

Porous One-Dimensional Photonic Crystals for Color Sensing of Vapors and Liquids*

T. Babeva

Acad. J. Malinowski Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl. 109, 1113 Sofia, Bulgaria

Received 3 November 2016

Abstract. One-dimensional photonic crystals are artificial structures, where refractive index varies periodically in one direction. Unlike Bragg stacks, they are characterized with omnidirectional reflectance, i.e high reflectance for all incidence angles and polarizations of light. Thus they are very suitable for utilization as color indicators of liquids and vapors, because the change of the color will be exclusively due to the presence of analyte, not to the change of viewing angle.

In the present study, chalcogenide glasses (GeSe_2) and sol-gel metal oxides (Ta_2O_5 and V_2O_5) are used as high refractive index material providing sufficient optical contrast, while zeolite and polymer (PMMA) films are employed for sensitive materials with low refractive index that change their optical properties or thicknesses upon exposure to analyte. Selective optical detection of acetone and chloroform based on monitoring of color change is demonstrated and discussed.

PACS codes: 78.67.Pt, 78.55.Mb, 42.70.Qs, 78.20.Ci

1 Introduction

One dimensional photonic crystals are artificial structures, where refractive index varies periodically in one direction. Usually they are fabricated in the form of Bragg stack, i.e as multilayers systems comprising alternating layers with high (n_H) and low (n_L) refractive index and quarter-wavelength thickness $n_H d_H = n_L d_L = \lambda_c/4$, λ_c – wavelength and d – thickness of the layers. Due to the periodicity and quarter-wavelength thickness all waves that reflected from the boundaries of the stack are in phase. Their interference leads to formation of high reflectance band that is centered at λ_c . When λ_c is within the visible range, the stack exhibits a bright color called structural color. Both the position of the band (λ_c) and the color of the stack depend on the parameters of the stack

*This article is based on a talk given at the 3rd National Congress on Physical Sciences, 29 Sep. – 2 Oct. 2016, Sofia.

(n_H , n_L and d). If the stack's parameters change due to an external stimulus, the reflectance band shifts and the color of the stack changes, thus indicating the presence of external stimulus. However, the position of reflectance band is very sensitive to the angle of incidence. This means that at different viewing angles the stack will be colored differently. When the detection is performed by visual inspection of the color the observer will be confused because he will not be sure if the change is due to the presence of some analyte or to slight change of the viewing angle.

One possible decision is the omnidirectional reflection (ODR), where high reflectance is obtained for all incident angles and polarization of light. Besides, the stack with ODR has the same color at different angles of observation. However, in order to reach omnidirectional reflection some restrictions on n_H and n_L exist: (1) the optical contrast (difference in refractive indices of both materials) has to be higher than 0.75 [1]; and (2) the value of high refractive index material to be greater than 2.264 [1,2]. Even if the first requirement is fulfilled by using appropriate pair of materials like TiO_2 and SiO_2 [3-5], it is not a trivial task to find porous material with refractive index higher than 2.264. Unfortunately the widely used materials such as porous metal oxides TiO_2 , ZnO etc., do not satisfy the second requirements. A careful selection of materials is demanded that should provide permeable materials with refractive index as high as possible that change their parameters upon exposure to external stimuli.

In this paper we present our results on development of building blocks for porous Bragg stacks. As high refractive index materials we use thermal evaporated thin films of chalcogenide glasses (GeSe_2) and sol-gel metal oxides (Ta_2O_5 and V_2O_5). As sensitive materials with low refractive index we utilize spin-coated thin films of zeolite and polymer (PMMA). Two types of color detection of vapors and liquids, based on the change in refractive index and thickness, are discussed and demonstrated.

2 Principle of Color Sensing of Vapors and Liquids

The principle of color sensing is illustrated in Figure 1. Upon exposure of one-dimensional photonic crystals to analyte, the molecules enter the empty pores and initiate change of refractive index or thickness of the layers comprising the 1D structure. As a result the optical thickness increases and leads to a shift of reflectance band and consequent change of the color of the stack. In an ideal case this change is proportional to the concentration of the detected analyte.

