

Liquid crystal infiltration of complex dielectrics

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Abstract

Liquid crystal infiltration is becoming an important tool to control the optical properties of complex dielectric systems like photonic crystals and disordered dielectrics. We discuss the technical aspects of liquid crystal infiltration in meso-porous structures, give some details of the sample preparation process, and discuss possibilities for tuning the optical properties of both ordered and disordered systems.

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1. Introduction

The transport of light in complex dielectric materials has several interesting similarities with electron transport (see for instance Ref. [1]). Complex dielectrics range from fully disordered materials in which light shows a diffusive type of propagation to ordered systems like photonic crystals or photonic band-gap materials. Interference effects turn out to be important in almost all cases. Interesting light transport phenomena for the disordered case include weak localization or coherent backscattering [2], Anderson localization of light [3], the optical Hall effect [4], and optical universal conductance fluctuations [5]. Interference in ordered photonic crystals allows for spectacular effects like the expected occurrence

of a photonic band gap, in analogy with the electronic band gap in a semiconductor [6].

Three-dimensional complex structures can be realized, for instance, by assembly of microspheres. The simplest technique makes use of slow sedimentation, which yields close-packed ordered structures (opals) if the diameter of the spheres is sufficiently monodisperse (variation of the diameter being typically less than 5%), and disordered samples otherwise. The opal can subsequently be infiltrated by high-index material to obtain, after removal of the original microspheres, inverse opal structures of high refractive index contrast [7,8].

The refractive index contrast between the sphere and its surrounding environment determines the scattering strength of the single building block and thereby determines the key parameters of the final complex dielectric. In the disordered case, the characterizing sample parameters are the mean free path and the diffusion coefficient. In the

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ordered photonic crystal case, the main parameters are the width and positions of the stopbands and/or band gap. One can gain control over these important parameters by infiltrating the sample with a liquid crystal [9]. The refractive index of a liquid crystal depends strongly on temperature and in the temperature range of the nematic phase also depends on an external electric or magnetic field. As a result the refractive index contrast of the single scattering element can be controlled externally via temperature or field after liquid crystal infiltration. Temperature control over the band gap of two-dimensional photonic crystals has been demonstrated experimentally, and shifts as large as 70 nm in the central wavelength of the band gap were observed [10]. Electric field tuning of the photonic stopband in opals was explored experimentally but the effects observed so far were limited by surface anchoring of the liquid crystal [11,12].

2. Liquid crystal infiltration

The refractive index of a liquid crystal is strongly temperature dependent due to the various liquid crystal phase transitions. The clearest effect occurs at the nematic-isotropic phase transition since the nematic phase is birefringent and the isotropic phase is not. In addition, all refractive indices of the liquid crystal are temperature dependent within the temperature range of a certain liquid crystal phase. For example, the phase sequence of the liquid crystal 8CB (Octylcyanobiphenyl) is crystalline (21.1) Smectic A (33.5) Nematic (40.8) Isotropic, where the numbers between brackets indicate the phase transition temperatures in degrees celsius.

If we fill the voids of either a photonic crystal material or a disordered structure with liquid crystal, the refractive index contrast between scatterer and surrounding medium changes and becomes temperature dependent. The nematic phase in the voids will be locally monodomain, but the nematic director orientation can, in principle, vary from void to void. Therefore this system consists of randomly oriented nematic domains. In addition, the nematic alignment inside the voids will be influenced by the coupling

between liquid crystal and the surface of the voids. Our systems of interest have relatively large pores with a diameter of more than 100 nm. At much smaller void sizes the liquid crystal phase transitions are strongly influenced, with phase transition temperatures being smeared out over a broad temperature range, and certain liquid crystal phases might even not be formed at all due to confinement effects. There is a broad interest in the behavior of liquid crystals in such confined geometries [13]. We limit ourselves in the work to the regime of relatively large pores.

In order to obtain a global anisotropy in the system, an external magnetic or electric field can be used to align the nematic director. The surface anchoring of the liquid crystal is, however, hardly ever negligible. Close to the pore surface the liquid crystal alignment will be dominated by the surface anchoring, even at high field strengths. This fixed surface alignment will persist over a distance that is about equal to the magnetic (or electric) coherence length ξ at the given field strength [14]. Therefore, ideally, the voids should be larger than the coherence length to enable external field switching of the photonic crystal and/or random system.

