One-dimensional tunable photonic crystals with spin crossover material for the terahertz range

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(Received 5 July 2006; accepted 11 September 2006; published online 26 October 2006)

The authors use a spin crossover material as a defect inserted into a periodic structure of alternating layers of glass and air. A single defect mode of this Bragg filter designed for the submillimeter wavelength can be tuned over 15 GHz by inducing the spin transition of the defect. This shows potential applications of spin crossover materials at terahertz frequencies. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2369535]

Applications in the so-called "terahertz gap" currently exhibit a tremendous development; it is due to a fast recent progress in the terahertz technology which contrasts with a lack of experimental tools for extensive exploration of this wavelength area. The need for terahertz devices based on compact photonic structures continuously grows especially since terahertz waveguiding was achieved with metal wires.[1] Frequently, terahertz wave propagation in dielectric materials suffers from an intrinsic limitation by absorption effect caused by residual conductivity or by tails of low-frequency phonon modes. Another limitation is related to the high divergence of spatially limited terahertz beams propagating over long distances. To overcome these drawbacks, waveguide devices with or without active functionality could take benefit of artificial media such as photonic materials.

Photonic crystals (PCs) belong to this family. They are artificial periodic structures that allow for tailoring band gaps and device designing for versatile applications. Their main particularity is a frequency region in which the propagation of electromagnetic radiation is prohibited.[2,3] In this context, PCs with controlled defects, which exhibit highly localized defect modes,[4] are useful for construction of filters with a narrow transmission band,[5] resonant cavities,[6] mirrors, and waveguides.[7] To expand the flexibility, the design, and the application range of these PCs, it could be convenient to use "smart" materials, which exhibit significant variation of the dielectric function tuned by external control parameters. The resulting devices are of great interest for optical routing and spectroscopic applications since one can easily tune the defect modes by modulating the dielectric properties.[8–10] In this letter, we present such a tunable structure composed of spin crossover material. We demonstrate the tuning of a 15 GHz defect mode at room temperature in a photonic Bragg structure. Model calculations are in a very good agreement with the experimental results and underline the dramatic consequences of absorption phenomenon of active material.

Recently, the complex refractive index of an iron (II) spin crossover (SCO) coordination polymer,[11] precisely the $[Fe(NH_2\text{-trz})_3]Br_2 \cdot H_2O$ with NH_2-trz=1,2,4-aminotriazole, was measured in the terahertz frequency range by terahertz time-domain spectroscopy (terahertz-TDS). By scanning the temperature from 288 to 333 K, the evolution of the terahertz spectrum within the low spin (LS)-high spin (HS) thermal hysteresis loop was recorded. The diamagnetic LS state is the ground state at low temperature, while the paramagnetic HS state is stable at high temperature, due to its larger entropy. Because of elastic interactions between the spin crossover molecular units, the entropy-driven spin crossover may result in a first-order thermal transition occurring with hysteresis. The spin state can as well be switched by pressure (of the order of kilobars), magnetic field (typically around 40 T), or irradiation in the visible spectral range.[12] The switching results in large changes in magnetic, optical, and dielectric properties, which are promising for future applications. Furthermore, these compounds offer many prospects for optical switches, which can be performed by the so-called direct or reverse-light-induced excited-spin state trapping (LIESST) effect.[13] This phenomenon is attractive as it combines (i) a low addressing power (about 5 mW/cm^2), (ii) a short addressing time (femtosecond scale, the spin transition being purely electronic in nature), (iii) a perfect reproducibility over successive cycles, even in a solid matrix, and (iv) an optical reversibility, since the LS→HS transition can be induced with a green light, while the reverse (HS→LS) state conversion can be addressed with a red light.

In the terahertz spectra the LS-HS transition of the $[Fe(NH_2\text{-trz})_3]Br_2 \cdot H_2O$ complex has a marked spectral signature in the millimeter wavelength range with a hysteresis of about 20 K close to room temperature.[11] In the

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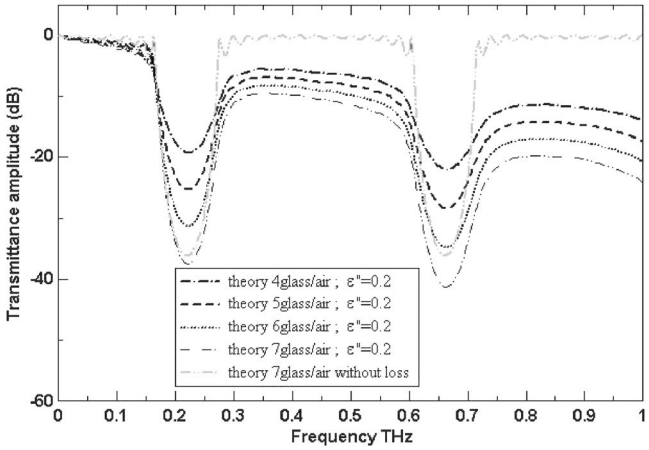

FIG. 1. Transmission spectrum of a photonic structure without defect. Absorption strongly affects the transmittance of the photonic structure. ε'' is the imaginary part of the complex permittivity.

