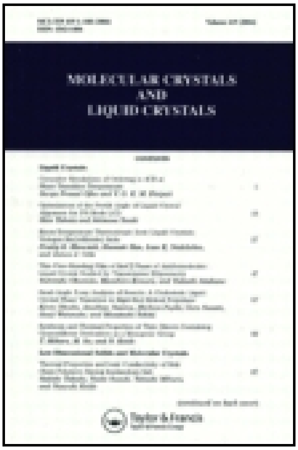

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# Temperature Tuning of Optical Stop Band of Liquid-Crystal Infiltrated Synthetic Opal

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# Temperature Tuning of Optical Stop Band of Liquid-Crystal Infiltrated Synthetic Opal

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The infiltration of a nematic liquid crystal into opal with a three-dimensional periodic structure has been studied. In the infiltrated opals, the stop band has been confirmed to be controlled by adjusting various conditions such as temperature. Opal replica has been prepared and it has been found that optical stop band of the opal replica also shifts upon infiltration with organic materials.

*Keywords:* photonic crystal; opal; replica; stop band; liquid crystal; refractive index

## INTRODUCTION

Photonic crystals with a three-dimensional ordered structure with a periodicity of optical wavelength have attracted much attention from both fundamental and practical points of view, because novel physical concepts such as photonic band gap have been theoretically predicted and various novel properties which are desirable for future electronics and opt electronics are expected in this new class of material [1-2].

To fabricate the three-dimensional periodic structure, we have adopted a simple method utilizing sedimentation of monodispersed nanoscale spheres of the order of optical wavelength in diameter.

Synthetic opals have been studied as pseudo photonic crystals or prototype photonic crystals in order to establish growth techniques and understand fundamental optical properties such as the stop band of the three-dimensional periodic structure of materials.

We have demonstrated that various materials can be infiltrated into interconnected nanosize voids in opals and various new functionalities can be realized in the infiltrated opals, and have proposed new concept of a tunable photonic crystal in which the photonic band gap can be tuned by controlling parameters such as periodicity, filling factor, refractive index and crystal structure [3-4].

In this paper, we report that liquid crystals can also be infiltrated into a three-dimensional periodic array of interconnected nanosize voids in the synthetic opal and the stop band can be tuned by controlling the refractive index, periodicity, or space filling factor.

We also discuss the infiltration of liquids and liquid crystal into a polymer replica of the synthetic opal.

## EXPERIMENTAL

Ordered colloidal crystal in a film was formed in sandwich cells composed of two glass plates with separation of 50 μm by sedimentation of the suspension of monodispersed silica spheres of 300 and 1000nm diameters [3-4]. In this paper, the opals made of 300nm and 1000nm $SiO_2$ spheres are named opal-300 and opal-1000, respectively. The obtained opal film was confirmed to have a face-centered cubic (f.c.c) structure and to contain interconnected voids of nanoscale by measuring the optical diffraction spectrum and also by electron microscope observation using a scanning electron microscope (S-2100, Hitachi). The transmission and reflection spectra were measured using a spectrophotometer (330, Hitachi or FT/IR-300E, JASCO).

The opal replica was prepared by infiltrating a liquid photopoymer (PN393, Merck) into the nanoscale voids in the synthetic opal and by removing silica particles using HF after polymerization [5].

A nematic liquid crystal ZLI1132 (Merck) was used for infiltration of the thin opal film.

## RESULT AND DISCUSSION

Figure 1 shows an electron microphotograph of the opal film made of $SiO_2$ spheres of 300nm in diameter. This opal film exhibits a beautiful opalescent color and clear diffraction peaks depending on the incident angle of the light, which support the existence of a regular periodic feature of the obtained opal.


FIGURE 1 Electron microphotograph of opal-300.

Figures 2 (a) and (b) show transmission spectra of the opal-300 and opal-1000 films for normal incidence, respectively. As is evident in these figure, clear stop bands appear at the wavelengths of around 650 and 2250nm in the opal-300 and opal-1000, respectively. The diameters of $SiO_2$ spheres of the opal-300 and opal-1000, evaluated from the observed transmission spectra by assuming f.c.c lattice as a crystal sturcture, coincide with those of the original silica spheres.

Figure 3 (a) indicates transmission spectra of the opal-300 (broken line) and the opal-300 infiltrated with the nematic liquid crystal (solid line). As is evident in this figure, the stop band of the nematic liquid crystal infiltrated opal appears at longer wavelength by about 70nm compared with that of the original opal-300. This stop band shift should originate from the large refractive index of the nematic liquid crystal.

