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Fiber Optic Temperature Sensor Based On Amplitude Modulation of Metallic and Semiconductor Nanoparticles in a Liquid Crystal Mixture

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***Abstract*—The response of an amplitude modulation temperature sensor based on a liquid crystal doped with either metallic or semiconductor nanoparticles has been theoretically analyzed. The effects of the concentration, the type of nanoparticle material and liquid crystal compound have been studied in detail. The high sensitivity of light resonances to refraction index changes, in collaboration with the high thermo-optic coefficients of liquid crystal materials, has resulted in the design of an optical fiber sensor with high temperature sensitivity. This sensitivity has been demonstrated to be dependent on nanoparticle concentration. A maximum theoretical sensitivity of 64•10-2 dB/ºC has been observed. Moreover the sensitivity is highly linear with a regression coefficient of 99.99%.**

***Index Terms*—Plasmons, optical fiber sensor, temperature sensors, nanoparticles, semiconductor nanostructures, liquid crystal.**

I. Introduction

TEMPERATURE sensing is one of the most demanding applications in the medicine and industry sector. The important influence of the temperature on common processes requires an accurate measurement of this physical parameter. Alongside precision, working conditions are some of the most important issues for the design of temperature sensors. For instance, typical temperature sensors, which work with electrical signals, are unsuitable for use in industrial processes where electromagnetic interferences are usually present; or in medical environments where the field strengths caused by some equipment can be very high, producing errors in metallic sensors. Optical fiber sensors have been used to solve these problems. Most fiber-optic techniques for temperature sensing are based on phase (coherent) or amplitude variations of a beam intensity (incoherent). Phase-based designs have been demonstrated by several works, for example, using interferometric configurations with sensitivities ranging from 0.01nm/ºC to 1.9nm/ºC [1] [2]. In a previous work, the authors proposed the use of the shift of plasmon resonances of metallic nanoparticles (NPs) as sensing element to achieve maximum sensitivities of 4nm/ºC [3]. Phase-based devices are highly sensitive. However, their most important drawback is that some of them are technologically complex to build. Moreover, they require conditioning circuitry or special equipment to measure the output signal (usually lambda shifts). On the other hand, amplitude-based devices use several physical phenomena such as light attenuation [4] or fluorescence [5]. Some of the most recent works on intensity sensors included a macrobend [6], fluorescence and glue [7], or a plastic optical fiber (POF) macrobend [8]. All of them have sensitivities around $3\cdot10^{-2}$ dB/ºC. In those studies, the temperature ranges are 20–73 ºC in POF fibers and 0–100 ºC in silica fibers.

In recent years, nematic liquid crystals (NLCs) have also been used in the temperature sensing field due to their interesting characteristics. NLCs are anisotropic materials whose optical properties could respond to an external stimulus [9]. In addition, it has been shown that their properties are also quite dependent on the temperature, through a high thermo-optic coefficient [10]. Taking advantage of this effect, NLCs are currently used in the design of new temperature sensors in Fabry-Perot systems [11], photonic crystal fibers [12] and chiral nematic polymer networks [13]. In addition, recent works have shown the possibility of performing stable and homogeneous mixtures of NLC and NPs (e.g. carbon nanotubes, gold NPs, etc.) [14]. Although these mixtures are mainly developed to produce controlled changes in the opto-electronic properties of NLC [15], they could also be used to modify the behavior of the NPs [16]. In particular, the interaction of light and metallic NPs (e.g. gold or silver) presents an interesting phenomenon; known as Localized Surface Plasmon Resonance (LSPR) [17]. This phenomenon,

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which produces a strong enhancement of both the absorption and scattering of the nanoparticle, is currently used for a wide range of sensors. This fact is possible due to the high dependence of the resonant frequency with any change of the surrounding medium [18]. This change could be produced by the presence of an analyte, as is the case of plasmon-based biosensors [19], or by an active medium, such as liquid crystals. Recently, it has also shown that semiconductor (SC) NPs, (e.g. silicon, germanium, etc.) present plasmon-like resonances and their use as a counterpart of plasmonic systems is currently being studied [20].

Joining the sensitivity of resonant phenomena to the refractive index of the surrounding medium and the high thermo-optic dependence of NLC, in this work we explore the effects of controlled changes of the external temperature on a light beam crossing a sample of an NLC doped with resonant NPs. In particular, the amplitude modulation of the beam and the resulting sensitivity of this response. In addition, we propose an optical fiber-based design for this sensor, looking for a cost-efficient and small device.