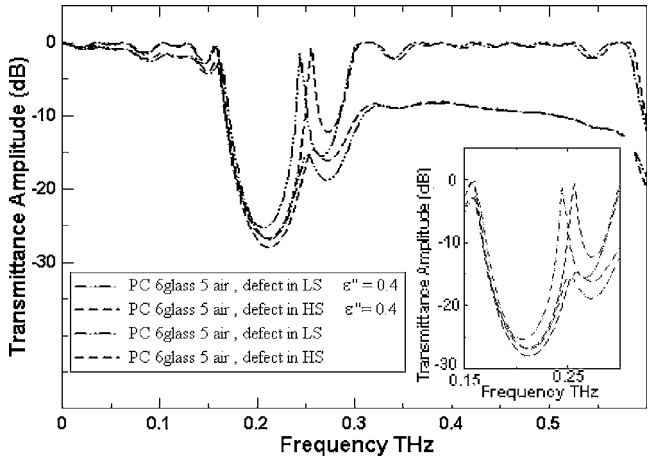

FIG. 2. Transmission spectra of the PC (glass 170 μm/air 350 μm) with SCO material as defect at the center. The calculation took into account strong absorption of the defect layer (−15 dB). Inset: Zoom of the forbidden band.

0.1–0.6 THz frequency range, the variations of real and imaginary parts of the index of refraction reach 6% and 20%, respectively. The origin of these variations of the dielectric function of SCO compounds is supposed to result from a spontaneous distortion of the coordination sphere of the metal center. In fact, upon the spin crossover phenomenon, a significant variation of the metal-ligand bond length occurs. It is induced by a deformation of the electronic molecular orbital between the LS and HS states. Therefore, the local electrical dipoles in the material are different in the two spin states, leading to a significant change in the permittivity of the material upon spin transition.[12,14] In this context, we propose to use this modulation of the dielectric function to achieve tunability of a Bragg structure.

The proposed structure forms an easy-to-fabricate compact and cheap Bragg structure working in the terahertz range. The investigated configuration can be considered as a one-dimensional PC with a defect layer symmetrically sandwiched between two Bragg mirrors. The device under test consists of a stack of alternating layers defined by their thicknesses t_i and their complex refractive indices N_i ($i=1,2$). In practice, the structure was fabricated by alternating glass slides and air layers (the thickness of the air layers was fixed by well defined spacers). The refractive index of glass $N_1=n_1+i\kappa_1$ in the terahertz frequency range was measured by stacking several wafers of the same kind and by measuring their transfer function by terahertz-TDS using the experimental setup described in Ref. 15. The glass does not show a strong dispersion within the frequency range studied: $n_1=2.1$ from 0.1 to 2 THz, while its absorption index κ_1 linearly increases up to 0.2 at 2 THz due to a significant amount of residual charges in commercial microscope slides.

On the basis of these experimental values, we performed a series of analytical calculations of the transmittance of a finite multilayered structure with N glass/air bilayers (i.e., without the defect layer) based on the transfer matrix formalism.[16,17] The targeted spectral range for the operation of the structure was around 200 GHz, where the losses of all the components of the PC remain reasonably low. $\tan\delta$ (which is $\varepsilon''/\varepsilon'$) of the spin crossover sample in LS and HS states are 0.06 and 0.18, respectively. The thicknesses of the structure layers are the following: a 170 ± 10 μm for glass and 350 ± 10 μm for air. These dimensions satisfy the Bragg reflection rule ($t_1n_1=t_2n_2=\lambda/4$, where t_1, n_1, t_2, n_2 are, respectively, the thickness and the refractive index of the glass and air layers and λ the operating wavelength). Figure 1 shows the calculated transmittance of the structure versus frequency for $N=6$. Note that losses resulting from glass plates induce only a weak influence on the first forbidden band. Above 300 GHz, absorption effect progressively becomes more pronounced and the transmission in decibels of the whole Bragg structure is linearly diminished by a factor directly related to κ_1 the extinction coefficient.