Figure 2 presents an example of omnidirectional reflectance for Bragg stack comprising layers with optical contrast of 0.8 ($n_H = 2.3$, $n_L = 1.5$). The short and long reflectance edges at level of 98% for both p- and s-polarization are plotted as functions of incident angle. It is seen that with increasing the angle of incidence, the reflectance band at normal incidence ($x = 0^\circ$) shifts

Porous 1D Photonic Crystals for Color Sensing of Vapors and Liquids

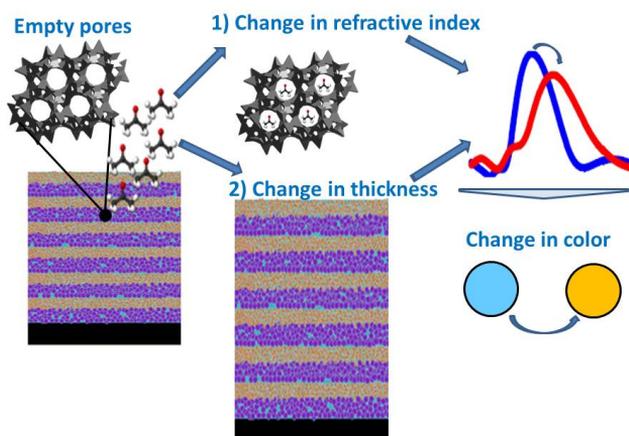


Figure 1. Principle of color sensing of vapors and liquids using one dimensional photonic crystals (color online).

towards shorter wavelength, widening for s-polarization and narrowing for p-polarization. The overlapping area of all bands is the omnidirectional reflectance band within which the stack has a reflectance higher than 98% (in this case) for all incidence angles and polarization types of light. ODR band for the particular case presented in Figure 2 is centered at 578 nm and has width of 4 nm. As the

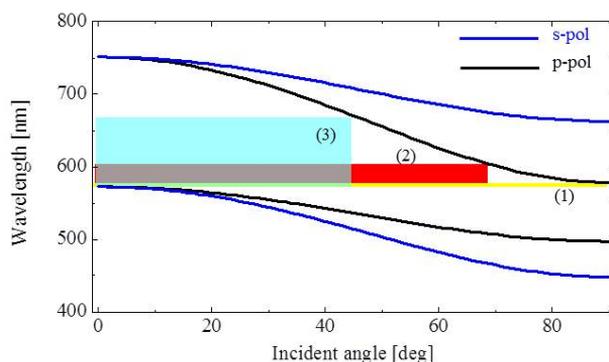


Figure 2. Long- and short-wavelength edges of the reflectance band at level of 98% for quarter-wave stack comprising layers with $n_H = 2.3$ and $n_L = 1.5$ as a function of the incident angle for p- and s-polarized light. The yellow rectangle (1) presents the omni-directional reflectance (ODR) band of the stacks, while the red (2) and blue one (3) are for quasi-ODR band corresponding to angles within the ranges of 0–70° and 0–45°, respectively (color online).

angle range gets narrower a quasi-omnidirectional band appears that shifts to higher wavelengths and widens with decreasing the angle range. Our additional calculations have shown that when n_L decreases from 1.5 to 1.2, the omnidirectional band disappears although the optical contrast increases from 0.8 to 1.1. For reappearing of ODR band n_H should be increased. Therefore, in order to achieve ODR it is very important the building blocks of Bragg stack to be appropriately chosen.

3 Materials and Methods

For materials with high refractive index we employ chalcogenide glass GeSe₂ [6], Ta₂O₅ [7,8] and V₂O₅ [9]. The bulk GeSe₂ glass was synthesized in a quartz ampoule by the method of melt quenching from the elements of purity 99.999% [10]. The layers were deposited by thermal evaporation with a deposition rate of 0.5–0.7 nm/s in a vacuum of 10⁻³ Pa.

Thin films from Ta₂O₅ and V₂O₅ with thicknesses in the range 50–150 nm were prepared by using methods of sol–gel and spin-coating [7-9]. The tantalum sol was prepared according to the previously developed water free procedure [7,8]. Briefly, 1.5 ml Ta ethoxide Ta(OC₂H₅)₅ (99.98%, Sigma-Aldrich) was dissolved in 50 ml of isopropyl alcohol and 3 ml of glacial acetic acid (CH₃COOH, Sigma-Aldrich). After 30 min stirring, 1 ml diethanolamine (HN(CH₂CH₂OH)₂, 98%, Sigma-Aldrich) was added. The obtained solution is subjected to slow stirring for 18 h.

Vanadium sol was prepared using 1.5 ml of Vanadium(V) oxytriisopropoxide (Sigma Aldrich) dissolved in a mixture of 17.5 ml acetone and 17.5 ml isopropanol for the dense films or 0.6% v/v solution of Pluronic PE6100 (BASF) for porous films, stirred for 2 h at room temperature [9].

For low refractive index material we used zeolite and polymer thin films. The former change their refractive index upon exposure to analyte, while polymer changes its thickness. Zeolites (molecular sieves) are crystalline materials with framework-type structures built of regular and uniform pores of molecular dimensions [11]. They have low refractive index (1.15-1.35) [12] and high affinity to organic solvents. Besides, thin films with good optical quality can be deposited by simple methods [12,13]. We use two types of zeolites synthesized in the Laboratory of Catalysis and Spectroscopy, Normandy University, ENSI-CAEN, CNRS, Caen, France.