II. Operation Principle and Theoretical Background

Localized surface plasmon resonances (LSPRs) in metallic NPs are produced by a collective oscillation of the free electrons at the surface of the nanoparticle with the incident light, at a certain frequency. However, resonances of SC NPs are produced by a joint effect between the size and shape of the particles with respect to the incident wavelength and the contrast of the optical properties of the particle and the surrounding medium [20]. However, both phenomena produce an extraordinary enhancement of both the light absorption and scattering of the nanoparticle and could be studied in the same way. While absorption dominates in very-small particles (r<<λ), scattering dominates for larger particles (r<λ) [21]. Despite the dominant process, the incident beam is extinguished and could be studied through the analysis of the extinction cross section (Q_{ext}). This parameter can be expressed as a multipolar expansion given by [22]:

$$C_{ext} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1)\,\mathrm{Re}(a_n + b_n) \tag{1}$$

Where a_n and b_n are the scattering Mie coefficients, depending on the properties of both the nanoparticle and the surrounding medium. k is the light wavenumber. In the range of sub-wavelength particles, the multipolar expansion can be approximated by the dipolar and quadrupolar ($n=1, 2$) terms, higher orders being negligible [22]. The excitation of a resonance produces a peak in the spectral evolution of C_{ext}, at the resonant frequency. Variations of the main characteristics of the peak: spectral position, height and width; could be directly related to changes in the surroundings conditions [19].

On the other hand, NLCs are complex media composed of anisotropic particles, such as rods or organic molecules. This composition produces an uniaxial optical symmetry depending on the orientation between the electric field and the main direction of the components that is characterized through the director. The director responds to external stimulus such as an external electric-field or a thermal effect, changing the macroscopic optical properties of the NLC [9].

There are several works in the literature concerning the preparations and analysis of different mixtures of NLC and NPs, both metallic and SC NPs. These works reported the possibility to obtain homogeneous samples of colloids of NPs in an NLC. Although the structured composition of the NLC, the size of these components with respect to the NPs, as well as the local effect of the NPs into the NLC, allows that some works consider the NLC as an effective homogeneous medium in which NPs are embedded [23].

In order to analyze the effect of an NLC doped with resonant NPs on an electromagnetic field crossing it, we have considered the attenuation of the transmitted beam. Classical theory established that the intensity of any field passing through a distance h of a dissipative medium is exponentially attenuated (2) [22].

$$I_{(z=h)} = I_{(z=0)} \cdot e^{-\alpha_{ext} \cdot h} \tag{2}$$

This attenuation is the result of both the absorption and the scattering of the beam into the medium, this is the extinction. In this sense, the attenuation α_{ext} and the extinction cross section (1) produced by the resonant NPs presented in the medium could be related in the following way

$$\alpha_{ext} = \Re \cdot C_{ext} \tag{3}$$

Where $\Re$ is the number of particles per unit of volume and C_{ext} is the extinction cross section of a nanoparticle embedded in the NLC.

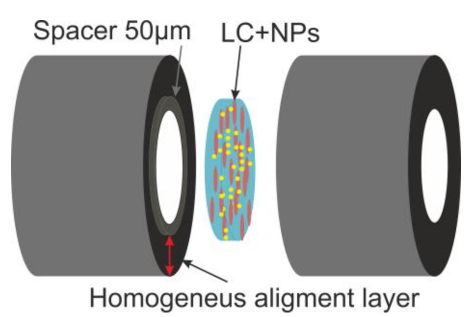

Fig. 1. Diagram of the fiber optic cavity.

The geometry considered in this work, as a proposed design of a potential temperature sensor, is a cavity in the optical path of a fiber optic. This cavity is filled with a mixture of an NLC doped with NPs of different composition and sizes by capillarity (see Figure 1). Two different NLC have been studied, E7 and TL296. A spacer of an optimized thickness is incorporated surrounding the fiber core. The fiber can be made of extruded glass (silica) or plastic. The size of the core determines some light losses but it should not affect the sensor sensitivity. The results presented in the next section reveal a static behavior of light seeing the ordinary refractive index of the NLC. This fact, indicates that the use of common fibers is possible. Despite this, in this case some molecules would have an ordinary refractive index and these molecules, and the NP surrounding them, would not contribute to the extinction ratio. This phenomenon could be compensated by increasing the NP concentration. Besides, the use of some kind of homogenous alignment layer (e.g. SiO_x, ZrO_2, etc.) and polarization maintaining fibers could lead to higher sensitivities if the extraordinary refractive index of the LC could be maintained during the measurements. The results of section III.B and section III.C consider this last case.

