

Three-Dimensional Bi-chiral Photonic Crystals

By Michael Thiel,* Michael S. Rill, Georg von Freymann, and Martin Wegener

Much work has recently been devoted to the design and fabrication of artificial materials (dielectric photonic crystals,^[1–4] as well as metallic metamaterials^[5–8]) aiming at achieving much larger optical activity and/or circular dichroism than observed in natural substances, such as milk or a sugar solution. This work has led to extremely large effects and even to negative-phase velocities^[5,6] but the vast majority of these structures were uniaxial. This low symmetry introduces a pronounced directional dependence of the optical properties which can be undesired for certain applications. A notable exception is a 3D arrangement of pieces of metal spirals with random orientation in three dimensions that has been demonstrated at microwave frequencies.^[9] The random orientation, however, leads to some degree of inherent scattering which can be avoided in periodic structures (“crystals”).

We aim at boosting chiral effects in tailored man-made crystalline materials, while avoiding uniaxial structures and maintaining isotropy as far as possible. The architectures that we propose and realize in this work are inspired by so-called blue-phase cholesteric liquid crystals,^[10–12] which come fairly close to our aim. They consist of left- or right-handed circular dielectric spirals that are arranged along the three orthogonal spatial axes of a cubic lattice with left- or right-handed so-called corners. Because of the two types of chirality, we refer to these structures as being “bi-chiral”. Out of altogether four possible bi-chiral structures, nature only provides those with opposite handedness, that is, left-handed motifs on right-handed corners and vice versa.^[13]

Here, we propose and experimentally realize a bi-chiral dielectric photonic crystal for the first time. Our structures, unlike blue-phase liquid crystals, can in principle be tuned to any desired operation wavelength. More importantly, our artificial structures give access to all four bi-chiral combinations, whereas only two are realized in nature. Moreover, we show that the ones missing in nature are the ones exhibiting the strongest effects.

The construction principle of our blueprint is illustrated in Figure 1. How have we arrived there? We have started from a 2D square array of left- or right-handed circular dielectric spirals

(strictly speaking helices), the optical properties of which have been discussed previously.^[1,4] A very large resonant enhancement of the chiral properties occurs if the dielectric spiral pitch matches the pitch of the light spiral, that is, the effective wavelength.^[4] As a result, light with the same handedness as the dielectric spirals is reflected for frequencies around the resonance, whereas light with the opposite handedness is transmitted (a “polarization stop band”).^[4] An obvious first extension of such a uniaxial structure is to arrange three sets of spirals along the three orthogonal directions in space (Fig. 1a). In general, however, this will not lead to mechanically connected structures, rendering the result essentially useless. By displacing the axes of the spirals by their radius as shown on the right-hand side of Figure 1a, a connection point of the three spirals in the center of each cubic cell can be enforced. After displacing two of the three axes, one is left with two non-equivalent options for positioning the third axis. This choice introduces a second type of chirality to the overall structure that is distinct from the chirality of the spirals. It is clear from this construction that the chiral optical properties will be identical for propagation of light along the three cubic axes—in sharp contrast to a uniaxial structure.

To test our concept of bi-chiral photonic crystals, we fabricated corresponding structures by means of standard 3D direct laser writing (DLW),^[14] which can be viewed as the 3D analogue of planar electron-beam lithography. We show a selection of electron microscopy images of fabricated structures in Figure 2 (further images are shown in the Supporting Information). Figure 2a depicts top-view images of all four bi-chiral combinations; Figure 2b shows an oblique view of a structure with right-handed corner and left-handed spirals (“right/left”). Note that the quality of these submicrometer structures is very high.

Next, we characterized these structures by normal-incidence optical transmittance spectroscopy using a Fourier-transform microscope–spectrometer (see Experimental).

The experimental results are shown in the left-hand column of Figure 3. For an ideal structure, we expect that, for instance, the transmittance of a right/right-handed structure for left-handed circular polarized incident light (LCP) is identical to that of a left/left-handed structure and right-handed circular polarized light (RCP). Our experimental results closely follow that expectation, indicating excellent reproducibility as well as sample quality. More importantly, it becomes evident that the differences between LCP and RCP are much more pronounced for the right/right and the left/left-handed photonic-crystal structures as compared to the mixed cases, that is, the right/left and the left/right-handed structures. The gray areas in Figure 3 highlight this aspect. As pointed out in the introduction, only the mixed cases are thermodynamically stable for the blue-phase cholesteric liquid crystals found in nature. Thus, our work on artificial materials allows us to access interesting and relevant structures that are simply not available in nature.

