Whispering gallery modes in a glass microsphere as a function of temperature

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Abstract: Microspheres of Nd^{3+} doped barium titano silicate glass were prepared and the whispering gallery mode resonances were observed in a modified confocal microscope. A bulk sample of the same glass was calibrated as temperature sensor by the fluorescence intensity ratio technique. After that, the microsphere was heated by laser irradiation process technique in the microscope and the surface temperature was estimated using the fluorescence intensity ratio. This temperature is correlated with the displacement of the whispering gallery mode peaks, showing an average red-shift of 10 pm/K in a wide range of surface temperatures varying from 300 K to 950K. The limit of resolution in temperature was estimated for the fluorescence intensity ratio and the whispering gallery mode displacement, showing an improvement of an order of magnitude for the second method.

OCIS codes: (130.3990) Micro-optical devices; (230.5750) Resonators; (280.6780) Temperature.

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1. Introduction

Optical sensors are an area of strong interest for applications. Conventional solid state temperature sensors are mainly based in thermoelectric materials like thermistors and thermocouples, the goal of optical sensors has significant advantages compared to them in terms of their properties like electrical passiveness, greater sensitivity, freedom from electromagnetic interference, wide dynamic range, point and distributed configurations and multiplexing capabilities [1]. Generally, accordingly to which property of the light beam changes when interacts with the optical sensors, they can be classified in two groups: interferometers in which optical phase is affected and intensity based devices in which optical intensity is modulated.

In the past decades, a number of optical temperature sensors have been presented and are principally based on the fluorescence intensity ratio (FIR) technique [1–11]. In this method, the fluorescence intensities of two closely spaced energy levels are recorded as a function of the temperature in order to be analyzed in a simple three-level system.

On the other hand, a group of optical micro-systems that presents morphology dependent resonances, known as Whispering Gallery Modes (WGM) micro-resonators, has been recently proposed and studied as temperature sensors in the interferometric category [12–17]. In these sensors, a microstructure made of a transparent dielectric of higher refractive index than the surrounding media (to generate total internal reflection) acts as resonant cavity. Experimentally in this work, sharp peaks corresponding to the resonances can be observed superimposed to the fluorescence emissions of Nd^{3+} ions. Any change in the temperature inside the micro-cavity causes a shift in the wavelength of the resonances.

Therefore, in the present study both techniques are combined to study the viability as temperature sensors of micro-sphere type resonators made of Nd^{3+} doped barium titano-silicate (BTS) glass. This is a glass with high refractive index and high melting point. Moreover, the BTS glass produces transparent glass-ceramic by thermal treatment [18,19] where the glassy and nanocrystalline phases are present; this property can be useful in future developments. One remarkable advantage of the microspheres reported is that due to their fabrication method they are not coupled to fibers or substrates, a fact that avoids geometrical irregularities that can affect to the WGM. Moreover the detection can take place remotely without the need of coupling the modes to a waveguide. As a result, the proposed technique allows to measure inside physical systems with a small perturbation by just introducing the microsphere and detecting a few centimeters away.

FIR measurements depend only of the temperature and the host matrix of the ions and so can be correlated very easily with the temperature of the glass. In the paper by Ma et al [14], a thermal insulated cell and a thermocouple near the microsphere was used is a small temperature range (297-310 K). However in the range of temperatures studied in this work (300-950 K), the FIR (although it is not a direct method as used by Ma et al [14]) is the only method that can ensure that the temperature is correctly estimated without air convection or other problems associated with our non coupled set-up. Thereafter it is possible to calibrate the WGM as function of the FIR and thus as function of temperature of the air-microsphere interface even when the variations of refractive index and radius of the glass with temperature are unknown.

2. Theoretical models

The FIR technique is a widely studied technique [1–11] where the relative luminescence of two radiative transitions is studied. One transition is between the electronic energy levels E_2 to E_1 and the other transition is from E_3 to E_1 (See Fig. 1a).

