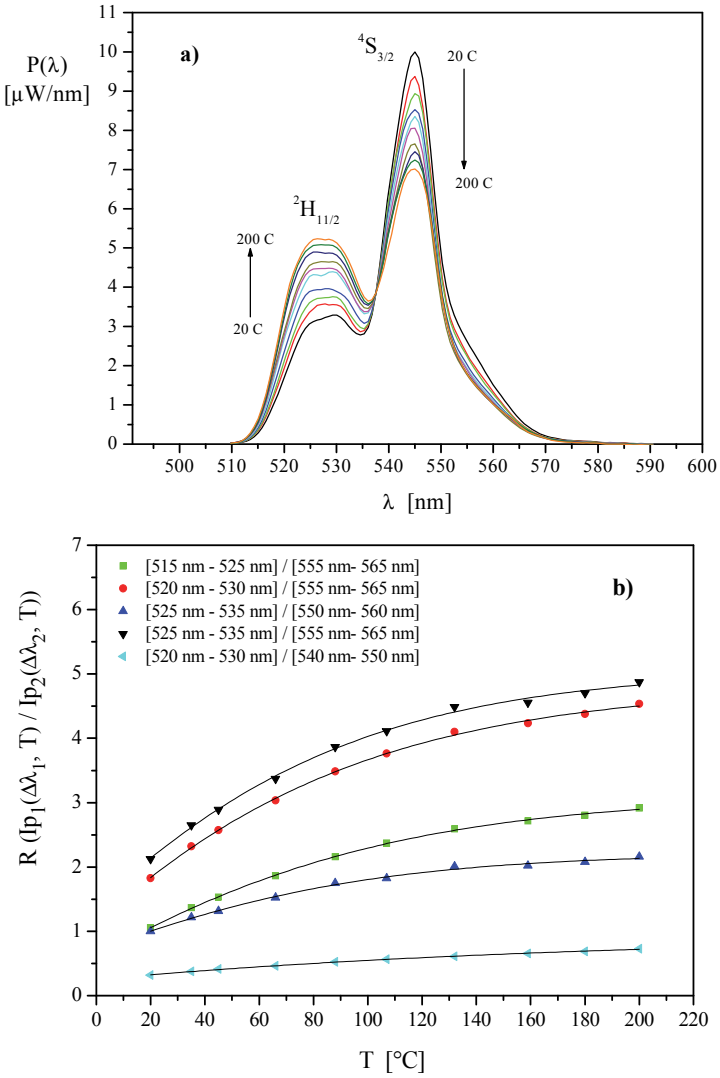

Fig. 7. a) Measured fluorescence spectrum of the erbium-doped silica fiber for different temperature values and b) measured power ratio for different fluorescence spectral bands, as a function of temperature. (Castrellon-Uribe & Garcia-Torales, 2010).

channel 2 ($^4S_{3/2}$ transition) for the different spectral bands as a function of the temperature. ΔT_{fiber} is the temperature change in the erbium-doped fiber.

The sensor sensitivity with the spectral bands [525 nm – 535 nm] / [555 nm – 565 nm] and [520 nm – 530 nm] / [555 nm – 565 nm] changed from approximately 35x10^{-3}/ºC to 9x10^{-3}/ºC and from approximately 33x10^{-3}/ºC to 8x10^{-3}/ºC, respectively. In addition, the sensitivities for the spectral intervals [515 nm – 525 nm] / [555 nm – 565 nm] and [525 nm –

535 nm] / [550 nm – 560 nm] changed from about $21x10^{-3}/^{o}C$ to $6x10^{-3}/°C$ and from about $15x10^{-3}/^{o}C$ to $4x10^{-3}/°C$, respectively. It was concluded that the sensor sensitivity exponentially decreases with an increase in the temperature.

