

# Temperature Sensor Based on Frequency Upconversion in $\text{Er}^{3+}$ -Doped Fluoroindate Glass

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**Abstract**—We describe the characterization of a temperature sensor based on the infrared-to-visible frequency upconversion process excited in a sample of  $\text{Er}^{3+}$ -doped fluoroindate glass. The present results demonstrate the feasibility of constructing a compact practical device using a low-power CW 1.48- $\mu\text{m}$  diode laser as the excitation source.

## I. INTRODUCTION

RARE-earth (RE) doped materials are of interest for temperature sensors because their absorption and emission properties are temperature dependent. To date a number of such sensors has been presented and the most successful approach is based on the study of RE fluorescence whose decay-time is a function of the sample temperature. For this kind of application the fluorescent material is excited by a pulsed light source of an appropriate wavelength and the fluorescence signal decay-time is determined by a time-resolved processing circuit. This method was introduced about ten years ago [1] and has been employed by several authors [1]–[5].

More recently a new approach also based on the temperature dependence of the RE fluorescence was proposed in [6]. The authors used a fluoride glass codoped with  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  and measured the sample's temperature by determining the signal ratio of two fluorescence lines of a Boltzmannian population associated to excited states. The signal processing was simplified since the temperature was determined from the ratio of two line intensities, instead of time-resolved measurements. However, an important requirement for practical application of the new method is the selection of an appropriate material that must present a large upconversion signal while

excited with low-power laser diodes. The use of oxide glasses, for example, is not practical because the large nonradiative relaxation suffered by the RE ions when incorporated in this class of host makes them poor upconverters. On the other hand, fluorozirconate glasses are not appropriate either because of their sensitivity to humidity.

In the present paper we report the use of a new class of fluoroindate glasses doped with  $\text{Er}^{3+}$  as a temperature sensor based on the method introduced in [6]. Accordingly, the efficient infrared-to-visible upconversion process is achieved using a 1.48- $\mu\text{m}$  CW low-power (5 mW) laser diode that excites a significant population to the thermally coupled excited levels  $^2\text{H}_{11/2}$  and  $^4\text{S}_{3/2}$ , which generate the double frequency fluorescence signal required.

The samples used were prepared following the procedure given in [7] and have the compositions (mol %):  $39 - x \text{InF}_3 - 20\text{ZrF}_2 - 16\text{BaF}_2 - 20\text{SrF}_2 - 2\text{GdF}_3 - 2\text{NaF} - 1\text{GaF}_3 - x\text{ErF}_3$  ( $x = 2, 3$ ). These fluoroindate glasses present high transparency from the ultraviolet to the middle-infrared and large resistance to atmospheric moisture. Moreover, our recent studies [8]–[11] have shown their large potential for photonic applications because their phonons have small energies ( $\leq 507 \text{ cm}^{-1}$ ), they present large frequency upconversion efficiency and it is possible to incorporate large concentrations of RE ions to the matrix.

Fig. 1 shows schematically the excitation and decay channels related to the states  $^2\text{H}_{11/2}$  and  $^4\text{S}_{3/2}$ , whose fluorescence intensity ratio is the basis of our sensor. As indicated by the solid arrows, the pump diode laser resonant with  $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$  transition initiates the upconversion process. The upconverted fluorescences at  $\approx 522 \text{ nm}$  and  $\approx 543 \text{ nm}$  are quite strong and readily visible by the naked eye. The spectra obtained for  $23 \text{ }^\circ\text{C}$  and  $175 \text{ }^\circ\text{C}$  are presented in Fig. 2. We have observed that when the glass temperature is raised, the intensities of both fluorescence lines at  $\approx 522 \text{ nm}$  and  $\approx 543 \text{ nm}$  decrease as well as their ratio. On the other hand, their peak positions did not change in the temperature range of our measurements ( $23\text{--}175 \text{ }^\circ\text{C}$ ). The behavior of the fluorescence signal,  $I_s$ , with the laser intensity,  $I_p$ , was also determined and the dependence,  $I_s \propto I_p^N$ , with  $N \approx 3$  was verified. This result indicates that three laser photons participate in the upconversion process. For the  $\text{Er}^{3+}$  concentrations and laser wavelength used, frequency upconversion is mainly due to energy transfer processes and the contribution of excited state absorption is negligible [11]. Accordingly, after excitation to the  $^4\text{I}_{13/2}$  state, energy transfer between three