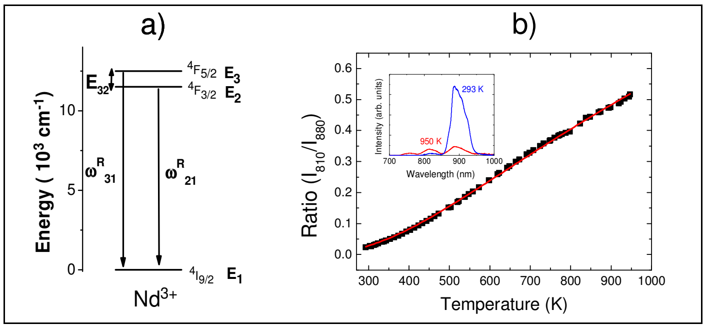

Fig. 1. a) Simplified scheme of Nd^{3+} energy levels involved in the experiment. b) Experimental values for the ratio of the intensities obtained with the emission spectra of the Nd^{3+}:BTS doped sample inside an electrical furnace (squares) and fit curve to Eq. (1) as described in text (red line). The inset in Fig. 1b shows the spectra obtained at RT and 950 K.

The small energy gap between the two close electronic levels E_2 and E_3 allows populating the upper level from the lower level by thermal excitation. The ratio of these intensities is independent of the source power intensity, since it is proportional to the population of each level involved. The relative population between the two levels, R, follows a Boltzmann-type population distribution given by [8,9]:

$$R = \frac{I_{31}}{I_{21}} = \frac{\omega_{31}^{R} g_3 h\nu_3}{\omega_{21}^{R} g_2 h\nu_2} \exp\left(\frac{-E_{32}}{KT}\right) = C \exp\left(\frac{-E_{32}}{KT}\right) \qquad (1)$$

where K is the Boltzmann constant, E_{32} is the energy gap between these two excited levels, g_3 and g_2 are the degeneracies $(2J+1)$ of the levels and ω^{R}_{31} and ω^{R}_{21} are the spontaneous emission rates of the E_3 and E_2 levels to the E_1 level, respectively.

Regarding the WGM micro-resonators, the resonance condition of a given resonance in the wavelength λ is approximately described by the following equation [15]

$$\lambda = \frac{2\pi n r}{l} \qquad (2)$$

where n is the refractive index and r is the radius of the sphere, l is the polar mode number that is the number of wavelengths that fits into the resonator. This geometrical approximation is valid only for high values of l [13].

One common parameter on optical temperature sensors is the “sensitivity” (S), defined as the variation of the measured parameter (MP) with the temperature.

$$S = \frac{1}{MP}\frac{d\,MP}{dT} \tag{3}$$

Using this definition, it is straightforward to obtain the sensitivities of the FIR and WGM displacement that are respectively,

$$S_{FIR} = \frac{\delta R}{R\ \delta T} = \frac{E_{32}}{kT^2} \tag{4}$$

$$S_{WGM} = \frac{\delta\lambda}{\lambda\ \delta T} = \left(\frac{1}{n}\frac{\delta n}{\delta T} + \frac{1}{r}\frac{\delta r}{\delta T}\right) \tag{5}$$

Many lanthanide ions are feasible for FIR experiments. As example, the Nd^{3+} ions used in the systems studied in this work are good candidates for the FIR technique [1,10,20]. These ions have many upper levels (not shown in Fig. 1) that can be easily excited by common lasers lines as green lines of Ar^+ or 532 nm line of doubled Nd^{3+} lasers. From these levels the nonradiative relaxation processes populate the $^4F_{5/2}$ and $^4F_{3/2}$ close levels.

Moreover, the temperature resolution ΔT_{min} in both methods can be estimated by [14]

$$\Delta T_{min} = \frac{\Delta MP_{min}}{MP\ S} \tag{6}$$

where ΔMP_{min} is the limit of detection of the measured parameter in each technique.