III. Results and Discussion

A. NLC response with temperature

The presented simulated results are obtained by estimations of the extinction coefficient (3) of metallic and SC NPs within a NLC E7 or TL296, for different temperatures. These types of NLCs have high temperature gradients of refractive indices and a broad range of temperature in the nematic phase (up to 55ºC and 80ºC). The Cauchy equation (4) and the Extended Cauchy equation (5) have been used to describe these variations with wavelength and temperature, respectively.

$$n_i(\lambda) \cong A_i + \frac{B_i}{\lambda^2} + \frac{C_i}{\lambda^4} \tag{4}$$

$$n_i(T) \approx A - BT - \frac{(\Delta n)_o}{3}\left(1 - \frac{T}{T_c}\right)^{\beta} \tag{5}$$

The estimated coefficients have been extracted from measured index of refractions reported on Ref. [10]. In the case of E7, the Cauchy coefficients, for different temperatures,

TABLE I
Coefficients for the Extended Cauchy Equation

λ\Coeff	450nm	486nm	546nm	589nm	633nm	656nm
A	1.63	1.62	1,61	1,60	1,60	1,59
B ($x10^{-4}$)	4,9	4,8	4,8	4,6	4,5	4,4
$(\Delta n)_{oe}$	0.25	0.23	0.19	0.18	0.17	0.16
$(\Delta n)_{oo}$	-0.12	-0.13	-0.15	-0.15	-0.16	-0.16
β_e	0.21	0.23	0.25	0.26	0.27	0.25
β_o	0.21	0.19	0.17	0.16	0.16	0.15

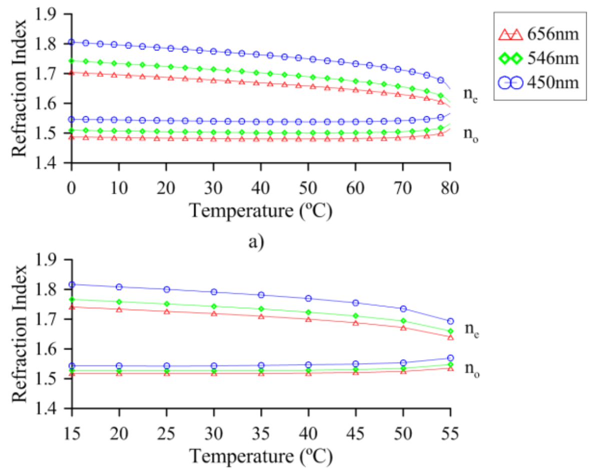

Fig. 2. Temperature dependences of the, a) TL296 (Extended Cauchy Equation) and b) E7 (Ref. [12]).

are directly estimated from the measured data with a least square fitting algorithm. For TL296 the use of the Extended Cauchy equation is required in order to estimate the index of refraction above 55ºC (Table. 1). The value of T_c is the clearing point of the NLC compound, in this case 80.3ºC. The result is a refractive index as a function of wavelength and temperature, as can be observed in Fig. 2. These LCs are materials with very high thermo-optic coefficients, as was commented above and it can be certainly concluded from the slope of these curves.

B. NLC doped with metallic nanoparticles

The plasmonic resonances of metallic NP produce a high extinction cross section for a determined wavelength. By combination with the high thermo-optic coefficient of nematic NLC, these resonances are tuned by temperature changes (see Fig. 3). This idea was the operating principle for a phase-

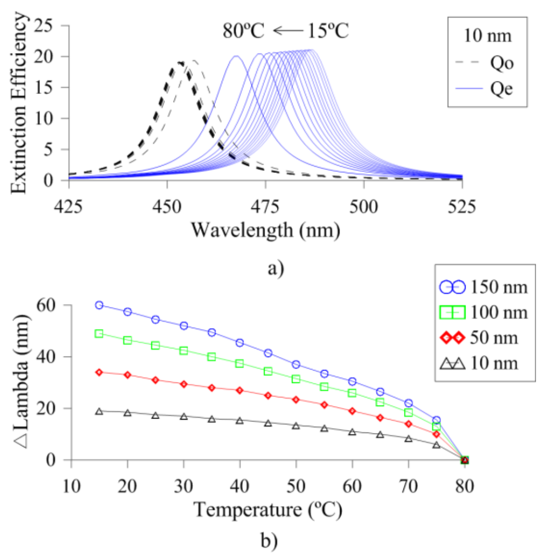

Fig. 3.Results of doped TL296 LC response [3]. a) Extinction efficiency spectra of a spherical Ag NPs for several temperature values. Particle sizes is R = 10nm. b) Resonant wavelength shift as a function of temperature for various NPs sizes for the ED mode.

