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Fiber optic fluorescence temperature sensors using up-conversion from rare-earth polymer composites

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We demonstrate an optical fiber sensor based on the green up-conversion emission of rare-earth active ions hosted by a polymer matrix. The temperature sensitive composite material is fabricated by simple mixing of the rare-earth ions in powder form ($NaY_{0.77}Yb_{0.20}Er_{0.03}F_4$) with the polymer (polydimethylsiloxane). This fluorescent material is then incorporated on the tip of silica-glass optical fibers to obtain a point temperature sensor probe. Temperature measurements are obtained through the fluorescent intensity ratio technique, yielding a linear response and minimizing spurious effects on the up-conversion fluorescence signal. The fiber sensors fabricated with this material provide good performance within a temperature range of 20–100°C, excellent linearity ($r^2 = 0.999$), and good thermal and fluorescent stability. © 2019 Optical Society of America

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Fiber optic temperature sensors have been extensively investigated because of their distinctive advantages over traditional sensors, including small size, lightweight, immunity to electromagnetic interference, and resistance to harsh environments. [1,2]. Although several approaches have been demonstrated for measuring temperature with fiber optic sensors, fluorescent-based measurements are one of the most commonly used techniques [3]. Fluorescence features that can be monitored as a function of temperature include lifetime [4], spectral shift [5], intensity decay [6], and the intensity ratio of a pair of fluorescent bands [7,8]. The latter technique is known as fluorescence intensity ratio (FIR) and has been widely used for optical thermometry due to its noise cancellation capabilities [9]. Because temperature is obtained through the ratio of the emission bands of two thermally coupled energy levels, the resulting readings are independent of the excitation power [8,9]. Hence, any fluctuations in the fluorescence signal and in the pump source are effectively eliminated, thereby simplifying the measurement procedure when compared to other techniques.

FIR measurements generally rely on the up-conversion (UC) luminescence observed in rare-earth (RE) ions [10]. Erbium (Er^{3+}) and ytterbium (Yb^{3+}), in particular, have proven to be a suitable co-doping pair for efficient generation of visible UC for temperature sensing [7,8]. This combination allows for increasing the pump absorption and effectively reducing the excitation power required to generate the fluorescence signal [11]. A number of Er^{3+}/Yb^{3+} FIR fiber optic temperature sensors have been demonstrated, aiming at incorporating the sensing material (typically a RE-doped glass) on the tip of the fiber probe [7–9,12]. This approach is preferred over using a RE-doped optical fiber in order to avoid the background signal generated along the length of the fiber itself, since this is known to favor fluorescence quenching limiting also the attainable spatial resolution [7,13]. While glass matrices have been the preferred choice for hosting the RE ions, other matrices may provide simpler means to fabricate fluorescence-based sensors. For example, RE compounds have been incorporated in a polymer matrix, allowing for obtaining temperature maps in microfluidic channels [14]. Hence, novel approaches for fabricating temperature sensors may arise upon incorporating RE-doped polymer materials on optical fibers.

In this work, we demonstrate a fiber optic temperature sensor based on a fluorescent polymer compound formed by polydimethylsiloxane (PDMS) hosting a sodium yttrium fluoride powder doped with Yb^{3+} and Er^{3+}. The composite polymer is fabricated by simple mixing and is subsequently incorporated on the tip of a dual fiber device, yielding a point temperature sensor. Temperature readings are obtained using the FIR technique with the green UC luminescence generated by the polymer compound. We provide details of the fabrication procedure and evaluate the performance of the sensors. Our results show that the proposed fabrication method together with the FIR technique yield fiber optic temperature sensors with excellent stability and linearity.

