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Liquid whispering-gallery-mode resonator as a humidity sensor

LUCÍA LABRADOR-PÁEZ,[1,2] KEVIN SOLER-CARRACEDO,[1] MIGUEL HERNÁNDEZ-RODRÍGUEZ,[1] INOCENCIO R. MARTÍN,[1,3] TAL CARMON,[4] AND LEOPOLDO L. MARTIN [4,5,*]

[1]*Departamento de Física, Universidad de La Laguna, La Laguna, S. C. Tenerife 38206, Spain*
[2]*Fluorescence Imaging Group, Departamento de Física de Materiales, Universidad Autónoma de Madrid, Madrid 28049, Spain*
[3]*MALTA Consolider Team and Instituto de Materiales y Nanotecnología (IMN), Universidad de La Laguna, La Laguna, S. C. Tenerife 38200, Spain*
[4]*Mechanical Engineering, Technion - Israel Institute of Technology, Haifa, 32000, Israel*
[5]*Fundación Galileo Galilei –INAF, Rambla José Ana Fernández Pérez 7, Breña Baja, S. C. Tenerife 38712, Spain*
**llmartin@tx.technion.ac.il*

Abstract: We experimentally demonstrate the high sensitivity of a novel liquid state, whispering-gallery-mode optical resonator to humidity changes. The optical resonator used consists of a droplet made of glycerol, a transparent liquid that enables high optical quality factor, doped with fluorescent material. As glycerol is highly hygroscopic, the refractive index and radius of the droplet change with ambient humidity. This produces a shift on the whispering gallery mode's wavelengths, which modulates the emission of the fluorescent material. This device shows an unpreceded sensitivity of 10^{-3} per relative humidity percent.

OCIS codes: (140.3948) Microcavity devices; (280.4788) Optical sensing and sensors; (160.2750) Glass and other amorphous materials.

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1. Introduction

While solid resonators were widely investigated, the pioneering research in optical Whispering-Gallery-Mode (WGM) resonators started with falling liquid droplets [1, 2], pumped by pulsed lasers. Recent progress in passive droplet resonators interrogated by continuous wave lasers [3–5] allowed observation of narrow and stable optical resonances. Therefore, we can benefit from the inherent differences of liquid resonators to improve the sensing capabilities. Ambient humidity sensing, unlike temperature or pressure, requires not only a physical change in the sensor itself, but also the diffusion of water molecules inside the sensor material and since the diffusion coefficient of water in miscible liquids is orders of magnitude larger than in silica, liquid droplets are excellent candidates to develop Relative Humidity (RH) sensors. RH is the most commonly used parameter to quantify ambient humidity, and is defined as the percentage of water vapor present in air over the amount of water vapor needed to saturate an equal volume of air at a given temperature [6]. Furthermore, the control of RH is extremely important in many industrial processes and scientific experiments. For that reason, many devices have been proposed in order to satisfy these requirements [6, 7].

Whispering gallery mode sensors consist of optical microcavities made out of a transparent material of refractive index higher than their surroundings, hence light is confined by total internal reflection with minimal losses, due to the natural smooth surface of the liquids; therefore the surface scattering losses are negligible and high optical quality factors (Q) are achieved [3–5, 8–10]When the refractive index and/or the radius of the optical resonator changes, the resonant wavelengths are shifted. Taking advantage of this fact, WGM optical sensors are commonly used as ambient conditions sensors [11–13].

Most WGM sensors consist of solid resonators [14]. To the best of our knowledge, there is only one preceding work concerning passive liquid resonators used as optical WGM sensors, where the WGM sensor was used to verify the chemical purity of diverse oils [3]. In liquid resonators, there is full interaction between the substance to be sensed (water, in our

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case) and the circulating light. As a result, the sensitivity of the WGM optical sensors is higher than on solid resonators, in which only the evanescent tail of the optical modes (about 1% of the energy) interacts with the outer medium. Moreover, this type of sensors is expected to show excellent sensitivity at all RH ranges including the extremes of RH (0-10% and 90-100%), where most sensors perform poorly [7, 15].