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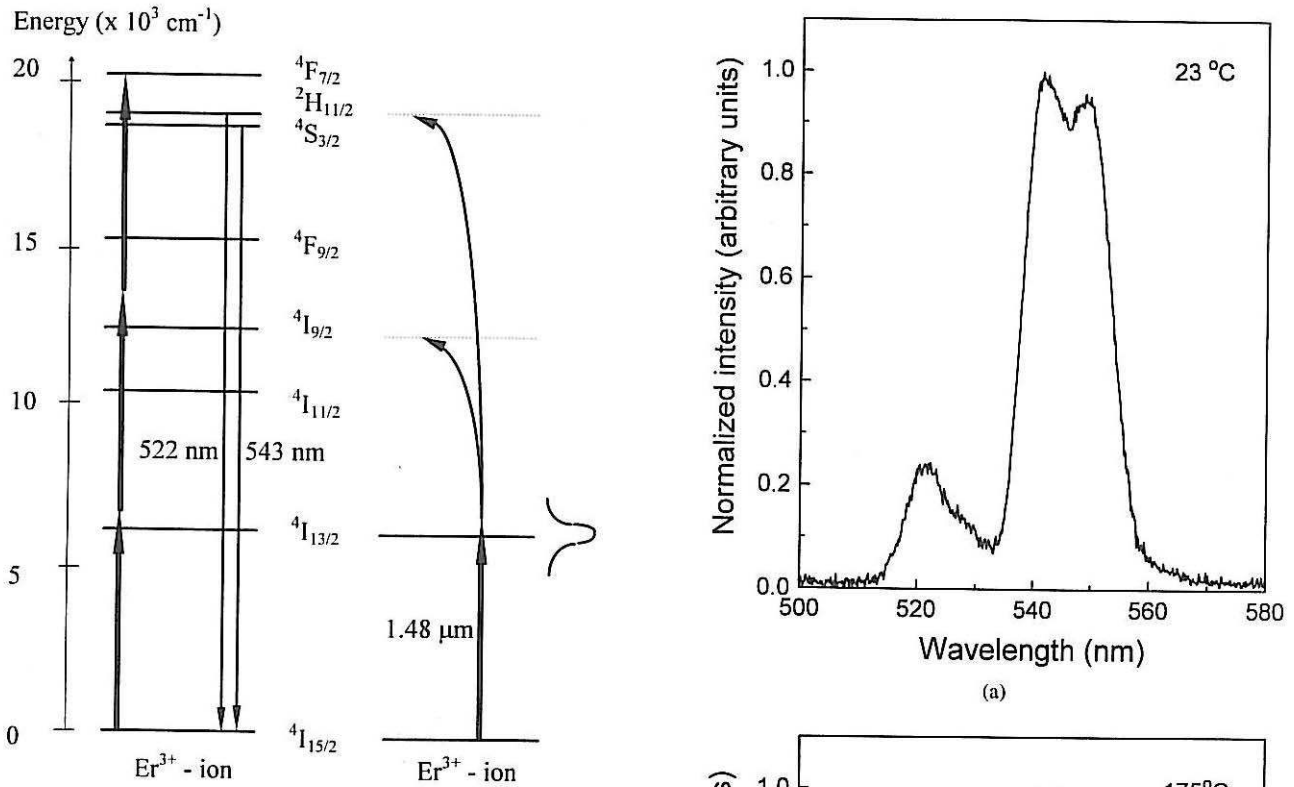


Fig. 1. Simplified energy levels scheme of Er<sup>3+</sup>. The downwards arrows indicate the upconverted fluorescence and the curved arrows on the right side stand for energy transfer.

excited Er<sup>3+</sup> ions at that level will take one ion to the states <sup>2</sup>H<sub>11/2</sub> or <sup>4</sup>S<sub>3/2</sub>. The energy transfer can be resonant or nonresonant with phonon emission or absorption compensating the energy mismatch. Afterwards, radiative transitions to the ground state give rise to the observed green fluorescence at ≈522 nm (<sup>2</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub>) and ≈543 nm (<sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub>). The temperature behavior observed is consistent with previous reports for fluorozirconate glasses [12]. Because of the small energy gap (≈750 cm<sup>-1</sup>) between the levels <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub>, the state <sup>2</sup>H<sub>11/2</sub> may also be populated from <sup>4</sup>S<sub>3/2</sub> by thermal excitation and a quasithermal equilibrium occurs between the two levels. As a consequence of the quasithermal equilibrium, the ratio of the two fluorescence intensities may be written as  $R = I_{522}/I_{543} = C \exp\{-\Delta E/kT\}$ , where  $\Delta E$  is the energy gap between the levels <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub>,  $k$  is the Boltzmann constant, and  $C$  is a parameter that depends on the levels lifetime and their electronic weight.