based design in a previous study [3]. In the referred work, a detailed study of the extinction efficiency for several NP sizes and NLCs was carried out. Some of the best results were obtained for the electric dipolar (ED) mode and the E7 (maximum sensitivities of 4nm/ºC were obtained in the non-linear range). TL296 was also studied (Fig. 2). The output sensing magnitude was the lambda shift produced by the change of the NLC refractive index with temperature. For these calculations, the concentration of NP was considered low enough to avoid multiple scattering effects.

In this work a different concept is introduced. In order to have an amplitude modulation sensor the NP concentration on the NLC mixture is considered. Following (2), and considering the number of NP per volume, an amplitude modulation is obtained for some specific wavelength ranges. An important consideration has to be taken into account, the NP size effect is directly related to the fill factor used. The absorption is really affected by the number of particles per volume. If the NP size is increased, and the fill factor is maintained, the number of NP on the sample is lower. For this reason, the NP size is recommended to be small; there will be more NP per volume for the same fill factor. In Fig. 4 the VIS spectrum of the cavity with NPs at different concentrations is shown. The NP size is R=10nm and the spacer distance is 10μm. The concentration varies in an achievable range (0.01%

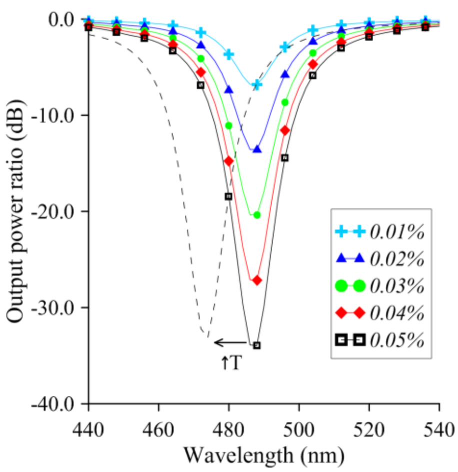

Fig. 4.Results of doped E7 LC response for several concentrations at room temperature.

to 0.05%). As can be seen, a higher number of NPs involves a higher extinction of the transmitted intensity at the resonant wavelength. Moreover, a change of the temperature produces a shift of the resonant mode due to the change of the NLC refractive index.

When no NPs are incorporated to the cavity, the transmission is only affected by the gap losses (0.13dB) and very small Fresnel reflections (not shown in the figure). Thus, it is clear that the main extinction effect is produced by the NPs at the resonance wavelength. As it was demonstrated above, these resonances can be tuned by the temperature. These two facts produce a very high sensitivity sensor when the light source has a spectrum of the same resonant wavelength. For instance, the output power ratio as a function of the temperature is shown in Fig. 5 when a NLC mixture consists of an E7 doped with Ag NP of 10 nm is considered. The fill factor is 0.05 %.

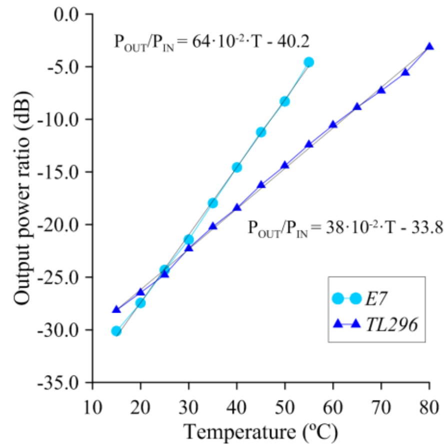

Fig.5.Output power ratio of Ag NP doped E7 and TL296 LC.

A light source of 490 nm and a spectrum bandwidth of ±2 nm is considered.

The refractive index change of the NLC with temperature is so high that it produces a huge difference between the extinction at different temperatures. For the case of E7, the result is a very high sensitivity of $64 \cdot 10^{-2}$ dB/°C. This is 42 times more than other related intensity sensors. Moreover the sensitivity is highly linear with a regression coefficient of 99.99%. For the case of TL296 a linear output response with a sensitivity of $38 \cdot 10^{-2}$ dB/°C is obtained from 0ºC to 80ºC. The use of other NLC compounds could increase the temperature range as well as the sensitivity.