The temperature sensitive polymer composite used for the sensors was fabricated using standard PDMS (Dow Corning, Sylgard 184) mixed with a green UC phosphor ($NaY_{0.77}Yb_{0.20}Er_{0.03}F_4$, Sigma Aldrich 756555-25G). This ytterbium- and erbium-doped

sodium yttrium fluoride powder has a particle size of 1–5 μm, is optimized to absorb in the wavelength range of 940–980 nm, and has been shown to provide high luminescence efficiencies [15]. Upon mixing the PDMS with $NaY_{0.77}Yb_{0.20}Er_{0.03}F_4$, we obtained a fluorescent composite polymer (PDMS–Yb^{3+}/Er^{3+}) that can generate the green UC emission typically observed when pumping this phosphor. Mixing was performed following a procedure reported previously for fabricating photothermal membranes [16], adding the fluoride powder to the PDMS in a concentration of 0.5% per weight. To reduce cluster formation, 1 ml of chloroform ($CHCl_3$) was added per gram of PDMS; this solution was then mixed with a magnetic stirrer while heated at 60°C until the $CHCl_3$ was evaporated.

A dual optical fiber probe was assembled to contain the PDMS–Yb^{3+}/Er^{3+} polymer composite. This was fabricated from a standard multimode fiber (62.5 μm core diameter) with a coupler manufacturing station (Dowson Corp., model OC2010), joining the two fiber claddings to form a fiber probe with a final diameter of approximately 150 μm (see Fig. 1). The transmission losses for this device were measured to be less than 0.2 dBm, and, since the cores of the waveguides are not coupled, one of the fibers is used to pump the polymer composite, and the other one is used to collect the UC luminescence. The steps followed to produce the temperature sensitive fiber probes are depicted in Fig. 1. A standard 21G butterfly catheter and a gastrointestinal polyvinyl chloride (PVC) tube (2 cm long, 2 mm external diameter, 1 mm internal diameter) were used as molds for housing the polymer composite. The catheter bevel was cut to obtain a 1.5 cm long tube that was subsequently inserted into the PVC tube, and both were then joined with an adhesive, yielding molds that were typically 3 cm long, allocating approximately 7.8 μl of the PDMS–Yb^{3+}/Er^{3+} composite. Once the fiber probe was inserted into the mold, the curing agent for the PDMS was added to the fluorescent composite in a 1:10 ratio, and both were mixed by hand for 3 min. This mixture was subsequently poured into the molds, and these were then heated at 75°C for 1 h for solidification. As a final step, the PVC tube was removed upon immersion in acetone for 3 min, leaving the temperature sensitive polymer compound exposed.

The experimental setup used for characterization of the sensors is shown in Fig. 2(a); a 975 nm laser diode (Thorlabs, 330 mW maximum output power) was launched into one

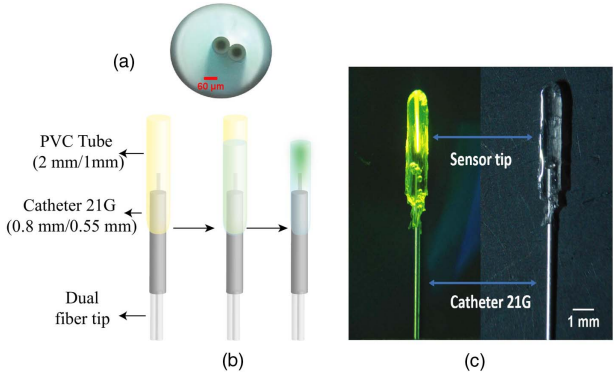

Fig. 1. (a) Cross section of a dual fiber tip, (b) sensor fabrication process, and (c) sensor probe showing the visible up-conversion emission of the polymer tip (left, laser on; right, laser off).