To determine the temperature behavior of the  $R$ -ratio under conditions similar to the ones required for a practical temperature sensor, the laser light was delivered to the glass sample through a single-mode-fiber. The fluorescence intensity was measured using an optical spectrum analyzer and for the signal capture the sample was butted to a two-meter-long multimode fiber. Thus, the temperature transducer was very compact. The behavior of the  $R$ -ratio is shown in Fig. 3 for the sample with  $x = 3$ . The exponential dependence of the  $R$ -ratio with temperature was asserted from the best fit presented in Fig. 3(a), which gives  $C = 11.2$  and  $\Delta E = 769$  cm<sup>-1</sup>.

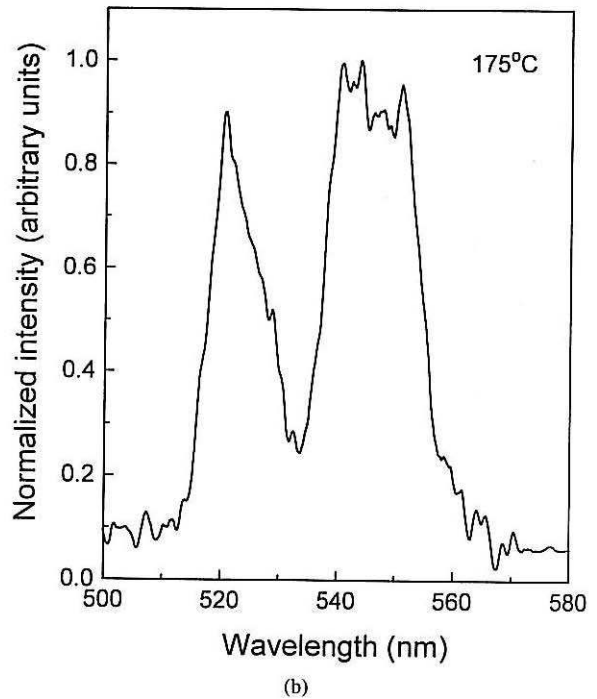
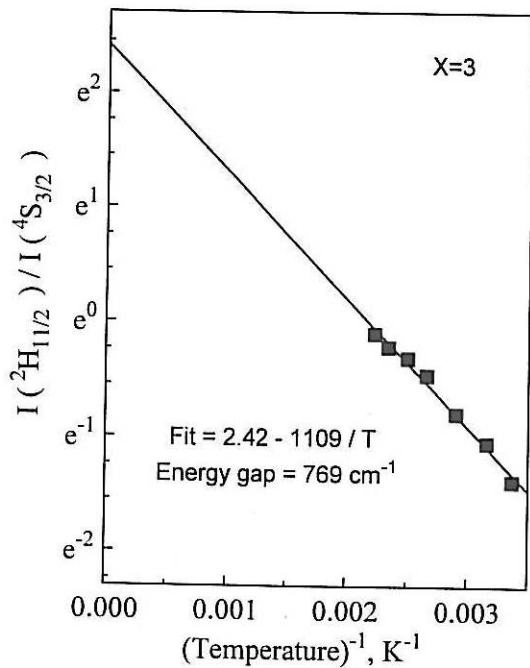
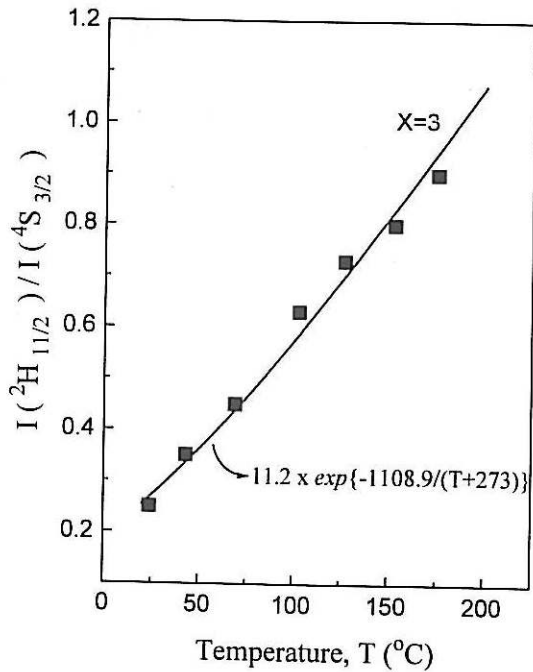


Fig. 2. Green upconverted fluorescence (normalized to the stronger line) corresponding to the transitions <sup>2</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub> (≈522 nm) and <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> (≈543 nm): (a) 23°C; (b) 175°C. Sample concentration:  $x = 3$ .

For the sample with  $x = 2$  we have obtained  $C = 7.39$  and  $\Delta E = 742$  cm<sup>-1</sup>. From the  $C$  values we obtain the ratio between the levels lifetimes  $\tau(^2H_{11/2})/\tau(^4S_{3/2}) = 2.36$ , and 3.59 for  $x = 2$ , and  $x = 3$ , respectively. The different values obtained are due to the dependence of the levels lifetime with the Er<sup>3+</sup> concentration [9]. From Fig. 3(b) we calculated the sensor sensitivity as 0.004/°C.



