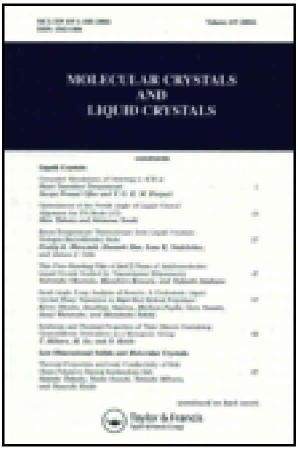

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Properties of Liquid Crystals in Photonic Crystal, Synthetic Opal

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Liquid crystals such as nematic liquid crystals and ferroelectric smectic liquid crystals are well infiltrated in photonic crystal, synthetic opal. Dielectric and optical properties of liquid crystals have been found to exhibit remarkable change upon infiltration in the opal. Diffraction and transmission of light through opals have been found to change upon infiltration of liquid crystal in opals and also upon field application. Relaxation of dielectric response in liquid crystals infiltrated in opal shifted to higher frequency and its temperature dependence has also changed. Electro-optic effect of the opal infiltrated with liquid crystals have been also discussed.

These results have been discussed in terms of interaction of liquid crystal molecule in nano-space and the inner surface of the nano-scale void in the photonic crystal, synthetic opal.

Keywords: liquid crystal; photonic crystal; synthetic opal

INTRODUCTION

Photonic crystals have attracted much interest from both scientific and practical view points, since novel concepts, such as photonic band gap, has been theoretically deduced and various novel applications of photonic crystals have been proposed[1, 2]. However, compared with theoretical studies, experimental studies have been limited. For example, ordered arrays of polystyrene spheres in aqueous solution, arrays of cylinders in a glass matrix and multilayered polymers have been studied as examples of three, two and one dimensional photonic crystals, respectively.

Recently we reported novel optical characteristics of synthetic opals that consist of well ordered three-dimensional arrays of SiO_2 spheres of diameters in the range of visible wave lengths as example of the photonic crystal[3]. In the same paper, we proposed to infiltrate organic materials in the nano-space formed in the synthetic opal and demonstrated unique characteristics in the opals infiltrated with dye molecules and also conducting polymers. It should be mentioned that liquid crystals themselves which have also periodic structure may exhibit some characteristic of photonic crystal. That is, liquid crystal can be one sort of photonic crystal.

In this paper, we demonstrate that liquid crystal is also well infiltrated in synthetic opals and liquid crystal infiltrated in the opals exhibits novel characteristics.

EXPERIMENTAL

Ordered crystals were formed by sedimentation of the silica suspension formed with monodispersed silica spheres of 430, 250, 210 and 160 nm in a diameter prepared by the well known procedures. These crystals were annealed at 120°C and sintered at 650°C to obtain a small degree of interparticle sintering, which mechanically stabilize the structure. The ordered crystals were also prepared between parallel ITO (In-Sn oxide coated) glass or quartz plates. The typical size of the crystal used for measurements was 8 mm in length, 5 mm in width and 50 μm in thickness.

Electron micro graphs were taken with S-2100C Hitachi electron-microscope. The reflectance and transmission spectra were evaluated using a CCD detector PMA-11 (Hamamatsu Photonics).

Dielectric constant of the sample in the heat bath controlled with a temperature controller FP21 (Shimden) on the stage of an optical microscope was measured with an impedance analyzer 4192A (YHP).

As an example of liquid crystals, both nematic liquid crystals, such as ZLI1132 (Merck), and ferroelectric liquid crystals (FLCs), such as 3MC2PCPOPB, whose molecular structure is shown in Fig. 1, were used.

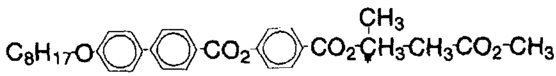

FIGURE 1 The molecular structure of 3MC2PCPOPB.