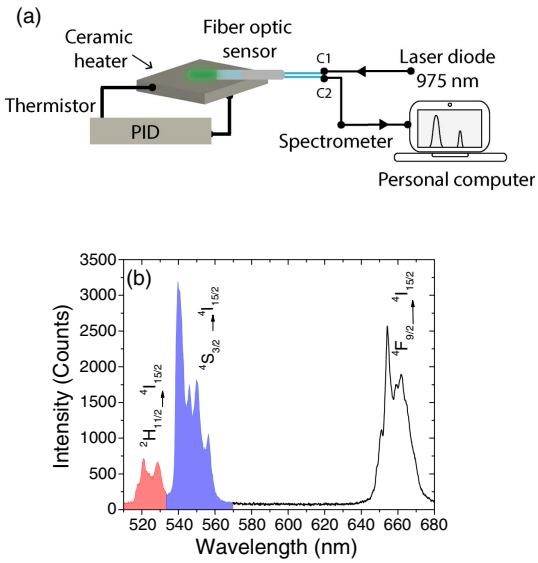

Fig. 2. (a) Experimental setup for fiber optic sensor characterization. (b) Emission spectrum obtained with the fiber optic probe under excitation at 975 nm with 75 mW laser power. The colored regions (red and blue) represent the transitions of interest for the FIR technique.

of the fiber leads, while the remaining fiber was connected to a solid-state spectrometer (Ocean Optics, USB4000). The fiber probes were placed on a ceramic heater connected to a proportional–integral–derivative (PID) controller (Thorlabs, TED200C) and a thermistor, allowing for controlling the temperature from 15°C to 120°C with 0.1°C precision. With this arrangement, we were able to obtain the spectral features of the UC emission from the polymer compound under different pumping conditions and for different temperatures.

A typical fluorescence spectrum obtained from the fiber probe at room temperature (27°C) is shown in Fig. 2(b). The spectral features obtained from the PDMS–Yb^{3+}/Er^{3+} polymer composite are comparable to those reported from some of the doped-glass materials used for temperature sensing [7,8], showing three intensity peaks located at 520, 540, and 654 nm. As indicated in the figure, these peaks correspond to the energy transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively. Since only the first two energy bands are thermally coupled [9], only the spectral features centered at 525 and 550 nm were used to evaluate the FIR. Hence, for each temperature, the FIR was evaluated as A_{525}/A_{550}, where A_{525} and A_{550} are obtained upon integrating the corresponding spectral bands (i.e., from 510 to 533 nm and from 533 to 570 nm, respectively).

A typical set of spectra of the relevant fluorescence bands obtained for different temperatures is presented in Fig. 3(a). As shown in the plot of Fig. 3(b), the FIR varies linearly as a function of temperature. The plot further includes the FIR obtained from four sets of experiments carried out with the same probe for temperatures ranging from 25°C to 100°C. Clearly, the probe provides repeatable readings for this temperature range, yielding an error within 0.2%. The material stability is consistent with the thermal features of the PDMS, as degradation for this host matrix is expected to occur for temperatures beyond 200°C [16].

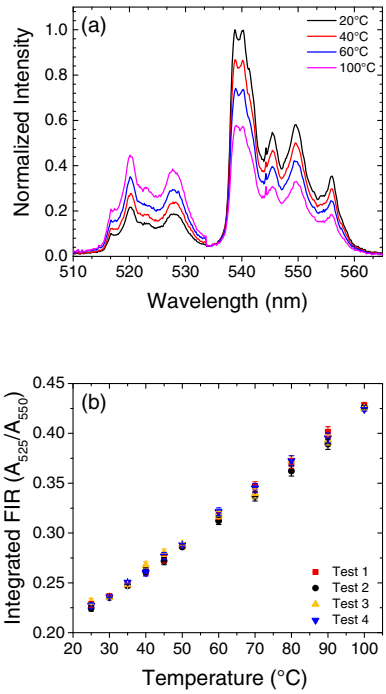

Fig. 3. (a) Typical normalized spectra for different temperatures. (b) FIR obtained with the thermally coupled bands as a function of temperature (25°C–100°C) for the same fiber probe in four sets of experiments.