Nevertheless, considering that the main characteristics for the best performance of any fiber optic sensor are a high SNR and excellent sensitivity, the authors also proposed to use the ratio of powers of spectral bands [520 nm – 530 nm] / [540 nm – 550 nm] with sensitivities from approximately $4x10^{-3}/^{o}C$ to $2x10^{-3}/°C$ in the temperature interval of 20°C – 200°C. These spectral bands exhibited smaller sensitivities and power ratio slopes than the others. However, they had a very high SNR and responsivity because these spectral bands corresponded with the maximum peaks of fluorescence for the $^{2}H_{11/2}$ and $^{4}S_{3/2}$ transitions (channels of the sensor).

Finally, the optimal spectral bands proposed to use in the sensor were [520 nm – 530 nm] and [525 nm – 535 nm] ($^{2}H_{11/2}$ transition) of the erbium-doped fiber with signal-to-noise ratios of 110 dB and 111 dB, respectively, at 20°C; while for the spectral bands [540 nm – 550 nm] and [555 nm – 565 nm] ($^{4}S_{3/2}$ transition) of the erbium-doped fiber, the signal-to-noise ratios were 120 dB and 104 dB, respectively, at 20°C. The highest sensitivity obtained for the sensor was from approximately $35x10^{-3}/^{o}C$ to $10x10^{-3}/°C$ for the temperature interval of 20°C – 200°C. Therefore, radiometric analysis is a powerful tool for predicting and comparing the performance of fiber optic sensors, and it allows one to determine the optimum sensor for specific applications.

5. New electro-optical materials for applications in chemical sensing

The development of new materials with non-linear optical properties (NLO) has been one of the main objectives of research and development in the field during the past few decades, due to their important applications mainly in photonics (Nalwa, 2001). The organic second-nonlinear optical materials have been widely investigated because of their great potential applications in optoelectronic devices and optical information processing, and many new NLO materials have been prepared and researched (Dalton, 1995; Yesodha et al., 2004). Generally, the organic materials are composed of a polymeric matrix in which the chromophores are distributed and produce the non-linear optical properties.

Polymers are normally used in electrical and electronic applications as insulators due mainly to the intrinsic property of covalent bonding present in most commodity plastics. These polymers with localized electrons are incapable of providing electrons as charge carriers or a path for other charge carriers to move along the chain. However, polymers are also widely exploited because of their special characteristics, such as low density, mechanical strength, ease of fabrication, flexibility in design, stability, resistance to corrosion, and low cost. Thanks to the investigations conducted by Shirakawa, Heeger, and Mac Diarmid since 1997 (prizewinners of the 2002 Nobel Prize in Chemistry), these polymers can also be synthesized in their conductive form (Shirakawa, 1977a, 1977b). Therefore, conjugated semiconducting polymers are a novel class of materials that combine optical properties with the electronic properties of semiconductors.

Since the early 1980s, conducting polymers, such as polypyrrole (PPy), polyaniline (Pani), polythiophene (PTh), and their derivatives, have been investigated due to their chemical, electrical, and optical properties (Skotheim & Reynolds, 2007). The conducting polymers are

easy to synthesize through chemical or electrochemical processes, and their molecular chain structures can be conveniently modified by copolymerization or structural derivations. One of the most important characteristics of these conducting polymers is their capacity to be oxidized or reduced when they are in contact with positive or negative ions. The change from the conductive state (oxidized) to the non-conductive (reduced) state of the polymer is reversible and is associated with its *redox* property. In addition, the conducting polymers combine interesting optical and electrical properties, such as photoluminescence (PL) and electroluminescence (EL), making them attractive for applications in optoelectronics.

Luminescence: Luminescence is defined as the de-excitation of an atom or molecule by the emission of photons. According to the origin of the excitation, the luminescent process can be photoluminescence, electroluminescence, chemo-luminescence, bioluminescence, or incandescence. Fluorescence is a photoluminescence in which the molecular absorption of a photon triggers the emission of a photon with a longer wavelength (less energetic). The luminescence can be classified according to the duration of the emission after the excitation. When the excitation is suspended, an exponential decay of the emitted light occurs. The luminescent process is called fluorescence when the time of decay of the emission has a duration on the order of 10^{-3} s or less; for decay times greater than this value, the process is called phosphorescence (Lakowicz, 2006). The conjugated polymers based on the luminescence can be used for several applications, particularly in chemical sensors (Lange et al., 2008; Liu et al., 2009).