[*] M. Thiel, M. S. Rill, Dr. G. von Freymann, Prof. M. Wegener
Institut für Angewandte Physik and DFG-Center for
Functional Nanostructures (CFN)
Universität Karlsruhe (TH)
Wolfgang-Gaede-Straße 1, D-76131 Karlsruhe (Germany)
E-mail: michael.thiel@physik.uni-karlsruhe.de

Dr. G. von Freymann, Prof. M. Wegener
Institut für Nanotechnologie, Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft,
D-76021 Karlsruhe (Germany)

DOI: 10.1002/adma.200901601

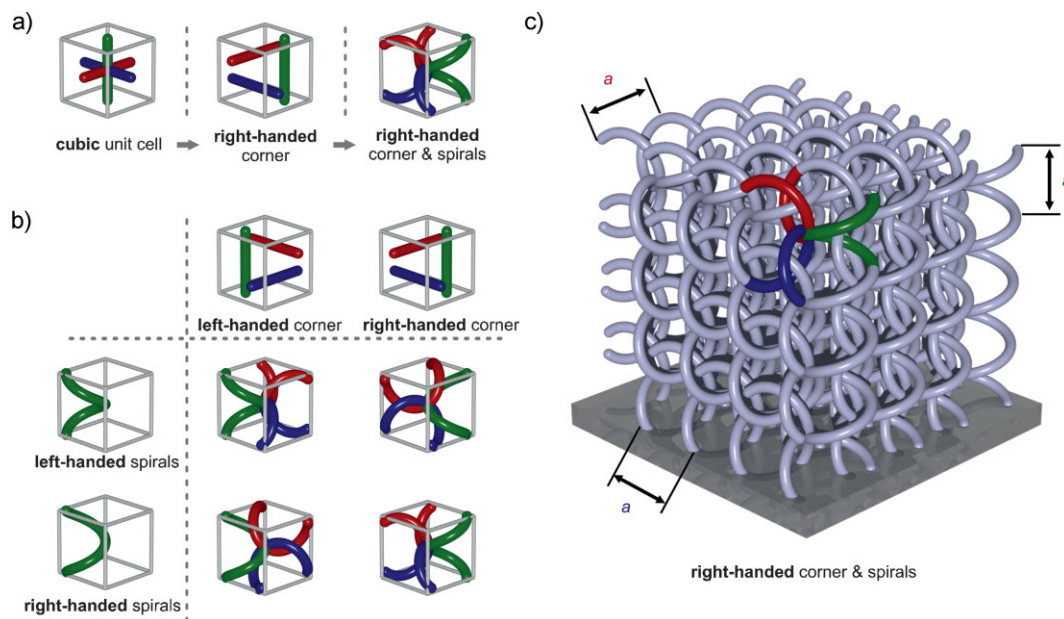


Figure 1. Our “bi-chiral” structures simultaneously exhibit two distinct types of chirality. The first type stems from the handedness of the circular spirals that are arranged on a simple cubic 3D lattice. a) Displacing the central spiral axes by half the spiral diameter enforces a mechanical connection point of the three spirals in the center of the unit cell. The orientation of these three fictitious spiral axes (the “corner”) introduces a second type of chirality. b) Combined with the chirality of the spirals, four distinct types of bi-chiral photonic crystals result, namely, left/left, right/right, left/right, and right/left-handed structures. c) Complete structure. The color coding is the same as in (a) and (b) and serves as a guide to the eye.

To further support our claims, we calculate the optical properties using a scattering-matrix approach,^[15,16] assuming a plane wave impinging under normal incidence. The refractive index of the polymer is taken as $n = 1.57$, that of the glass substrate as 1.52. The structure follows our above blueprint and the ellipticity of the “voxels” (a voxel is the smallest polymerized volume element and corresponds to the ellipsoidal laser focus)

in DLW is explicitly accounted for (aspect ratio of 2.7). The volume-filling fraction is 27.6%. The theoretical results shown in the right-hand column of Figure 3 agree well with the experimental values (Fig. 3, left-hand side). In particular, much more pronounced effects are found for the two cases where motif and corner have the same handedness as compared to the two mixed cases. The remaining small quantitative discrepancies