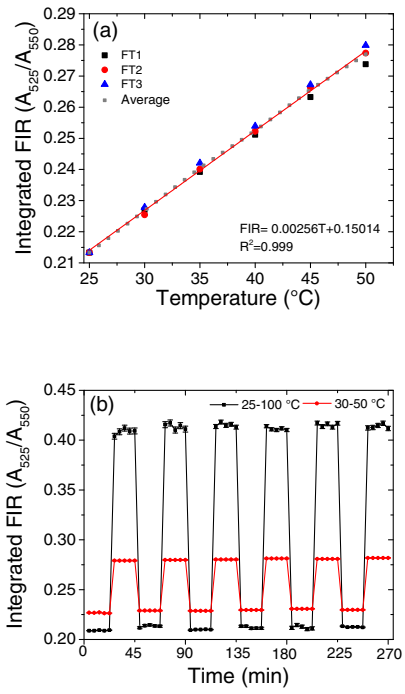

Fig. 4. (a) FIR as a function of temperature for three different fiber probes (FT1, FT2, FT3). (b) FIR reading for thermal cycles obtained with FT1.

Three sensors were fabricated following the same process in order to verify the reproducibility of the proposed method. The emission spectrum was obtained for temperatures ranging from 25°C–50°C, and, as seen in Fig. 4(a), the sensors show a similar temperature response and excellent linearity ($r^2 = 0.999$) owing to the FIR technique. From the slope of these curves, the resulting sensitivity is 0.00256/°C, which is comparable to that reported for fiber optic fluorescent sensors based on RE-doped glass [8]. We further evaluated the thermal stability by conducting experiments at two different thermal cycles: one from 30°C to 50°C and then from 25°C to 100°C. As seen in Fig. 4(b), the sensors showed repeatable readings when exposed to periodic temperature changes over a total time of 4.5 h. Nonetheless, small FIR fluctuations (within 0.3%) are apparent for the cycles reaching temperatures of 100°C.

Further tests were conducted to evaluate the stability of the FIR measurements. Using the PID controller, the temperature was set to fixed values of 35°C, 40°C, 50°C, and 100°C, for 3 h while keeping a constant power for the laser diode (75 mW). As seen in Fig. 5(a), the FIR obtained from the fiber sensor remained stable even when sustaining a maximum temperature of 100°C. In a similar experiment, the temperature was fixed at 50°C over a period of 3 h, and the FIR from the sensors was evaluated for three different powers of the laser diode (90, 100 and 125 mW). The results are shown in Fig. 5(b), and, as before, the FIR remained stable and showed only small variations (0.1%) when the laser power was increased. Hence, the FIR technique used with the PDMS–Yb^{3+}/Er^{3+} composite polymer effectively minimizes the sensor's reading fluctuations.

The response time of the fiber sensors was compared with a thermistor and a resistance temperature detector (RTD) to assess their temperature tracking capabilities. We first set the temperature to 25°C and then increased it to 50°C. Once a stable temperature reading was obtained from the thermistor, the temperature was lowered to 35°C. This cycle was carried

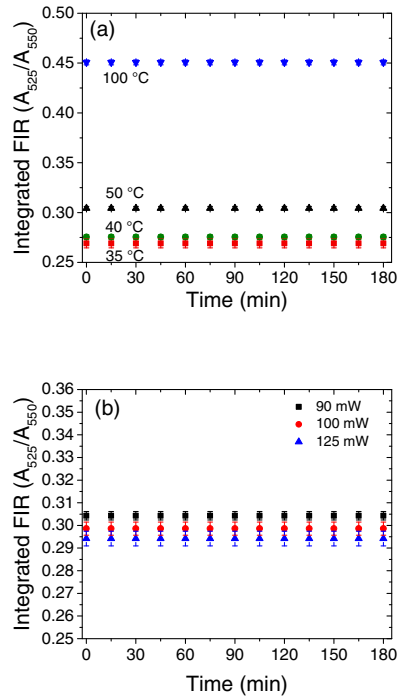

Fig. 5. Sensor stability during 3 h: (a) constant pump power (75 mW) and four different temperatures; (b) constant temperature (50°C) and three different pump powers.