In most cases, optical humidity sensors give as output parameter the variation of power registered at the exit of an optical fiber or waveguide optically coupled to the resonator [6, 16]. For instance, Zhang et al. have demonstrated the use of non-resonating hydrogel spheres coupled to an optical fiber core as RH optical sensor, due to the fact that the refractive index of hydrogel changes with the ambient humidity, the light is scattered out from the core of the fiber in a different amount and, consequently, the tapered fiber transmittance changes [16]. In a similar way, the spectral displacement of WGMs can be observed as a function of humidity in nanoparticle coated solid resonators, where a layer of water is adsorbed by analyzing the transmittance of a tapered fiber evanescently coupled to the resonator, in which, only 0.5% of the circulating light interacts with the water in the outer layer [17]. This technique, in addition, has two drawbacks: it requires a tunable narrow-line laser and a tapper fiber whose transmission decays when exposed to humidity in matter of hours or days [18]. By using fluorescent doping of liquid resonators, however, we enable direct observation of WGMs without coupling to a tapered optical fiber and using a simple multimode laser for the fluorescent dopant excitation, which simplifies the measurement process, although a spectral device such a CCD spectrograph is required.

2. Experimental

The material used for the liquid WGM fabrication, should be transparent in the excitation and emission wavelengths of the fluorescent dopant and show volumetric and refractive index changes with the RH along a wide range of RH, as well as stable properties in time and temperature, and in presence of chemical species existing in air [6]. In this work, glycerol (also known as glycerin) has been chosen because this polyalcohol is hygroscopic, that is, it attracts and absorbs water from the surrounding environment forming a stable solution. Moreover, this material is non-toxic, water-soluble, stable, viscous, and compatible with many other compounds [19]. As fluorescent material, we used a common laser dye (rhodamine 6G) but any other fluorescent material as: transparent nanocrystals, other dyes or quantum dots could be used. Glycerol was mixed with a solution of rhodamine 6G in methanol (3 10-4 mol/l as typical in pulsed dye lasers) in a ratio of 1 part of rhodamine solution in 9 parts of glycerol. In order to observe the shifts in the wavelength of the WGMs overlapped in the emission spectrum of this dye, due to the well-known Purcell effect [20], which produces an increase in the emission at the resonant wavelengths. Using a similar technique, spectral tuning of glycerol-water-rhodamine B resonators has been already demonstrated, by electrical excitation [21].

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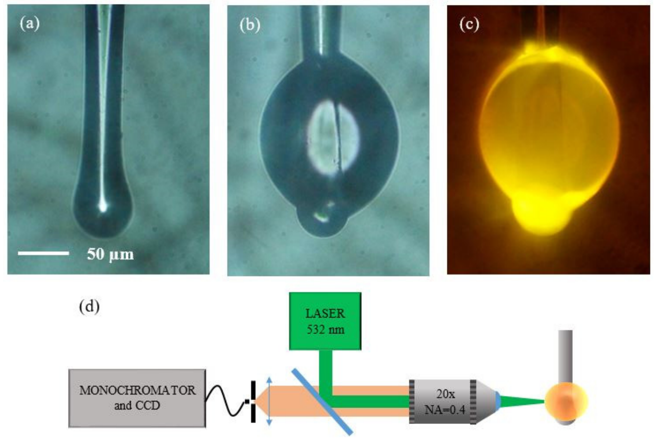

Fig. 1. (a) Optical image of the modified optical fiber, (b) optical image of the liquid resonator made in the tip of the modified optical fiber, (c) optical image of the liquid resonator under excitation at 532 nm, and (d) schematic representation of the confocal microscope.

The liquid resonator characterized in this work, consists of a 160 µm droplet of glycerol and rhodamine 6G (with a 90% by weight of glycerol) formed in the tip of a modified optical fiber, which is made by heating the end of a tapered optical fiber until it is slightly melted, so that superficial tension acts modifying its shape (see Fig. 1(a)). This facilitates the formation of the droplet once the modified optical fiber is dipped into the liquid and also enhances its stability since silica is hydrophilic and the droplet resonator trends to move to thicker parts of the tapered fiber, when is not terminated as a sphere [22]. The presence of the optical fiber used to generate and manipulate the droplet originated slight deformations in the spherical form expected for the resonator (see Fig. 1(b)) that had no significant influence on the resonances [3].

The sensor was calibrated for the usual ambient RH range (approx. from 40% to 65% RH). The process was executed without any special insulation of the resonator and at room temperature, which was kept constant within 2 K. Given the large area to volume ratio of the microresonators we assume that the resonator's and ambient temperatures are identical and any heating of the glycerin by water dilution is negligible. Before the calibration started, the ambient RH was lowered slightly below 40% RH. Then, during the process, a controlled and steady increase of ambient moisture was held until 65% RH was reached. Meanwhile, the ambient RH was measured using an electronic RH meter with a resolution of 0.5% RH. At the same time, a set of measurements of the spectra of rhodamine 6G in the range from 550 to 650 nm were taken with a confocal microscope (spectral resolution 0.3 nm; spacial resolution 0.7 µm) and pumping the rhodamine 6G at 532 nm with a commercial continuous wave solid state laser (see Fig. 1(d)) [12] about 3 mW to minimize the heating and the photobleaching of the dye, this issue is inherent to dyes and can be avoided in other fluorescent materials as nanoparticles or quantum dots.