Pure silica MFI-type zeolite (Si-MFI) was synthesized according to the procedure described in [14]. The synthesis was performed at 90°C for 3 days. After the hydrothermal treatment, the zeolite nanoparticles were purified by two steps centrifugation (24.500 rpm, 1 h) and redispersed in double distilled water. MEL zeolite crystals were synthesized from a colloidal precursor suspension with the following chemical composition: 1.0SiO₂: 0.3TBAOH: 4.0EtOH:

18.0H₂O (TBAOH – tetrabutylammonium hydroxide, EtOH – ethanol). The precursor suspension was heated at 90°C for 68 h [15]. After the synthesis, the precursor suspension was purified using high-speed centrifugation, and finally redispersed in ethanol.

For deposition of thin films, the zeolite-ethanol suspensions and metal sols were spin-coated on silicon wafer (2500 rpm and 30 s), followed by annealing at 320°C for 30 minutes. The stacks were prepared by alternative deposition of oxide and zeolite films. After deposition of each layer a thermal treatment was applied in order to avoid its destruction during the deposition of the next layer.

The sensing properties of the films and stacks were investigated through measurements of reflectance spectra of the films with CARY 05E UV-VIS-NIR spectrophotometer and homemade sensor set-up [16]. CIE (Commission Internationale de l’Eclairage) tristimulus color coordinates were calculated using the measured reflectance spectra at normal and oblique incidence of unpolarized light through already developed program codes [17,18].

4 Results and Discussions

4.1 Color sensing of liquids

Here we are going to present two examples of color sensing of liquids. The first one employs bi-layered stack of GeSe₂ (130 nm) and MEL thin films (260 nm). Our calculations (not shown here) proved that Bragg stack comprising GeSe₂ ($n = 2.65$ at 600 nm) and MEL zeolites ($n = 1.18$ at 600 nm) has an omnidirectional reflectance (ODR) band with width of 6 nm and wider quasi-ODR band of 55 nm for angle ranging from 0 to 70 degrees. However, it is interesting to check how the color of the stack changes when it is illuminated with white light. Figure 3(a) shows CIE coordinates calculated for 7-layers stack as a function of incident angle. As the incident angle increases the color of the stack changes from yellow-green to blue-green. Nevertheless, there are ranges of angles (0-30°, for example) where the color is the same thus providing the possibility for color sensing. The red shift of reflectance band when the stack is immersed in methanol and acetone was presented in Figures 3(b) and 3(c), respectively. In the case of methanol the shift is 12 nm, that is 3 times more as compared to acetone. The shift leads to 7% change of the signal at fixed wavelength in the case of methanol and 4.5% for acetone. The shift is accompanied with detectable change of the color from blue to blue-violet in the case of methanol immersion and insignificant color change in the case of acetone (Figure 3(d)).

The inconvenience of GeSe₂-MEL building block of Bragg stack is the requirement of two different techniques for films deposition: thermal evaporation and spin-coating. It will be a real advantage if both films are deposited by the same simple method. Thus using sol-gel and spin-coating we prepared 5-layers stack