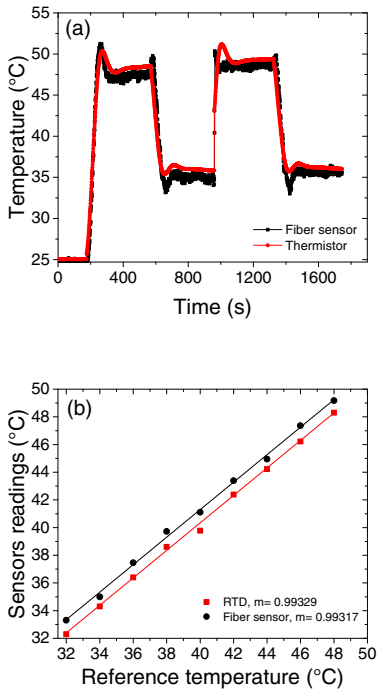

Fig. 6. Fiber sensor response: (a) tracking the response time of a commercial thermistor; (b) tracking temperature readings of a RTD.

out twice over a total of 30 min and spectra from the fiber sensors were acquired every second. The temperature reading was subsequently calculated using the FIR and then compared with the reading of the thermistor. The results are presented in Fig. 6(a), showing that the readings from both sensors are similar; thus, the fiber sensors track the transient readings registered by the thermistor. From these data, the response time of the sensor, defined as the time required to reach 95% of the set temperature, was estimated to be approximately 56 s. Similarly, the time constant, defined as the time required to reach 63.2% of the set temperature, was calculated to be 21 s. Both of these features are comparable to those reported for the thermistor used in our experiments. As for the RTD, this was used for comparing the temperature sensitivity over a range from 32°C to 50°C. The temperature was increased in steps of 2°C, and, as shown in Fig. 6(b), the slope for both devices is very similar. Thus, the fiber sensors perform well when compared to their electronic counterparts.

In spite of using a simple mixing procedure for obtaining the fluorescent polymer, the composite performs remarkably well for temperature sensing. The basic structure of the green UC phosphor remains unaffected when hosted by PDMS, thus retaining its green UC fluorescent features. This polymer composite is easy to process and can be readily incorporated on fiber devices. Most temperature sensors involving fiber optics with RE dopants usually rely on glass matrices (e.g., tellurite glass, fluorotellurite glass, fluorinated glass, oxyfluoride glass, etc. [8]); albeit providing large temperature measurement ranges, glass processing involves more elaborated techniques compared to the proposed method using the PDMS–Yb^{3+}/Er^{3+} polymer composite. Furthermore, only small amounts of the polymer composite (7.8 μl) are needed to obtain a sensor with comparable performance to that reported for some of the RE-doped glass devices.

A fluorescent temperature sensor using compounds with RE embedded in a polymeric matrix was demonstrated. The temperature sensitive compound ($NaY_{0.77}Yb_{0.20}Er_{0.03}F_4$) retains its fluorescence features when mixed into a PDMS matrix, thus providing a material that can be easily incorporated on the tips of optical fiber devices. The proposed temperature probe is easy to fabricate with commercially available materials. Tests were conducted in a temperature range from 25°C to 100°C, and the sensors showed an excellent linearity ($r^2 = 0.999$) and a sensitivity of 0.00256/°C. Furthermore, the use of the FIR technique for temperature measurements allowed for minimizing reading fluctuations due to pump noise and other spurious effects. The proposed fabrication method is simple and yields sensors with highly reproducible features, which can be further reused since the compound presents good fluorescence stability. Thus, the incorporation of temperature sensitive polymer compounds onto conventional optical fibers provides a simple means to fabricate point temperature sensors.

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