3. Results and discussion

In order to calibrate the droplet resonator as RH sensor, the emission of the rhodamine 6G had to be recorded (see the liquid resonator emitting in Fig. 1(c)). An emission spectrum of the droplet resonator under excitation at 532 nm is plotted in Fig. 2(a). As expected, the emission band of rhodamine 6G (centered approximately at 600 nm) is modulated by the sharp peaks of the WGMs in the resonator.

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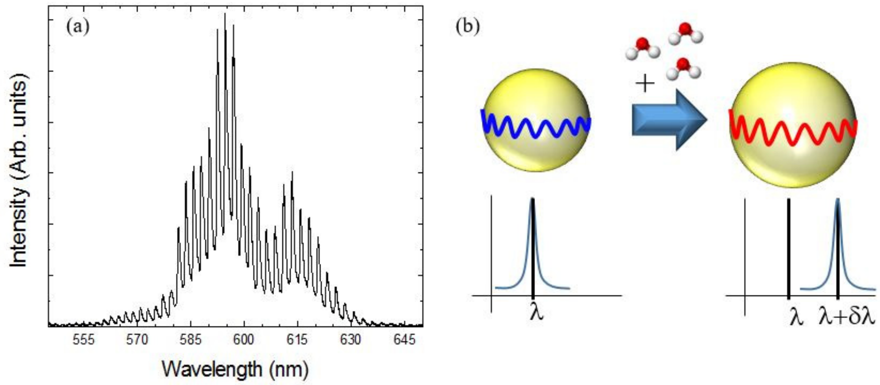

Fig. 2. (a) Emission spectrum of rhodamine 6G present in the droplet resonator, where WGMs modulate the emission, at 45% RH. (b) Scheme of the WGM shift due to water absorption in the drop.

In WGM resonators, the resonant wavelengths follow the following relation:

$$m\lambda = 2\pi R\ n_{eff} \tag{1}$$

Where an integer number m of resonant wavelengths λ, fits the circular optical path length in the resonator, which depends on its effective refractive index n_{eff} and size 2πR, being R the radius. Therefore, the shift in the wavelengths of the WGMs is a consequence of the change in the refractive index of the resonator as the glycerol absorbs/desorbs water from/to ambient depending on the RH. This effect effectively increases/decreases the radius of the droplet (the more water absorbed, the larger is the radius) and consequently decreasing/increasing the refractive index (because the refractive index of water is lower than that of glycerol) [19]. This behavior is depicted in Fig. 2(b). The observed Q in this work is about 10^3, this value is limited by our experimental set-up.

With this work we aim to demonstrate the capability of glycerol doped with rhodamine 6G liquid WGM optical resonators as RH sensors using, for the first time, liquid resonators as ambient conditions sensors.

The wavelength of the most intense peak of the rhodamine 6G emission, located in 595 nm at 45% RH (see Fig. 2), was followed as the ambient RH was being slowly increased. As a result, the calibration shown in Fig. 3 was obtained. A common figure of merit is sensitivity, S, defined for this particular sensor according to Eq. (2) as the displacement of the wavelengths of the WGMs per RH percentage, relative to the wavelength value. Therefore, this value can be obtained as,

$$S = \frac{1}{\lambda}\frac{\delta\lambda}{\delta RH} \tag{2}$$

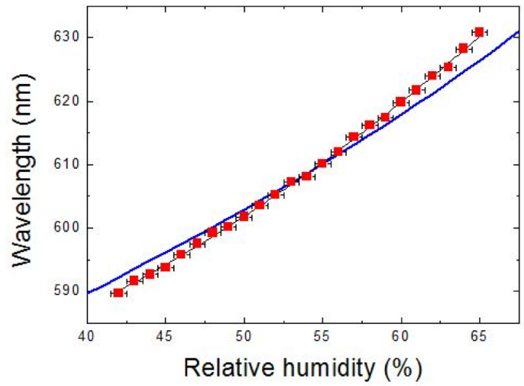

Fig. 3. Calibration of the variation of the wavelength of a WGM peak with increasing RH (red squares) obtained from emission spectra of rhodamine 6G (see Fig. 2), its fit to a quadratic polynomial (black line), and estimation of the displacement of the wavelength of the WGM peak from the expected variation of the refractive index and the radius of the resonator with RH (blue line).