3. Experimental

A glass with the composition of 40%BaO–20%TiO_2–40%SiO_2 and doped with 1.5% of Nd_2O_3 (in the molar ratio) was prepared using a conventional melt-quenching method. Commercial powders of ACS reagent grade (purity ≥99.9%) $BaCO_3$, TiO_2, SiO_2, and Nd_2O_3 were mixed and melted in a platinum-rhodium crucible at 1500 °C for 1 hour in an electric furnace. After that, the melt was poured between two bronze plates. Obtaining a bulk glass from which microspheres have been made.

Microspheres can be made by different methods; these ones include polishing, chemical etching and rapid quenching of liquid droplets [21,22]. In this letter, the microspheres are fabricated by the method exposed by Gregor R. Elliott et al. [22] from the glass mentioned above. Using this technique, microspheres of diameters ranging from 5 µm to 100 µm can be obtained.

The BTS microsphere and bulk samples were excited with a commercial continuous wave 532 nm Diode Pumped Solid State laser. The Nd^{3+}: $^4F_{5/2}\rightarrow{}^4I_{9/2}$ (810 nm) and $^4F_{3/2}\rightarrow{}^4I_{9/2}$ (880 nm) transitions were recorded using a CCD spectrograph.

The spectral measurements to compute the FIR, were performed by placing the BTS bulk glass sample inside an electric furnace to increase the temperature from room temperature to 950 K at a rate of 2 K/min.

Microsphere measurements were carried out in a modified confocal microscope. In this set-up the excitation zone can be shifted from the detecting zone (with a volume about 1 μm^3) by moving the detection pinhole. In the configuration used, the laser pumping zone was the center of the microsphere and the detection zone was the sphere-air lateral interface as described in a previous work [23] which is schematized in the inset of Fig. 2. In this configuration it is obtained the best visibility of the resonances, measure the FIR on the surface and heat up the microsphere.

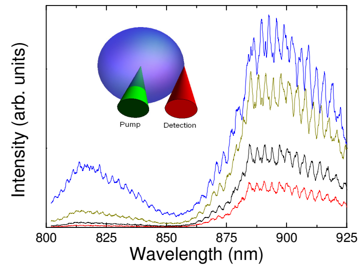

Fig. 2. WGM resonances superimposed to Nd^{3+}: $^4F_{5/2}\rightarrow{}^4I_{9/2}$ (810 nm) and $^4F_{3/2}\rightarrow{}^4I_{9/2}$ (880 nm) transitions at different pump powers (power increases from red to blue spectrum). The inset is a schematic view of pumping and detecting geometry of the experiment.

In our experiment, while the polar mode number l is in the order of 300 [23] so the geometrical approximation is applicable, Eq. (3) is not fully satisfied because the temperature of the microsphere is non homogeneous due to the laser heating nature. As the microsphere is heated by the pumping laser, the heating is non-homogeneous yielding a temperature gradient from high temperature in the centre to low temperature in the surface of the sphere.

4. Results and discussion

From spectral measurements completed in the bulk sample inside an electric furnace, the areas of the emission bands associated to the $^4F_{5/2}\rightarrow{}^4I_{9/2}$ (810 nm) and $^4F_{3/2}\rightarrow{}^4I_{9/2}$ (880 nm) transitions are obtained and fitted to Eq. (1) giving a value of 887 cm^{-1} for the energy gap E_{32} and a pre-exponential parameter C with a value of 1.982. The experimental values and the fit curve are shown in Fig. 1b. The E_{32} energy gap value is similar to the one obtained from absorption spectrum, that is 944 cm^{-1} which is also in good agreement with other Nd^{3+} doped matrices [19,24–26]. This calibration will be employed to estimate the temperature of the microsphere surface in the laser heating process.

In Fig. 2 it is shown the spectra of the microsphere during the heating process with the laser, the WGM peaks are superimposed to the emission bands associated to the $^4F_{5/2}\rightarrow{}^4I_{9/2}$ and $^4F_{3/2}\rightarrow{}^4I_{9/2}$ transitions of Nd^{3+}. Under the assumption of that the WGM peaks do not modify in a significant way the overall area of the Nd^{3+} emission bands, it is possible to compute the temperature of the surface by the FIR method. This dependence of the wavelength of several WGM peaks with the surface temperature is displayed in Fig. 3. It is observed that the wavelength of the WGM peaks have a monotonic increase behavior with the surface temperature in agreement with the Eq. (5) and previous works [14]. This fact is due to the BTS as many other optical materials have positive coefficients for $\delta n/\delta T$ and $\delta r/\delta T$.