C. NLC doped with semiconductor nanoparticle

As was commented above, it has also been shown that SC NPs present plasmon-like resonances. Their use as a counterpart of metallic NP is currently been studied. The resonances produced in this type of NP are usually more numerous, but they occur for bigger sizes (~100nm).

In this study several SC materials have been studied. Most of the SC NP resonances do not change at all with temperature. The main reason is that, unlike metallic NP, the SC NP are more stable under any change of the refractive index of the surrounding medium [22]. Moreover the extinction coefficient produced by SC NP is considerably

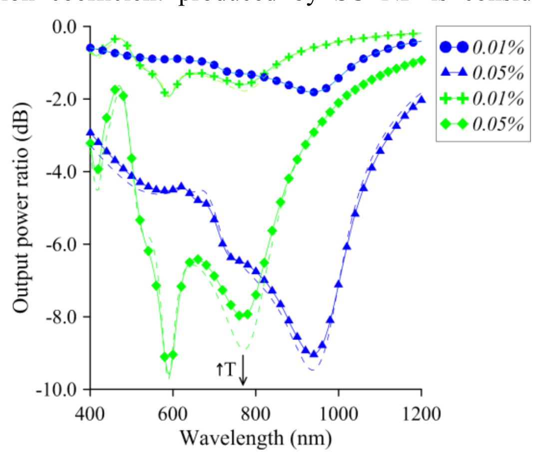

Fig.6.Results of doped E7 LC response for several concentrations. Blue color is for germanium and green for silicon. The arrow indicates an increase in the applied temperature.

lower than that caused by the metallic ones. For this reason a cavity of 100 µm is considered in this case. After a study of several SC materials, two of them seem to have an interesting response, the silicon and the germanium. In Fig.6 the response of a 100 nm NP, for several concentrations and both materials, is shown. As commented above, SC NPs are not affected in the same way by changes in the refractive index of the surrounding medium. For this reason the result, when a temperature change is produced, is very different. In Fig. 4 a wavelength shift was produced by temperature. In Fig. 6, it can be observed how the temperature does not change the resonance wavelength but it changes the absorption coefficient.

In consequence, the requirement of the light source bandwidth is reduced. In this case, a 770 nm light source with a ±10nm is enough to achieve a linear range sensitivity of $1.6\cdot10^{-2}$ dB/°C for the case of silicon (Fig. 7). This sensitivity is similar to other reported works based on amplitude modulation. The wavelength can be tuned by changing the NP size. The sensitivity can be maintained if the number of particles per volume is the same. Similar results are observed for germanium NPs. Thus, in this case, the use of SC NPs do not produce remarkable advantages with respect to metallic ones, despite the reduction of bandwidth requirements.

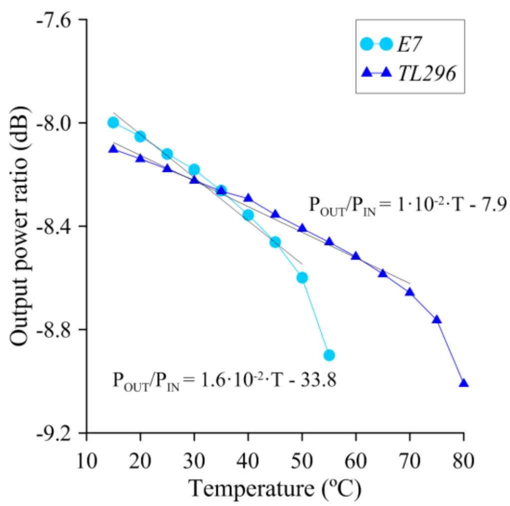

Fig.7.Output power ratio of Si doped E7 and TL296 LC.

IV. Conclusions

An amplitude modulation optical fiber sensor for temperature sensing has been theoretically analyzed. The dependence of the resonant frequency with the changing refractive index of NLC with the temperature is used as sensing parameter. Different kinds of NLCs, NP materials and concentrations have been studied. The operating range and sensitivity of the sensor depend on the NPs concentration and the NLC type. Temperature ranges up to 55ºC and 80ºC have been considered. Maximum sensitivities of $64\cdot10^{-2}$ dB/ºC are obtained when metallic NP are used. This is 42 times more than other related intensity sensors. Moreover, the sensitivity is highly linear with a regression coefficient of 99.99%. The design of the proposed sensor could be low cost, and have all the typical advantages of fiber optic sensors.

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