3. Infiltrated photonic crystals

Liquid crystal infiltration in direct opals of silica was studied carefully by Kang et al. [11], who found a modest shift of the band edge upon applying an external electric field over the sample. The limited effect of the external field was attributed to confinement effects inside the complicated shaped voids in a direct opal. One might expect that inverse opal structures, having spherical voids, are favorable for external field switching since a spherical void does not impose a preferred alignment direction. In addition, at fixed lattice constant, the inverse opal voids are bigger than those of the direct opal. To further exploit the possibilities of electric field tuning of photonic crystals we characterized the stopband of infiltrated titania inverse opals.

The titania inverse opals were based on self-organized direct opals of monodisperse

polystyrene spheres. These direct opals were infiltrated with TiO_2 , via a precursor solution (tetra-propoxy-titane). Calcination of the TiO_2 by heating to 450°C subsequently also removes the polystyrene and leaves a clean titania inverse opal (air spheres in a TiO_2 backbone). See for more details Ref. [8]. The lattice constant a of the resulting titania inverse opals was 451 nm and their pore radius was 160 nm.

The titania inverse opal was infiltrated overnight with the liquid crystals 5CB or E7. The infiltrated samples were mounted between two glass slides coated with a thin transparent layer of indium doped tin oxide (ITO) on the glass surface facing the sample. Before mounting the glass slides, part of the ITO coating was carefully removed in order to avoid regions of facing ITO layers without sample in between. The sample thickness equals the distance between glass plates and ranges from 0.2 to 0.5 mm in our case.

The electric conductance of the tin oxide allows to apply an electric field over the sample

perpendicular to the sample plane. Without the electric field the optical properties of the sample are expected to be isotropic, whereas at high enough field the nematic director should obtain some global alignment and hence the stopband of the infiltrated photonic crystal is expected to shift towards higher wavelengths. Since the sample is a very good insulator (much better than air), and facing ITO layers always have sample material in between, we can apply an electric field as high as $24 \text{ V}/\mu\text{m}$ to the sample (ac at 500 Hz).

A good way to characterize the stopband of a photonic crystal is via angular and wavelength resolved reflection measurements. A stopband appears as a wavelength regime where the reflectivity is high. In Fig. 1 we report angular resolved reflection spectra of a liquid crystal infiltrated titania inverse opal. If the system were to exhibit a complete photonic band gap, there would exist a wavelength region in which all reflection spectra overlap. This is not the case for our liquid

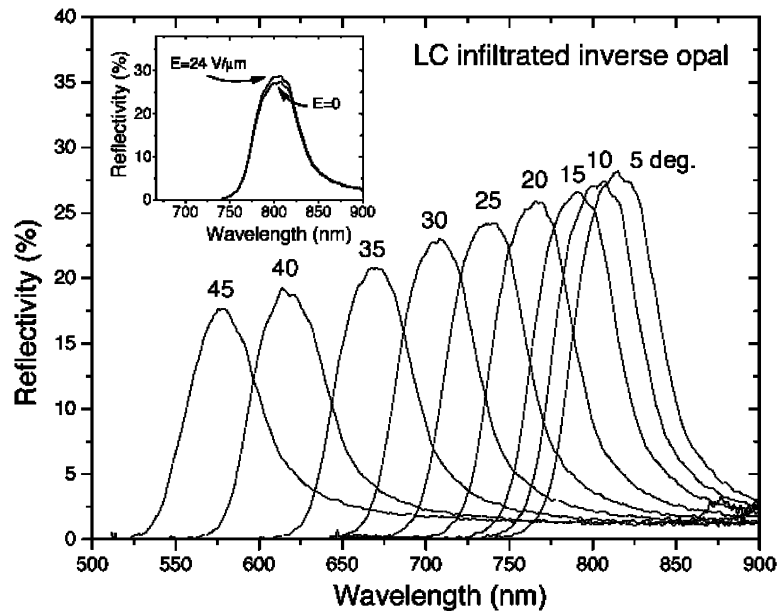


Fig. 1. Reflection spectra of titania inverse opals infiltrated with the liquid crystal E7. The emission of a broad band lamp was collimated via an optical fiber on the sample (spot size on the sample surface $100 \mu\text{m}$), and the reflected light was detected via an optical fiber by a spectrometer (spectral resolution 1 nm). The incoming and detection angle are equal and given in the graph with respect to the sample normal. The inset shows the tiny red-shift and increase of the reflection peak at 10° upon switching on the electric field. (Field strength $24 \text{ V}/\mu\text{m}$.)