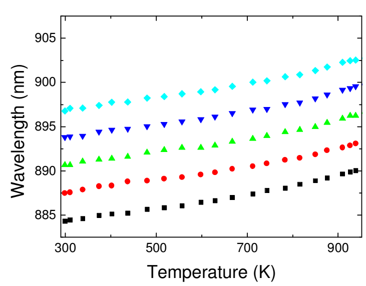

Fig. 3. Plot of the wavelength of five resonance peaks related to the surface temperature by the FIR technique.

When the surface temperature increases until 950 K, the WGM peaks experiences a wavelength increase of 7 nm. As consequence, the estimated variation of the wavelength results an average 10 pm/K shift in our BTS glass, which is similar to 11 pm/K observed at room temperatures in silica microspheres [17].

In Fig. 4, it is shown the temperature resolution ΔT_{min}, computed as described in Eq. (6) for the FIR and WGM displacement. The estimated WGM displacement temperature resolution of a homogeneous heated fused silica microsphere is also shown evaluated using Eqs. (5) and (6) with equal radius to the measured microsphere (30 μm) and constant parameters $\delta n/\delta T = 1.28\text{x}10^{-5}$/K and $\delta r/\delta T = 5.5\text{x}10^{-7}$/K obtained from literature [27]. As can be seen in this figure, the temperature resolution obtained in this work with the BTS microsphere is similar to the calculated values for a silica microsphere.

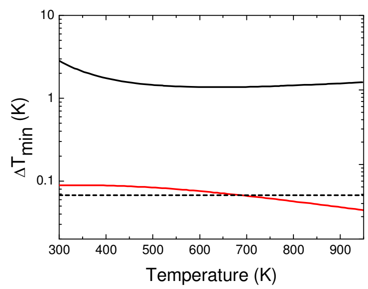

Fig. 4. Temperature resolutions for the FIR technique in the glass (solid line), WGM displacements in the measured microsphere (red line) and the calculated ones for a homogeneous heated fused silica microsphere (dashed line).

The FIR sensitivity of the Nd^{3+} ions in the BTS glass can be calculated by Eq. (3) and it reaches a maximum of 0.01 in the measured range which is similar to the sensitivity of FIR technique achieved in other host glasses [1,10]. This yields a temperature resolution about 1 K using Eq. (6) and an estimated error of 5%. This error is due to the inaccuracy of the areas due to the overlap between the thermalized bands.

On the other hand, in the WGM the limit of detection of the displacements is about 0.01% of the line-width of the resonances [28]. Therefore, the achievable resolution limit on temperature is about 0.1 K (independently of the calibration technique) that probes an increase near one order of magnitude in the detection limits respect to the FIR technique. However, using a narrow line tunable laser or a high resolution spectrograph, the resolutions obtained can be as high as [14] and [17] specifies.

The conjunction of both techniques, allows a coarse temperature estimation by the FIR and a fine temperature estimation by the WGM and avoid the penalty that can be caused by rapid heating cooling proceses, where a incorrect temperature sampling can lead to a jump in the WGM peak.

5. Conclusions

Microspheres made from Nd^{3+} doped BTS glass were prepared, and the WGM resonances were observed in a modified confocal microscope. A bulk sample of the Nd^{3+}:BTS glass was used to calibrate as temperature sensor by the FIR technique. The microsphere was heated by laser irradiation process and the surface temperature was computed using the FIR technique. This temperature is correlated to WGM peak displacement, showing an average red-shift of 10 pm/K. The limit of resolution on temperature measurements was estimated about 1 K for the FIR technique and about 0.1 K for the WGM shift technique.

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