Electroluminescence: The electroluminescent conjugated polymers are materials that emit light when they are excited by the flow of an electric current. Conjugated polymers are particularly versatile because their physical properties, such as color and emission efficiency, can be fine-tuned by the manipulation of their chemical structures. The research on these new fluorescent materials has contributed to the development of organic light-emitting diodes (Akcelrud, 2003; Friend et al., 1999; Kraft et al., 1998). Organic thin-film electroluminescence devices were developed in the 1980s by Tang and Van Slyke (Tang & Van Slyke, 1987) and Saito and Tsutsui et al. (Adachi et al., 1988).

In recent years, research has been focused on thiophene-based polymers due to their structural versatility, solubility upon functionalization, and environmental stability (Chan & Ng, 1998). The polythiophenes are electroluminescent and photoluminescent materials, and their electro-optical properties are of considerable interest due to their potential applications, particularly as fluorescent chemical sensors based on fluorescence quenching (Li et al., 2005; Marti, 2009a, 2009b; Somanathan & Radhakrishnan, 2005; Tang et al., 2006).

Generally, the polythiophenes are excited with UV radiation, and the fluorescence signal is observed in the visible region of the electromagnetic spectrum. Fluorescence quenching refers to any process that decreases the fluorescence intensity of a sample. There are a wide variety of quenching processes; they include excited state reactions, molecular rearrangements, ground state complex formation, and energy transfer (Lakowicz, 2006).

In these conducting polymers, the quenching efficiency increases with an increasing tendency of the polymer to associate with the quencher in solution. This association can occur either through the formation of a non-luminescent complex between the polymer and the quencher (static quenching) or through collisions between the photo-luminescent macromolecule and the quencher (dynamic quenching).

In general, conjugated polymers have become an important class of materials employed in a wide variety of applications, including light-emitting diodes (LEDs) (Adachi et al., 1988; Akcelrud, 2003; Friend et al., 1999; Kraft et al., 1998; Tang & Van Slyke, 1987), light-emitting electrochemical cells (LECs) (Pei et al., 1995), plastic lasers (Hide et al., 1997), solar cells (Gunes et al., 2007), field effect transistors (FETs) (Sirringhaus, 2005), and more recently, chemical or biological sensors (Achyuthan et al., 2005; Castrellon-Uribe et al., 2009; Liu & Bazan, 2004; McQuade et al., 2000; Pinto & Schanze, 2002; Thomas et al., 2007).

Particularly, conducting polymers, such as polypyrrole, polyaniline, polythiophene, and their derivatives, have been investigated and used as the sensitive materials for developing gas sensors (Ameer & Adeloju, 2005; Bai & Shi, 2007; Maksymiuk, 2006; Nicho et al., 2001; Rahman et al., 2008).

Sensors composed of conducting polymers have important characteristics, such as high sensitivities and short response times. Conducting polymers are easy to synthesize through chemical or electrochemical processes, and their molecular chain structure can be conveniently modified by copolymerization or structural derivations. Furthermore, conducting polymers have good mechanical properties, which allow for the facile fabrication of sensors. Chemical sensors are devices that allow the continuous and reversible measurement of chemical parameters. The conducting polymers are conjugated macromolecules that exhibit electrical and optical property changes when they are protonated/deprotonated by certain chemical agents. In recent years, conducting polymers, such as polypyrrole and polyaniline (PANI), have been proposed as chemical sensors based on the changes in their electric conductivity when they are exposed to ammonia (Agbor et al., 1995; Brie et al., 1996; Koul & Chandra, 2005).

Recently, sensors of polyaniline films that are based on the change in their optical absorption have been investigated for the measurement of ammonia (Jin et al., 2001; Lee et al., 2003; Nicho et al., 2001). In these chemical sensors, the optical absorption at a wavelength of about 630 nm changes with an increasing ammonia concentration. Nevertheless, these sensing materials are not suitable to carry out remote measurements with optical fibers because the attenuation of the multimode fibers is 9 dB/km at 600 nm and 1 dB/km at 980 nm (Keiser, 1991).