As plotted in Fig. 4(a) with a red line, the sensitivity of the calibrated droplet WGM sensor increases with RH, with a mean value about $2.8 \cdot 10^{-3\%}$ RH^{-1}. Other WGM resonators acting as RH sensors have achieved sensitivities of $2 \cdot 10^{-4\%}$ RH^{-1}, as did Zhang et al. using tubular hybrid optical microcavities [23]. Consequently, it can be said that, to the best of our knowledge, the droplet WGM sensor is one order of magnitude more sensitive to RH change than prior works with solid WGM RH sensors.

The relative displacement of the resonances can be estimated from experimental data obtained in thermodynamical and optical studies of glycerol showing the equilibrium of the glycerol + water concentration for a given ambient RH and the refractive index of glycerol + water solutions for a given concentration of glycerol [19], for the same conditions of radius (80 µm) and wavelength of the experimentally studied resonator, and assuming that only a small volume of the drop is occupied by the silica stem. The hygroscopicity of glycerol produces an increase in the radius and a decrease in its refractive index with the rise of the RH, due to the incorporation of water, which has lower refractive index than glycerol, from the ambient moisture to the drop. As a result of this, the sensitivity of the displacement of the wavelengths of the WGMs with the RH depends on these parameters, as expressed in Eq. (1), and therefore has two components, that can be obtained from Eq. (2) resulting in the following:

$$S = S_{Radius} + S_{Refractive\ index} = \frac{1}{\lambda}\left(\frac{1}{R}\frac{\delta R}{\delta RH} + \frac{1}{n_{eff}}\frac{\delta n_{eff}}{\delta RH}\right) \tag{3}$$

where R is the radius and n_{eff} the effective refractive index of the droplet resonator. The estimated sensitivity was found to be in good agreement with the result obtained from the experimental calibration, with a mean value of $S = 2.5 \cdot 10^{-3\%}$ RH^{-1}, as shown in Fig. 4(a) with a blue continuous line. The estimated sensitivities of the two variable parameters (refractive index and radius) obtained from Eq. (3) and the data obtained from literature [19] that includes the volumetric ratio of glycerol and water for a range of RH from where the volumetric expansion can be inferred and the refractive index of the glycerol-water mixtures from where the refractive index at each RH can be inferred. Both sensitivities are plotted individually in Fig. 4(a), with a blue dotted line for S_{Radius}, the sensitivity of the increase of the radius of the droplet with the RH, and a blue dashed line for $S_{Refractive\ index}$, the sensitivity of the decrease of the refractive index of the liquid resonator with RH. From this, the displacement of the wavelength of the WGM peak has been estimated in order to compare it with the experimental data of the calibration in Fig. 3.

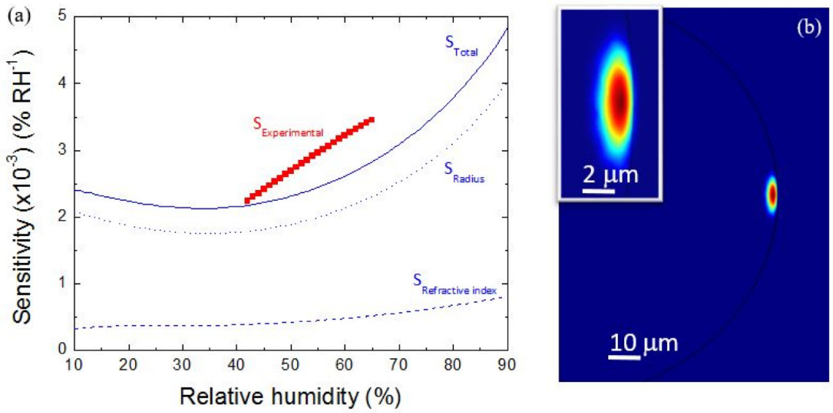

Fig. 4. (a) Sensitivity of the displacement of the wavelengths of the WGMs calculated from the experimental data from the calibration using Eq. (1) ($S_{Experimental}$, red squares) and from the estimation (S_{Total}, blue continuous line) of the sensitivity of the decrease of the refractive index ($S_{Refractive\ index}$, blue dashed line) and the sensitivity of the increase of the radius of the resonator (S_{Radius}, blue dotted line). (b) Numerical simulation of the first radial optical mode in a spherical droplet.