RESULTS AND DISCUSSION

Chiral Smectic Liquid Crystal as Photonic Crystal

Figure 2(a) shows the temperature dependence of transmission spectra through the thin film of ferroelectric liquid crystal 3MC2PCPOPB[4]. As evident in this figure, this liquid crystal exhibits selective reflection, that is, stop band at some wavelength which depend on temperature. This liquid crystal 3MC2PCPOPB shows ferroelectric characteristics in the chiral smectic C phase, in which helicoidal structure is formed under bias-free state (no applied field and no effect from the boundary of a substrate). The observed results indicate that the helical pitch of this material is ranged in the length of the order of wavelength of visible light and it changes drastically with temperature (Fig. 2(b))[4]. Helical pitch was also dependent on applied pressure. Therefore, this type of chiral smectic liquid crystal, chiral nematic liquid crystal and some sorts of cholesteric liquid crystal also should show characteristics of some sorts of photonic crystals.

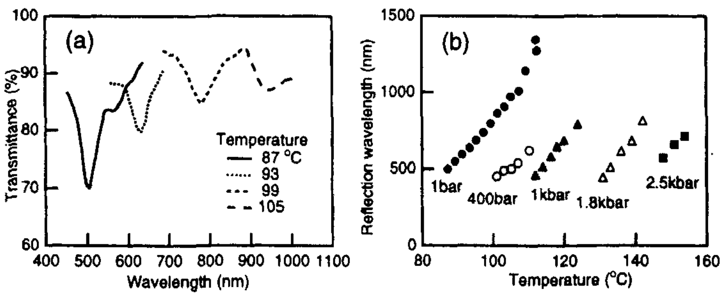

FIGURE 2 The temperature dependences of 3MC2PCPOPB. (a) The transmission spectra. (b) The helical pitch.

We are studying the characteristics of this material as photonic crystal and also studying the characteristic of functional behavior to photonic crystal. For example, we are studying spectral narrowing and lasing of various dyes such as Rhodamine 6G and highly fluorescent conducting polymers dissolved in a liquid crystal as matrix of photonic crystal as function of temperature and helical pitch[5]. Detailed results will be reported separately.

Synthetic Opal, Photonic Crystal, Infiltrated with Liquid Crystal

We are also studying properties of synthetic opals, photonic crystal, infiltrated with a liquid crystal.

Figures 3 indicates electron micrographs of the opals composed of regular arrays of SiO_2 spheres of 250 nm and 430 nm in a diameter. Because of the face centered cubic (f.c.c) structure of these opals, they contain an interconnected structure of tetrahedral and octahedral voids. For example, in an ideally structured opal made of SiO_2 spheres of 250 nm in a diameter, tetrahedral and octahedral voids were evaluated to be 56 nm and 104 nm in diameter, respectively. These voids are fully interconnected by channels of a smallest diameter of 38 nm. However, because of the sintering process, real sizes of voids and connection channels should be smaller than the calculated values. This percolated porous structure permits the infiltration of a liquid crystal in the opal.

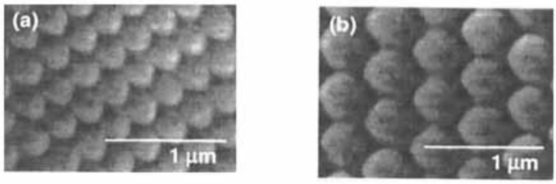

FIGURE 3 The electron micrographs of the opals consist of SiO_2 spheres of 250 nm (a), and 430 nm (b) in a diameter.

Figure 4 shows the reflection spectra of the opal imbedded in chloroform as a function of incident angle θ. In the spectra, sharp diffraction peaks shift with changing incident angle.

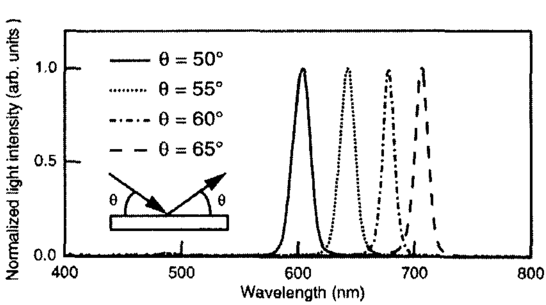

FIGURE 4 The reflection spectra of the opal imbedded in chloroform as a function of incident angle θ.

The interplanar spacing of the opal lattice evaluated from the diffraction peaks with Bragg diffraction condition utilizing a refractive index of chloroform was consistent with that of (110) planes calculated with the diameter of SiO_2 spheres and f.c.c structure.