Similar stop band shift due to the infiltration of the liquid crystal was also confirmed in the opal-1000, as shown in Fig. 3 (b). In this case, the center wavelength of the stop band was red-shift by 250nm.

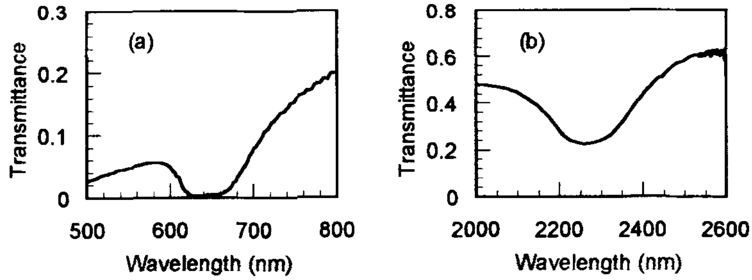


FIGURE 2 Transmission spectra of opal-300 (a) and opal-1000 (b).

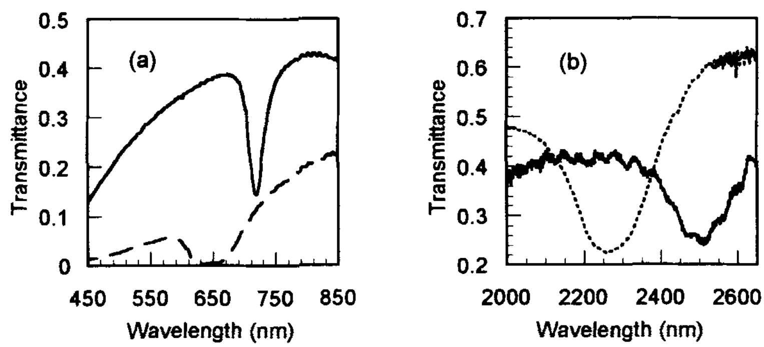


FIGURE 3 Transmission spectra (solid line) of nematic liquid crystal infiltrated opal-300 (a) and nematic liquid crystal infiltrated opal-1000 (b). Broken lines show the transmission spectra of original opals.

It should be noted that the stop band depends on the phase of the liquid crystal as shown in the inset of Fig. 4. The stop band of the opal film infiltrated with the nematic liquid crystal shifts drastically at the phase transition point between the isotropic and nematic phases. From these spectral changes, we can evaluate the refractive index of the liquid crystal as a function of temperature by utilizing the periodicity of the opal and the refractive index of $SiO_2$. Figure 4 shows the temperature dependence of the refractive index of the nematic liquid crystal. With decreasing temperature, stepwise increase in the refractive index was observed at the phase transition point between the isotropic and nematic phases.

The stop band of the opal-1000 infiltrated with the nematic liquid crystal also depends on temperature, as shown in the inset of Fig. 5. From the temperature dependence of the stop band wavelength, the refractive index of the nematic liquid crystal infiltrated in the opal-1000 can also be evaluated. As is shown in Fig. 5, the stepwise change in the refractive index was also observed at the phase transition point.

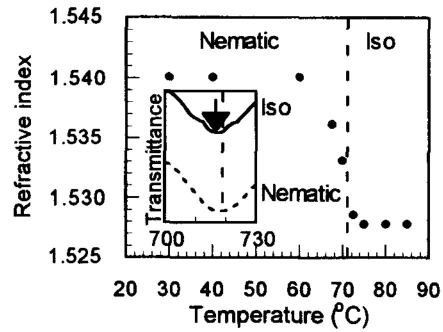


FIGURE 4 Temperature dependence of evaluated refractive index of nematic liquid crystal (ZLI1132) in voids of opal-300. The inset shows the temperature dependence of transmission spectra.

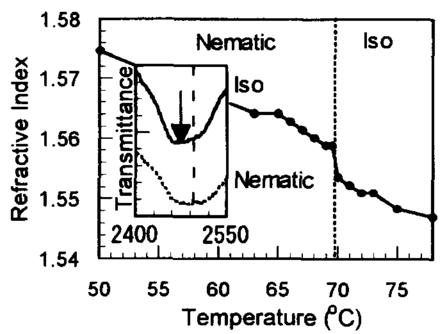


FIGURE 5 Temperature dependence of evaluated refractive index of nematic liquid crystal (ZLI1132) in voids of opal-1000. The inset shows the temperature dependence of transmission spectra.