crystal infiltrated samples as can be seen in Fig. 1. Although the density of states in un-infiltrated titania inverse opals is strongly reduced [15], after liquid crystal infiltration the refractive index contrast is diminished. This is the reason that the stopbands in Fig. 1 are not overlapping.

When we apply the electric field, the position of the stopbands is not changed considerably within the accuracy of our experiment (resolution about 1 nm). When we apply the maximum electric field of $24 \text{ V}/\mu\text{m}$ we observe only a minor increase of the reflected intensity. (See inset of Fig. 1.) These data might indicate also a tiny red shift of the reflection peak which however can not be considered significant. This increase and red shift could be mistakenly interpreted as a switching effect of the stopband of the sample by the electric field. We observe that it sets in slowly after applying the electrical field, which suggests an interpretation in terms of a heating effect of the sample and not a field effect. Heating effects on the reflection spectra from infiltrated photonic crystals were studied by Mertens et al. [16]. Apparently, the alignment of the liquid crystal due to the electric field is too small to induce any appreciable global anisotropy in our system. A possible improvement of the coupling with the external electric (or even magnetic) field could be obtained by a low-concentration addition of highly dielectric (or magnetic) nano rods suspended in the liquid crystal.

In Fig. 2 we report the reflection spectrum of an titania inverse opal that has intentionally been infiltrated in an inhomogeneous way. Although the spot of the incident light on the sample surface is small ($100 \mu\text{m}$), one can clearly see two reflection peaks corresponding to micro regions of the sample which were either infiltrated or not. The peak wavelength of both peaks (606 and 803 nm) corresponds with the expected reflection maximum for an either fully infiltrated sample or completely non-infiltrated sample. One can see that there is no reflected light in the intermediate regime. This is an indication that any specific void is either fully infiltrated or completely empty and that partial infiltration of a single void does not occur.

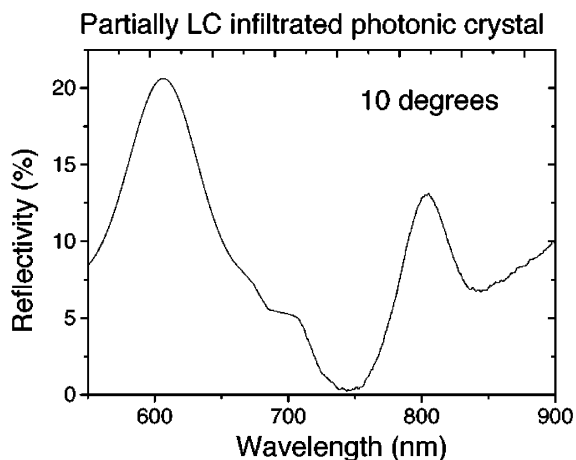


Fig. 2. Reflection spectrum at fixed angle of a partially infiltrated titania inverse opal. The double reflection peak is a good indication for the inhomogeneous infiltration of the sample. The low-wavelength peak at 606 nm corresponds to the reflection at 10° , of a non-infiltrated titania inverse opal whereas the high-wavelength peak at 803 nm corresponds to a fully LC infiltrated region. The appearance of two distinct peaks indicates that voids of the sample are either fully infiltrated or empty and that partial infiltration of a single void does not occur.