Recently, a study of the optical response of polyaniline films that had been exposed to low concentrations of aqueous ammonia was reported (Castrellon-Uribe et al., 2009). The synthesis of the PANI films was carried out by the chemical bath method. In that work, polyaniline films were exposed to different concentrations of aqueous ammonia (10–4000 ppm), and their optical transmittances were measured in the wavelength interval of [350–1100 nm] to determine their optical sensitivities. In addition, an optical sensor system was developed based on the power ratio of transmittance for monitoring low concentrations of aqueous ammonia; it employed a polyaniline film, a pigtailed laser diode at 975 nm, photodetectors, and a multimode optical fiber.

Figure 8 shows the laser sensor system based on the optical power of transmittance for the optical detection of ammonia with PANI films. Generally, optic sensors that are based on change in intensity are susceptible to the variation of the optical signal of the source, causing errors in the measurement. Thus, the authors proposed the use of the optical power ratio technique to carry out the remote optical detection of ammonia.

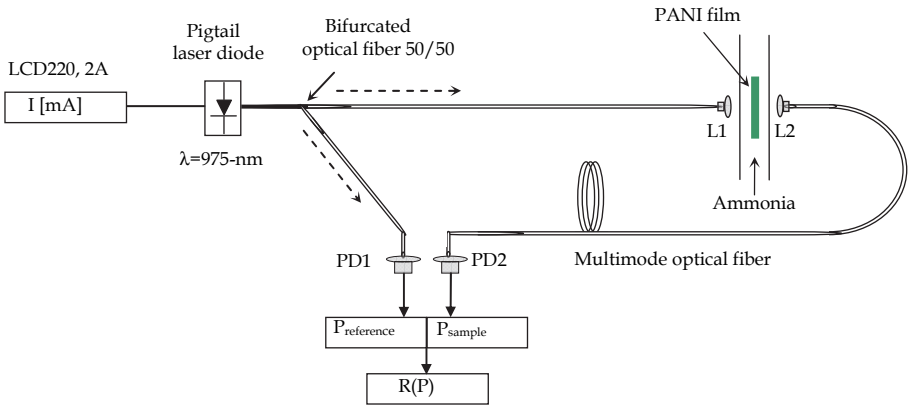

Fig. 8. Laser sensor system for the remote optical detection of ammonia with PANI films employing the optical transmittance ratio technique. (Castrellon-Uribe et al., 2009).

To evaluate the optical response of the PANI films, the sample was exposed to 4000 ppm of aqueous ammonia; immediately, the PANI film showed a chromatic change (from green to blue) when in contact with the ammonia. The PANI (EB) samples (blue color) were then treated with 0.2 M hydrochloric acid to chemically return them to their (ES) state (green color). When the PANI (ES) film was exposed to a basic solution, such as ammonia, it underwent a deprotonation process and was converted to an emeraldine base (EB) state with a blue color. In contrast, if the reaction medium was acidic, such as with hydrochloric acid, the polymer was in a protonated state, known as the emeraldine salt (ES), which had a green color. The optical transmittance of the PANI film in the (ES) and (EB) states is observed in Figure 9a. Afterward, the optical transmittance of the PANI film was measured to determine its optical sensitivity to different concentrations of ammonia (see Fig. 9b). In the visible region (VISR), the signal of transmittance showed a gradual shift in wavelength with increasing ammonia concentrations. The PANI (ES) film exposed to different concentrations of aqueous ammonia presented a better optical response at the wavelength centered at 975 nm (NIR), as observed in Figure 9b.

The response time and the recovery time of the PANI film when in contact with the ammonia and its regeneration in hydrochloric acid were also investigated. The response time and the recovery time of the PANI film exposed to a basic solution (such as ammonia) and an acid medium (such as hydrochloric acid) were less than 10 sg at room temperature. The response of the PANI film when exposed to aqueous ammonia, as well as its recovery when regenerated in hydrochloric acid, was immediate, as shown in Figure 10a. Finally, the calibration curve of the optical sensor system was obtained from the change in the power ratio of transmittance ratio, ($P = P_{Sample}/P_{ref}$), at different concentrations of ammonia as is observed in Figure 10b.