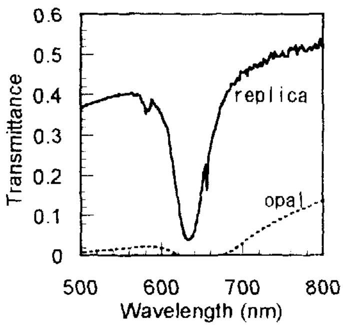


FIGURE 6 Transmission spectra of opal-300 (broken line) and opal-300 polymer replica infiltrated with water (solid line).

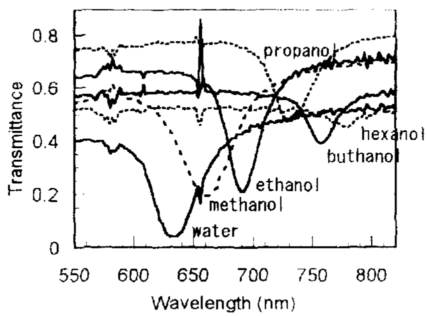


FIGURE 7 Transmission spectra of opal-300 polymer replica infiltrated with various solvents.

We have proposed an opal replica as one of candidates for photonic crystal material. The opal replica has following advantage. For the fabrication of the replica, a variety of materials such as polymer, semiconductor, and metal can be used. This means that, in the liquid crystal infiltrated replica, the surface interaction in the voids between the liquid crystal and replica can be controlled by selecting the replica matrix material.

In addition, a volume of the interconnected voids in replica is larger than that in original opal. In such larger spaces, infiltrated liquid crystal can respond more easily to the external stress such as an electric field. We performed a preliminary study on the spectral change of the infiltrated polymer replica.

Figure 6 shows the transmission spectra of opal-300 polymer replica infiltrated with water. As is evident in this figure, clear stop band appears at wavelength of around 640nm.

We investigated the solvent effect on the stop band in the infiltrated replica. Figure 7 shows transmission spectra of the opal-300 polymer replica infiltrated with various solvents. The stop band of the opal polymer replica shifts drastically by infiltrating solvents into the voids.

Reflection spectra of opal-300 polymer replica infiltrated with ethanol-methanol mixture are shown in the inset of Fig. 8 as a function of the concentration ratio of ethanol in the mixture. The reflection peak shifts drastically by changing the concentration ratio of the mixed solvent. Figure 8 shows the wavelength of the reflection peak as a function of the ethanol concentration in the mixture. With increasing the ethanol concentration, the peak wavelength monotonously red-shifts.

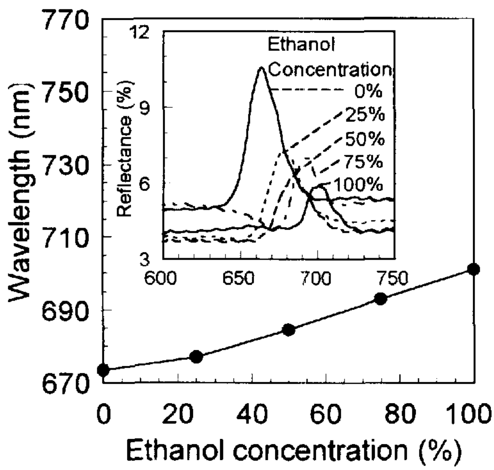


FIGURE 8 Dependence of wavelength of the stop band of replica infiltrated with methanol and ethanol mixture on ethanol concentration. The inset shows transmission spectra dependence of methanol-ethanol mixture infiltrated opal-300 polymer replica on ethanol concentration.

If the peak shift of the infiltrated opal replica originates from the difference in the refractive index of the solvent, the shift is calculated to be about 10nm. However, reflection peak shifts by more than 30nm upon changing the solvent from methanol to ethanol. Therefore, the change in periodicity of the polymer replica should also be taken into account for the large peak shift shown in Fig. 8.

## CONCLUSION

We fabricated synthetic opal thin film, which has a three dimensional periodicity as a photonic crystal by the self-assembly method. We also fabricated opal polymer replica using synthetic opal as a template.

We demonstrated that the stop band of the opal can be clearly tuned by infiltrating liquid crystals and changing the temperature, and the stop band of the opal polymer replica can also be changed by infiltrating organic solvents.

These results seem to support the possibility of the tunable photonic crystals. It should also be mentioned that we demonstrated a measurement method for the refractive index using opal. That is, by observing the transmission spectra through infiltrated opals, the refractive index of the infiltrated material can be evaluated.

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