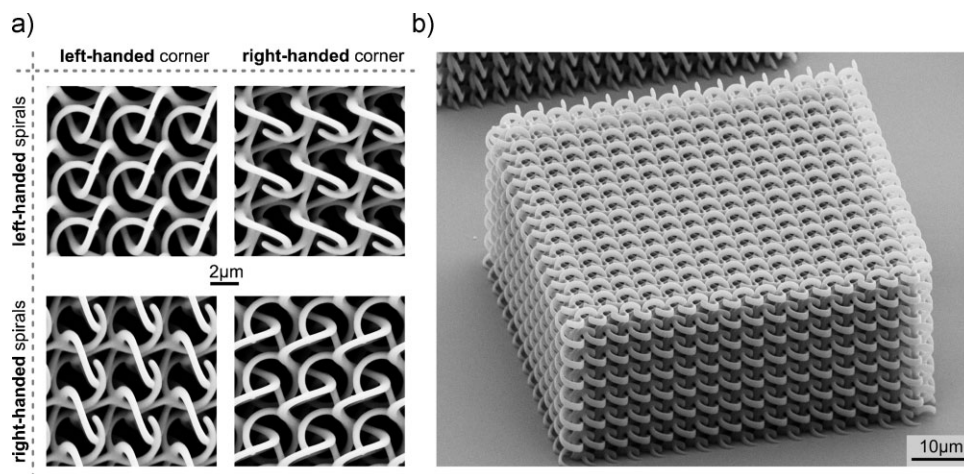


Figure 2. Electron microscopy images of fabricated bi-chiral photonic crystals. a) Top views on left/left, right/left, left/right, and right/right-handed photonic crystals. b) Oblique view on a right/left-handed polymer structure made by direct laser writing. The cubic lattice constant of all structures is $a = 4 \mu\text{m}$, their footprint is $60 \mu\text{m}$ times $60 \mu\text{m}$, and they contain seven lattice constants normal to the glass substrate plane. The diameter of every spiral is $L = 0.9a$.

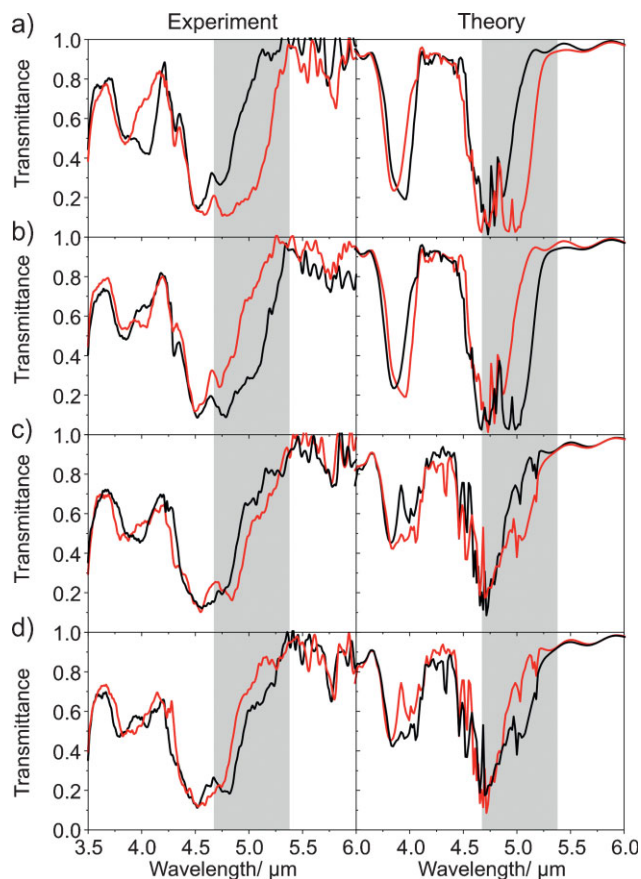


Figure 3. Transmittance spectra of the samples shown in Figure 2 taken/calculated under normal incidence for circular polarization of the incident light. Left-handed circular polarization (black) and right-handed circular polarization of the incident light (red) are shown for all four different bi-chiral structures. a) Right-handed corner/right-handed spirals (right/right), b) left/left, c) left/right, and d) right/left. Note that much larger circular dichroism is observed (see highlighted gray areas) for the right/right and the left/left-handed structures compared to the mixed cases left/right and right/left.

between experiment and theory are likely due to the finite opening angle of light in the optical measurements and/or due to small structural imperfections.