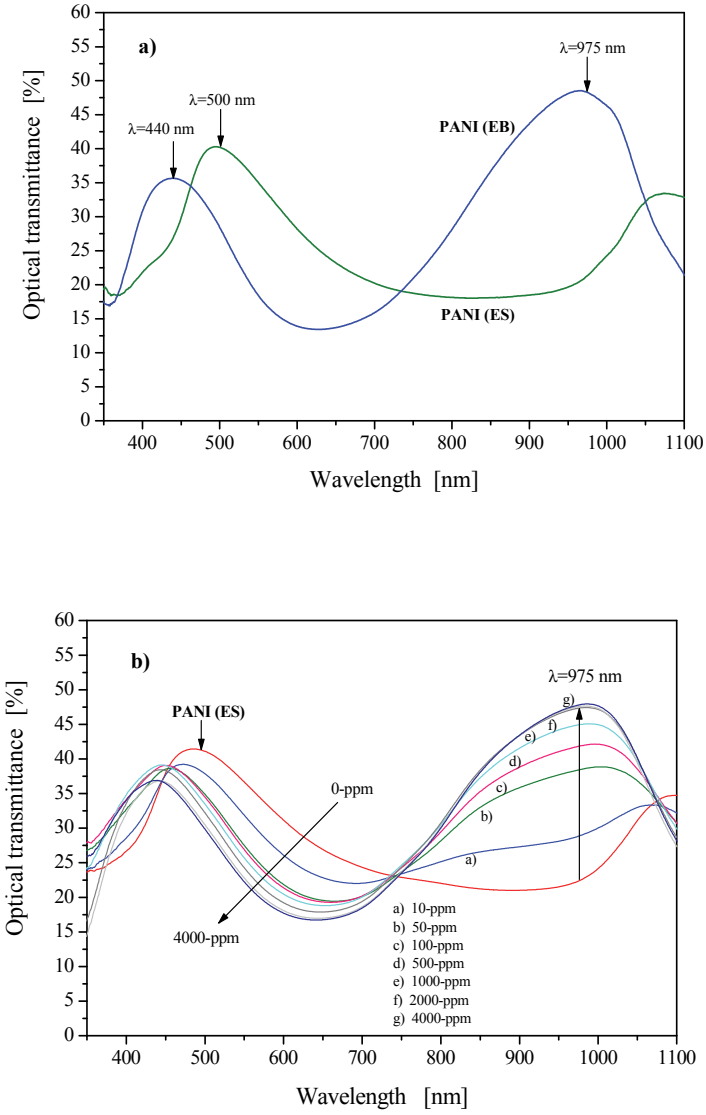

Fig. 9. a) Optical transmittance of the PANI film upon protonation and deprotonation reactions and b) optical response of the PANI film exposed to different concentrations of aqueous ammonia as a function of wavelength. (Castrellon-Uribe et al., 2009).