The next step consists in studying the opportunity offered by the introduction of a defect layer and its active control through the molecular bistability of the spin crossover system. For this purpose, we replace the central air layer by our SCO material. Maximum tunability of this structure, i.e., tuning capability over the entire forbidden band, will be achieved if the optical thickness of the defect can be changed by an amount comparable to the central wavelength of that forbidden band.[16] In order to design the layer for an optimum tuning, the material chosen for the defect should exhibit a large change in dielectric properties, and its losses should be as weak as possible to simultaneously yield high peak transmission and good quality factor. Knowing the permittivity and loss tangent by the use of time-domain terahertz spectroscopy, the design of the layers enclosing the defect is also important for the terahertz properties of the structure. The higher the reflectivity of the Bragg mirrors is, the narrower the defect mode and the higher the effective losses in the defect are. Consequently, Bragg mirrors with moderately high reflectivity constitute a good compromise for a high peak transmission.

Calculation of a transmission spectrum of the structure with a 350-μm-thick SCO layer defect is shown in Fig. 2. One can clearly identify the defect mode occurring at 255 GHz in the first gap. After SCO transition, the defect transmission window shifts to 240 GHz due to the change in refractive index. Also presented in this figure is the impact of losses in the SCO materials which can dramatically reduce the peak transmission at the defect mode frequency. The defect level appears at the center of the first forbidden band for a SCO layer thickness of 450 μm. That is why we prepared samples with a defect layer of thickness 350 μm, which is a good trade-off with respect to the SCO material losses.

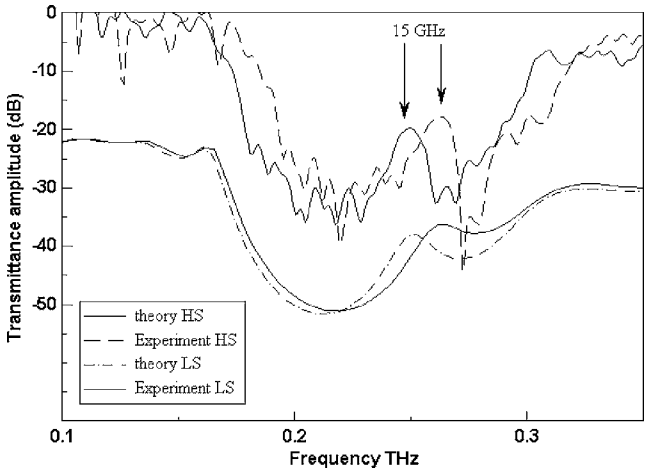

FIG. 3. Experimental transmission spectra of the PC with SCO material acting as a defect. Tuning of 15 GHz is measured while SCO transition occurs. For clarity we shifted theoretical calculations by 20 dB.

For comparison, an example of experimental transmission spectrum of the structure with a 350-μm-thick defect layer is shown in Fig. 3. One can clearly identify the first band gap between 150 and 300 GHz (higher order band gaps are not shown). The frequency resolution of the terahertz-TDS is about 4 GHz for 250 ps long scans performed in this study. To reduce experimental error source related to sample positioning, we made our measurements on the same sample and quantified the transmitted field through the PC with and without the defect level by simply translating the PC located at the terahertz focus. Calculations show that as soon as the absorption index κ of the defect is larger than 0.1, the peak defect level is reduced by 15 dB in transmission for the first band and practically disappeared in the second and the third band. This underlines the critical aspect of losses in order to preserve the benefit induced by the insertion of a defect level in a PC and probably opens future work concerning the use of SCO as active material at terahertz wavelength. From experimental data, we detected a shift of 15 GHz of the defect frequency induced by the spin transition. These results are in very good agreement with calculations except for the experimental transmission which is lower than that predicted by theory above 300 GHz (we measured −5 dB in comparison with −10 dB calculated).

In conclusion, we have shown that the terahertz-TDS technique can be efficiently used to quantitatively characterize the far infrared properties of one-dimensional photonic crystals. Moreover, we have theoretically and experimentally demonstrated control over the defect level position by sweeping the dielectric hysteresis property of spin crossover materials. This effective evidence indicates the potential use of spin crossover materials in electronic devices up to 500 GHz. Then these results provide opportunities to read out information in the terahertz domain. Furthermore, these compounds offer many prospects for optical switches, which can be performed by the so-called direct or reverse-LIESST effect.

The work of one of the authors (P.K.) was supported by the Ministry of Education of the Czech Republic (Project No. LC512). Two of the authors (J.F.L. and E.F.) would also like to thank the Aquitaine Region of Bordeaux and the network of excellence MAGMANet (FP6-515767-2) for supporting the technical development of the photomagnetic platform.

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