Diffraction peaks of the opal infiltrated with a nematic liquid crystal ZLI1132 change slightly compared with chloroform infiltrated opal. This originates from the difference in refractive indices of a nematic liquid crystal and chloroform and also the change of scattering of light. It should also be mentioned that the diffraction and transmission changed slightly with application of electric field (this result is described below). This should be due to the change of refractive index of the liquid crystal in the opal on account of the reorientation of liquid crystal molecules by applied field.

Based on these observations, we propose new concept of an anisotropic photonic crystal. That is, synthetic opals infiltrated with liquid crystal should exhibit anisotropy in electric and optical properties due to anisotropic characteristics of the liquid crystal. The orientation of liquid crystal molecules can be controlled by applied field and temperature, resulting in the change of anisotropic characteristics of the photonic crystal infiltrated with the liquid crystal. Various functionality may be realized by the control of anisotropy of this anisotropic photonic crystal, such as anisotropic photonic band gap etc.

Figure 5 shows the temperature dependence of transmission light intensity through the opal infiltrated with the liquid crystal ZLI1132. Compared with a liquid crystal in the usual sandwich cell in which clear change of the transmission intensity was observed at the phase transitions, the change of the transmission was relatively smooth in the opal infiltrated with the same liquid crystal. This may suggest that the liquid crystalline order is not suddenly lost at the phase transition point, partly due to the interaction of liquid crystal molecules with the inner surface of the nano-scale cavity in the opal.

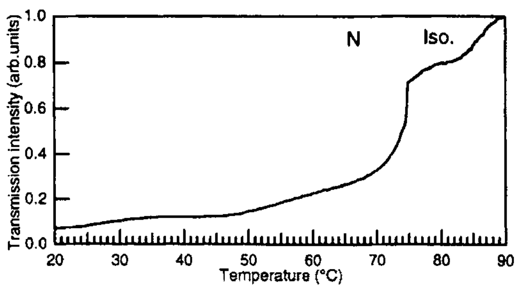

FIGURE 5 The temperature dependence of transmission intensity of the opal infiltrated with ZLI1132.

It should also be mentioned that the transmission intensity through the opal infiltrated with liquid crystal also change upon voltage application as shown in Fig. 6. This type of electro-optic effect without optical polarizers may be originated from the change of light scattering due to the change of refractive index of the liquid crystal relative to that of SiO_2 associating with molecular reorientation.

Figure 7 shows the response of transmission intensity of the opal infiltrated with the liquid crystal ZLI1132 upon voltage application and removal. The sample was set between the crossed polarizers. The response time of the electro-optic effect of the infiltrated opal was different from that in the usual sandwich cell.

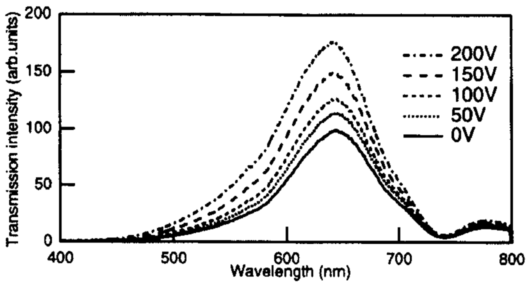

FIGURE 6 The transmission intensity of the opal infiltrated with ZLI1132 as a function of applied field.

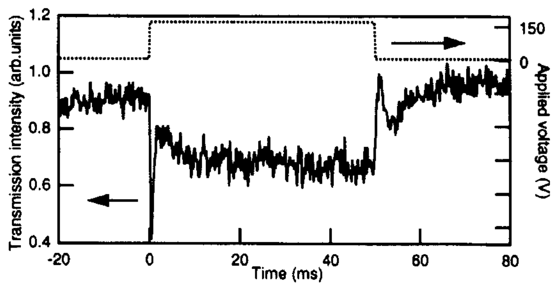

FIGURE 7 The response of transmission intensity of the opal infiltrated with ZLI1132 upon voltage application and removal.