In conclusion, we have introduced, fabricated, and characterized bi-chiral dielectric photonic crystals. In these structures, one type of handedness stems from the motif (the spirals in our case) and the other one from the corner, that is, from the fictitious skeleton onto which the motif is arranged. We find much more pronounced chiral effects if motif and corner have the same handedness as compared to the mixed cases. Our concept of bi-chiral dielectric photonic crystals with cubic symmetry avoids the strong directional dependence of previous uniaxial structures while maintaining strong circular dichroism via pronounced polarization stop bands.

Experimental

Direct laser writing was carried out using a commercially available negative-tone photoresist SU-8 (MicroChem Corp.) and a commercial DLW system (Nanoscribe GmbH, see www.nanoscribe.de).

Optical spectra were taken on a Fourier-transform microscope-spectrometer (Bruker Tensor 27 with Hyperion 1000 microscope). Importantly, we custom modified this commercial instrument by constructing polarization optics that could be inserted and that allow broadband transmittance spectroscopy to be carried out with incident circular polarization of the light. The heart of this add-on was a super-achromatic quarter-wave plate (Bernhard Halle Nachfl.), with a retardation of $\lambda/4 \pm 14\%$ in the spectral regime of 2.5–7.0 μm wavelength. Furthermore, we modified the reflective Cassegrain optics by introducing a diaphragm such that the full opening angle of the incident light was reduced to around 5° . Normalization of all spectra was carried out with respect to the transmittance of the bare-glass substrate.

Acknowledgements

We thank Isabelle Stauder for help with the optical spectroscopy, Stefan Linden for writing the original version of the scattering-matrix approach computer program, and Joachim Fischer for valuable discussions in the early phase of this project. We acknowledge support by the Deutsche Forschungsgemeinschaft (DFG) and the State of Baden-Württemberg through the DFG-Center for Functional Nanostructures (CFN) within subproject A1.4. The research of G.v.F. is further supported through a DFG Emmy-Noether fellowship (DFG-Fr 1671/4-3). The Ph.D. education of M.T. and M.S.R. is embedded in the Karlsruhe School of Optics & Photonics (KSOP). Supporting Information is available online from Wiley InterScience or from the author.

Received: May 13, 2009

Published online: July 24, 2009

- [1] K. Robbie, M. J. Brett, A. Lakhtakia, *Nature* **1996**, 384, 616.
- [2] A. Chutinan, S. Noda, *Phys. Rev. B* **1998**, 57, R2006.
- [3] S. R. Kennedy, M. J. Brett, O. Toader, S. John, *Nano Lett.* **2002**, 2, 59.
- [4] M. Thiel, M. Decker, M. Deubel, M. Wegener, S. Linden, G. von Freymann, *Adv. Mater.* **2007**, 19, 207.
- [5] S. Zhang, Y.-S. Park, J. Li, X. Lu, W. Zhang, X. Zhang, *Phys. Rev. Lett.* **2009**, 102, 023 901.
- [6] E. Plum, J. Zhou, J. Dong, V. A. Fedotov, T. Koschny, C. M. Soukoulis, N. I. Zheludev, *Phys. Rev. B* **2009**, 79, 035407.
- [7] N. Liu, H. Liu, S. Zhu, H. Giessen, *Nat. Photonics* **2009**, 3, 157.
- [8] M. Wegener, S. Linden, *Physics* **2009**, 2, 3.
- [9] F. Mariotte, S. A. Tretyakov, B. Sauviac, *Microwave Opt. Technol. Lett.* **1994**, 7, 861.
- [10] W. Cao, A. Muñoz, P. Palfy-Muhoray, B. Taheri, *Nat. Mater.* **2002**, 1, 111.
- [11] H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang, T. Kajiyama, *Nat. Mater.* **2002**, 1, 64.
- [12] H. J. Coles, M. N. Pivnenko, *Nature* **2005**, 436, 997.
- [13] S. Meiboom, J. P. Sethna, P. W. Anderson, W. F. Brinkman, *Phys. Rev. Lett.* **1981**, 46, 1216.
- [14] S. Kawata, H.-B. Sun, T. Tanaka, K. Takada, *Nature* **2001**, 412, 697.
- [15] D. M. Whittaker, I. S. Culshaw, *Phys. Rev. B* **1999**, 60, 2610.
- [16] S. G. Tikhodeev, A. L. Yablonskii, E. A. Muljarov, N. A. Gippius, T. Ishihara, *Phys. Rev. B* **2002**, 66, 045102.