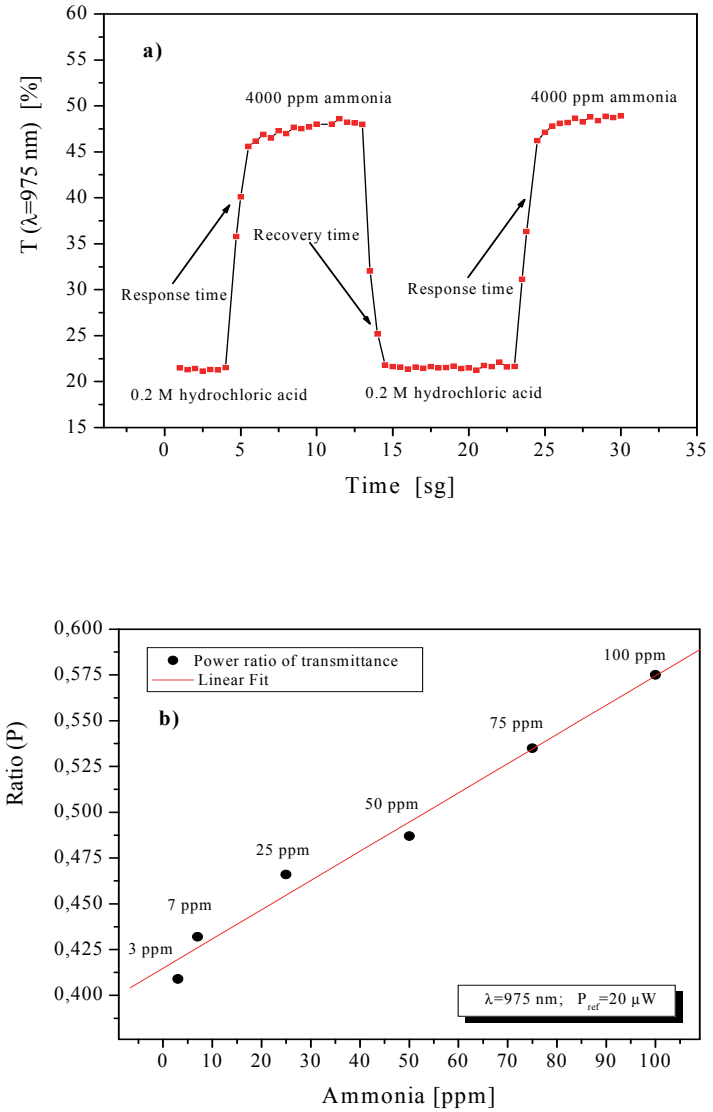

Fig. 10. a) Response time and recovery time curve of a polyaniline film measured at 975 nm and b) calibration curve of the power ratio of transmittance of the optical sensor system employing a pigtail laser diode at 975 nm. (Castrellon-Uribe et al., 2009).

6. Conclusions

In conclusion, the main advantages of the optical sensor system proposed for monitoring ammonia with PANI films are the following: its insensitivity to the intensity variations of the optical source signal, which helps to avoid errors in measurements; its simple detection system of the signal with the ammonia information; and the possibility of utilizing a light-emitting diode (LED) as the optical source instead of a laser diode. Therefore, the feasibility of employing polyaniline polymers in the development of intrinsic optical fiber sensors for the remote optical detection of ammonia was shown.

The development and commercialization of optical fiber sensors has increased in recent years. The area of application of optical fiber sensors is now well identified, and its extension toward sensor systems optoelectronics has contributed to a wide range of applications in diverse fields. However, the continuous technological progress in diverse fields establishes new challenges for the development and instrumentation of reliable optical fiber sensor systems and devices with high performance. The investigation and development of new materials that combine electrical and optical properties, such as the conductive polymers, open the possibility of new optoelectronic devices, such as sensor systems and their implementation with optical fibers (Cao & Duan, 2005; Castrellon-Uribe et al., 2009; Christie et al., 2003; Scorsone et al., 2003).

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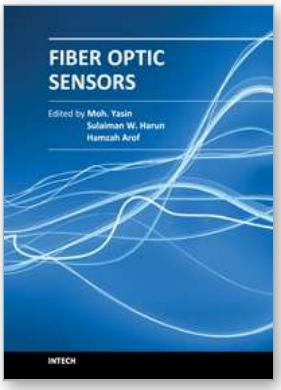

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This book presents a comprehensive account of recent advances and researches in fiber optic sensor technology. It consists of 21 chapters encompassing the recent progress in the subject, basic principles of various sensor types, their applications in structural health monitoring and the measurement of various physical, chemical and biological parameters. It also highlights the development of fiber optic sensors, their applications by providing various new methods for sensing and systems, and describing recent developments in fiber Bragg grating, tapered optical fiber, polymer optical fiber, long period fiber grating, reflectometry and interefometry based sensors. Edited by three scientists with a wide knowledge of the field and the community, the book brings together leading academics and practitioners in a comprehensive and incisive treatment of the subject. This is an essential reference for researchers working and teaching in optical fiber sensor technology, and for industrial users who need to be aware of current developments and new areas in optical fiber sensor devices.

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