Given the underlying principles for this kind of sensor, there is no saturation in the extremes of the range of RH, as can be seen in the sensitivity (Fig. 4(a)). At low RH, the shift of the resonant wavelength is small, but, according to Eq. (2) the sensitivity is nonzero even at very low RH. At high RH, the shift of the resonant wavelength is large, since the radius changes very fast due to the high amount of water that is being incorporated to the drop, so sensitivity also increases. The difference between calculated and experimentally measured sensitivity is within the experimental error, furthermore it should be noted that the calculated sensitivity is based on experimental volumetric measurements for the glycerol-water mixture at different RH [19] and refractive index at different glycerol-water concentrations [19] being susceptible to errors. Besides that, the order of magnitude is correct.

Another parameter that could characterize the performance of the sensor is the resolution or limit of detection, that is, the magnitude of the minimum change in ambient RH that could be transduced, which can be calculated by means of Eq. (3),

$$\Delta RH_{\min} = \frac{\Delta \lambda_{\min}}{\dfrac{d\lambda}{dRH}} \qquad (4)$$

The common spectral shift sensitivity is about 1% of the full width at half maximum of the WGM peaks [17, 24]. According to this, Ma et al. estimated for a coated silica microsphere acting as WGM RH sensor a detection limit of $3\cdot 10^{-3\%}$ RH [17]. However, quality factors of at least $Q = \lambda / \Delta\lambda_{\min} = 5\ 10^{5}$ have already been experimentally demonstrated in liquid optical WGM resonators [3]. Having these facts into account in Eq. (4), the droplet WGM RH sensor is expected to resolve a shift of $7\cdot 10^{-6\%}$ RH, under the ideal condition of constant temperature and using $Q = 5\ 10^{5}$.

Regarding thermal stability it should be noted that we assume good thermal contact between the air and the resonator and that we kept the excitation laser at very low power, therefore we assume negligible change in the resonator's temperature and no WGM shift due to this effect. Moreover, unlike solid resonators, the photothermal coefficient of glycerol is

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negative [25], so the temperature shifts are not as large as could be expected given the large thermal volumetric expansion of glycerol.

About the dynamics of the process, the stabilization time can be estimated by using a random walk diffusion model given the diffusion coefficient, D, at room temperature and the penetration depth, x_p, which is reached in the stabilization time by the 68% of the molecules.

$$x_p = \sqrt{2\ D\ t} \tag{5}$$

The coefficient D at room temperature for water in silica is about 10^{-21} cm^2 s^{-1} [26] and for water in glycerol is about 10^{-5} cm^2 s^{-1} [27]. If the penetration depth is reduced to the depth of the WGMs in the drop, making the silica holder bigger in order to occupy the rest of the volume, the stabilization time could be drastically reduced (see Eq. (5)). As the amount of glycerol is severely reduced having the same resonator volume, less water would be included and no significant change of volume will happen. As a result of this, only refractive index changes will modify the WGM resonant wavelengths, although it would reduce the sensitivity of the device. In order to estimate the thinnest glycerol layer that can support WGMs in the glycerol without any light traveling inside the silica, a COMSOL simulation shown in Fig. 4(b) displays the spatial distribution of the optical field (first radial mode, azimuthal 1200) in a perfect sphere. As can be seen, all the mode is within 2 µm from the surface. Using this as penetration depth, the stabilization time becomes 2 ms. In this scenario, the sensitivity decreases to the one associated to the refractive index change, that as can be seen in Fig. 4(a) is about 10^{-2} per RH %, and lacks of significant volumetric change contribution, since this one depends on the amount of glycerol, that would be considerably reduced with this structure. In order to estimate the thinnest glycerol layer that can support WGMs in the glycerol without any light traveling inside the silica, a COMSOL simulation shown in Fig. 4(b) displays the spatial distribution of the optical field (first radial mode, azimuthal 1200) in a perfect sphere. As can be seen, all the mode is within 2 µm from the surface. Using this as penetration depth, the stabilization time becomes 2 ms. In this scenario, the sensitivity decreases to the one associated to the refractive index change, that as can be seen in Fig. 4(a) is about 10^{-2} per RH %, and lacks of significant volumetric change contribution, since this one depends on the amount of glycerol, that would be considerably reduced with this structure.

4. Conclusion

A liquid optical WGM droplet resonator made out of glycerol, a hygroscopic liquid, shows a dependence of the refractive index and the radius of the resonator on the ambient relative humidity. We support this evidence with experimental results and straight-forward models based on thermodynamical data of glycerol. Furthermore, a fluorescent material, rhodamine 6G is added to the resonator to enable non coupled observation of the WGM via Purcell effect. We estimate a sensitivity of the displacement of the resonant wavelengths with environmental humidity of $2.8\cdot10^{-3}$ per relative humidity %, and could achieve a resolution of $7\cdot10^{-6\%}$ of relative humidity under ideal condition of constant temperature and using Q factor of 10^5.

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