Dielectric properties of liquid crystal infiltrated in the opal were also studied in comparison with those of the usual sandwich cell. Figure 8 shows temperature dependences of dielectric constant of ferroelectric liquid crystal 1MC1EPOPB in the sandwich cell and that infiltrated in the opal. As evident in this figure, the change of dielectric constant at the phase transition points is sharp in the sandwich cell. On the other hand, the change in the opal infiltrated with the same liquid crystal becomes not so sharp but dielectric constant changes relatively gradually even at the phase transition. Moreover, the peak of dielectric constant, which appears at phase transition point from SmA to SmC* in the usual sandwich cell, was much suppressed in the FLC infiltrated into the opal. Since this peak is due to softmode motion of molecules, this may suggest that softmode motion of liquid crystal molecules was hindered.

To confirm the suppression of softmode motion, the frequency dispersion was measured. Figure 9 shows frequency dispersion of dielectric constant of the FLC infiltrated in the opal in the SmA phase (ε' and ε'' indicate the real and imaginary part of dielectric constant respectively). As evident in this figure, the dispersion of the softmode is not observed. That is, the softmode motion of molecules should hardly occur in the nano-size voids.

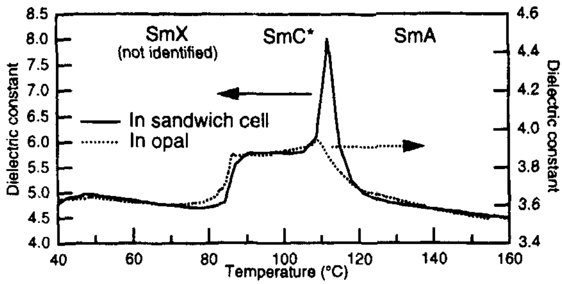

FIGURE 8 The temperature dependences of dielectric constant in 100kHz of 1MC1EPOPB in the sandwich cell and that infiltrated in the opal.

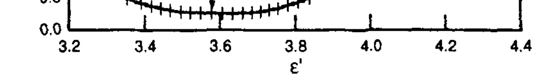

FIGURE 9 The frequency dispersion of dielectric constant of 1MC1EPOPB infiltrated in opal in the SmA phase.

Dielectric response was also measured in the nematic liquid crystal infiltrated in the opal. Figure 10 shows frequency dispersion of dielectric constant of the nematic liquid crystal in the sandwich cell and in the nano-size voids of the opal. As evident in this figure, relaxation frequency of the opal infiltrated with the nematic liquid crystal is located at 630kHz, which is higher than that in usual sandwich cell (360kHz) as shown in Fig. 10. This may also come from the strong interaction of liquid crystal molecules with the inner surface of the nano-scale voids in the opal, resulting in the strong recovering force. This situation seems to be similar to the polymer dispersed liquid crystal in which higher response speed of electro-optic effect was observed for smaller size of liquid crystal droplet of μm range. That is, the change of response dynamics of electro-optic as already mentioned may be related with this change of dielectric relaxation in the opal.

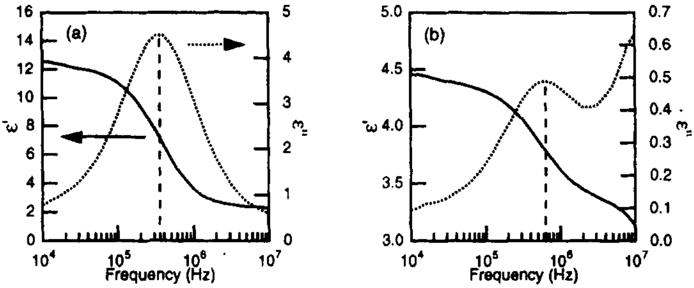

FIGURE 10 The frequency dispersions of dielectric constant of ZLI1132. (a) In the sandwich cell. (b) In the opal.

CONCLUSION

New structure of photonic crystals, synthetic opals infiltrated with a liquid crystal were proposed and unique characteristics of diffraction, transmission of light and electro-optic response have been demonstrated. The phase transition behavior and dielectric relaxation process in the liquid crystal infiltrated opals were much different from those of liquid crystal in the usual sandwich cell. The results are interpreted in terms of effects of wall on the liquid crystalline molecular alignment order and also strong interaction of liquid crystal molecules with the inner surface of nano-scale voids in the opal.

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