(a)



(b)

Fig. 3. (a) Logarithmic plot of the relative intensities of the transitions at 522 nm and 543 nm ( $I_{522}/I_{543}$ ) versus the inverse temperature; (b) Relative intensities versus the sample temperature. Sample concentration:  $x = 3$ .

The present results for the upconversion efficiency can be favorably improved if  $\text{Yb}^{3+}/\text{Er}^{3+}$  codoped samples are used.

Another important aspect to consider is the suitability of the fluoroindate glass to be fibered, and the possibility to use the doped fiber as the active sensing element.

Finally, we mention that a practical device will require a simple and inexpensive electronic circuit to process the ratio between the two signals instead of the elaborate circuitry used in the devices based on the analysis of decay-time temperature dependence. From the calculated sensor sensitivity, a precision  $\geq \pm 1^\circ\text{C}$  can be obtained if the electronic circuitry allows division with four digits or more. Moreover, the temperature sensor is insensitive to light intensity variations of the pumping source as well as possible fluctuations and losses of the optical signal during propagation through the addressing fiber coupled to the sensor.

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#### REFERENCES

- [1] K. T. V. Grattan and A. W. Palmer, "Infrared fluorescence decay-time temperature sensor," *Rev. Sci. Instrum.*, vol. 56, pp. 1764–1787, 1985.
- [2] M. C. Farries, M. E. Fermann, R. I. Laming, S. B. Poole, D. N. Payne, and A. P. Leach, "Distributed temperature sensor using  $\text{Nd}^{3+}$ -doped optical fiber," *Electron. Lett.*, vol. 22, pp. 418–419, 1986.
- [3] L. Scrivener, P. D. Maton, A. P. Appleyard, and E. J. Tarbox, "Fabrication and properties of large core, high NA, high  $\text{Nd}^{3+}$  content multimode optical fibers for temperature sensor applications," *Electron. Lett.*, vol. 26, pp. 872–873, 1990.
- [4] W. Quoi, R. A. Lieberman, L. G. Cohen, D. J. Shenk, and J. R. Simpson, "Rare-earth doped optical fibers for temperature sensing," *J. Lightwave Technol.*, vol. 10, pp. 847–852, 1992.
- [5] F. Wysocki, M. J. F. Digonnet, B. Y. Kim, and H. J. Shaw, "Characteristic of erbium-doped superfluorescent fiber sources for interferometric sensor applications," *J. Lightwave Technol.*, vol. 12, pp. 550–558, 1994.
- [6] H. Berthou and C. K. Jorgensen, "Optical fiber temperature sensor based on upconversion-excited fluorescence," *Opt. Lett.*, vol. 15, pp. 1100–1102, 1990.
- [7] Y. Messaddeq, A. Delben, M. Boscolo, M. A. Aegerter, A. Soufiane, and M. Poulain, "New fluoroindate glass compositions," *J. Non-Crystall. Solids*, vol. 161, pp. 210–212, 1993.
- [8] R. M. Almeida, J. C. Pereira, Y. Messaddeq, and M. A. Aegerter, "Vibration spectra and structure of fluoroindate glass," *J. Non-Crystall. Solids*, vol. 161, pp. 105–108, 1993.
- [9] R. Reiche, L. A. O. Nunes, C. C. Carvalho, Y. Messaddeq, and M. A. Aegerter, "Blue and green upconversion in  $\text{Er}^{3+}$ -doped fluoroindate glasses," *Solid State Commun.*, vol. 85, pp. 773–777, 1993.
- [10] L. E. E. de Araújo, A. S. L. Gomes, Cid B. de Araújo, Y. Messaddeq, A. Florez, and M. A. Aegerter, "Frequency upconversion of orange light into blue light in  $\text{Pr}^{3+}$ -doped fluoroindate glasses," *Phys. Rev. B*, vol. 50, pp. 16219–16223, 1994.
- [11] Cid B. de Araújo, L. de S. Menezes, L. H. Acioli, A. S. L. Gomes, Y. Messaddeq, A. Florez, and M. A. Aegerter, "Infrared-to-visible CW frequency upconversion in  $\text{Er}^{3+}$ -doped fluoroindate glasses," to be published.
- [12] D. Shinn, W. A. Sibley, M. G. Drexhage, and R. N. Brown, "Optical transitions of  $\text{Er}^{3+}$  ions in fluorozirconate glass," *Phys. Rev. B*, vol. 27, pp. 6635–6648, 1983.