4. Disordered materials

In disordered systems liquid crystal infiltration can be successfully applied to tune the diffusion coefficient and/or the transport mean free path of the system, via temperature or via an external field [17]. Since the diffuse transport of light through a disordered dielectric obeys a similar transmission law as Ohm's law of resistance in electronics [1] one can describe such temperature sensitive diffusion as optical NTC (or PTC)-resistance [18]. The ideal systems to obtain temperature tuning of the diffusion constant are liquid crystal infiltrated strongly scattering powders or porous glasses. It is well known that polymer dispersed liquid crystals (PDLC) and liquid crystal/aerosil networks allow for electric field tuning of the scattering cross section [19]. Such systems have been studied extensively, but almost always in the regime of single (or very low order) scattering. By decreasing the transport mean free path of such systems or increasing by at least an order of magnitude the sample

Table 1

Various disordered material that are suitable for liquid crystal tuning of the transport mean free path

System	Remarks	Typical void size	Range ℓ (with LC)	Thickness
Porous glass	Robust discs	≤ 100 nm	10, ..., 200 μm	0.1, ..., 10 mm
Sintered glass	Robust discs	1, ..., 50 μm	8, ..., 100 μm	0.1, ..., 5 mm
Inorg. powders	Fragile	0.3, ..., 10 μm	5, ..., 50 μm	0.01, ..., 5 mm
Semic. powders	Fragile	0.3, ..., 10 μm	1, ..., 20 μm	0.01, ..., 5 mm
PDLC ^a	Thick film	1 μm ^b	50 μm , ..., 1 mm	200, ..., 1000 μm

Typical void sizes are given together with some values of the transport mean free path that can be obtained after liquid crystal infiltration. Most samples can be used both at visible and infrared wavelengths apart from the semiconductor powders which usually absorb strongly in the visible regime. The powders are obtained from sedimentation on a glass plate and can be pressed into self-standing discs (thickness range in that case about 0.5, ..., 5 mm).

^a Polymer dispersed liquid crystal. Particularly suitable for electric field tuning providing highly anisotropic mean free path values.

^b Optimum droplet size.

thickness of a PDLC one can obtain electric field tuning of the diffusion constant as well.

In Table 1 we give some examples of disordered systems that are well suitable for liquid crystal infiltration and that provide enough scattering to obtain samples in the diffusion regime. A range of typical values of the transport mean free path is given as an indication. The tuning range that is obtained depends strongly on the type of liquid crystal that is chosen. High values of the transport mean free path ℓ can be obtained relatively easily by index matching the liquid crystal at a certain temperature with the porous host. Small values of ℓ (strong scattering) are more difficult to achieve. In disordered systems, problems from surface anchoring are less important since the scattering mechanism randomizes the propagation direction anyway.

Porous glasses have the advantage that they are commercially available in the form of robust solid blocks that can be machined easily into any sample geometry. Usually, these materials have relatively small pore sizes of only a few nanometers (very weak scattering), so that the pore size has to be increased to at least 100 nm by chemical etching. Sintered glass has similar mechanical properties to porous glass but pore sizes are generally much bigger. Powdered materials generally offer more possibilities in the choice of dielectric properties and higher values of the refractive index contrast and hence stronger scattering can be achieved. In particular semiconductor powders are very suitable

for this task with negligible absorption in the band gap region and high refractive index values. Powers can be compressed into discs which remain however very fragile especially after infiltration with a liquid crystal. Stability can be somewhat improved by adding a polymer at cost of refractive index contrast. Polymer dispersed liquid crystals (PDLCs) offer good switching properties but relatively weak scattering so that extremely thick samples ($> 200 \mu\text{m}$) are required to be in the multiple scattering regime at all. (PDLCs are commonly only applied at thicknesses of several micro meters.) For more details regarding temperature tuning of the diffusion constant we refer to Ref. [17].

The physical infiltration of our porous samples with various liquid crystals is relatively simple in practice. At the pore sizes of interest one is greatly helped by the capillary forces. The voids must obviously be percolating in order to let the liquid crystal penetrated fully into the sample. We immerse the samples partially in the liquid crystal so that some openings are available to let the air out. The temperature is chosen such that the liquid crystal is in the isotropic phase during infiltration. If air bubbles inside the sample turn out to be a problem, the infiltration process can be assisted by working in a modest vacuum environment.

Since the transport mean free path and diffusion constant are the key parameters that characterize a disordered sample in light transport studies, having external control over these parameters

open up interesting possibilities. Interesting applications of temperature tuning of the diffusion constant include the temperature tunable random laser [20], in which the temperature control over D is used to bring a random laser system below and above threshold via temperature changes. Another fascinating application of a tunable mean free path would be in the study of Anderson localization of light, where the tunability would allow to explore the localization transition on one single sample.

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