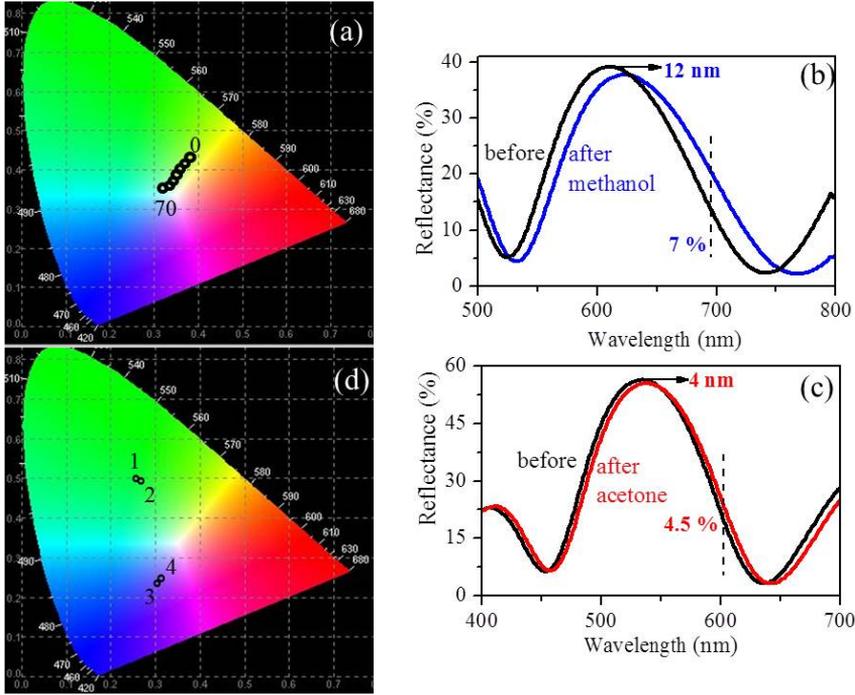


Figure 3. (a) Calculated CIE coordinates for 7-layers stack comprising GeSe₂ and MEL thin films as a function of incident angle; Reflectance spectra of GeSe₂ – MEL bi-layers measured prior to and after exposure to liquid methanol (b) and acetone (c); CIE color coordinates for GeSe₂ – MEL bi-layer before (points 1 and 3) and after (points 2 and 4) acetone (points 1 and 2) and methanol (points 3 and 4) exposure (color online).

consisting of Ta₂O₅ and MEL films with thicknesses of 72 nm and 102 nm, respectively. In order to achieve higher reflectance the stack starts and ends with Ta₂O₅ film. After immersion in analyte the effective refractive index of zeolite increases because the air inside the pores with refractive index 1 is replaced with liquid with higher refractive index. As a result reflectance band shifts towards longer wavelengths and a change of color of the stack is expected. The shift of high reflectance band in the case of immersion of 5-layers Ta₂O₅ / MEL stack in acetone and methanol is presented in Figures 4(a) and (b). A selective shift of 30 nm is obtained in the case of acetone and only 9 nm for methanol. In the case of water the change is even smaller – less than 4 nm. As it is expected the shift of reflectance band is accompanied with substantial change of the stack's color from blue-greenish to yellow-green (Figure 4(c)), while there is no color change in the case of methanol and water. Our additional calculations have shown that the optical contrast in the case of Ta₂O₅ / MEL stack is 0.7 [7] that is insufficient for ODR band to open. The calculated CIE coordinates for the reflectance of the

Porous 1D Photonic Crystals for Color Sensing of Vapors and Liquids

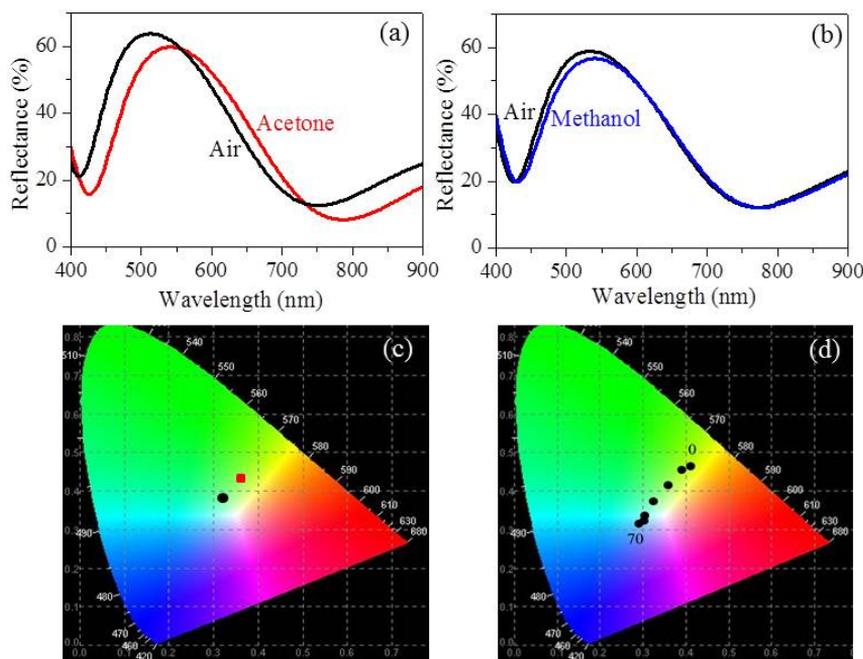


Figure 4. Reflectance band of 5-layers stack consisting of Ta_2O_5 (72 nm) and MEL zeolites (102 nm) layers prior to and after immersion in acetone (a) and methanol (b); Calculated CIE coordinates for reflectance spectra measured before and after acetone immersion (c) and of the stack as a function of incident angle (d) (color online).

stack at different incident angles (Figure 4(d)) show that the color of the stack changes from yellow to blue-green as the viewing angle increases from 0 to 70 degrees. Still, there is a narrow range of viewing angles (0–20°) inside which the color is independent of the angle. With the current advances in technology, it will not be difficult the detection of color to be performed with the camera of a smartphone [19]. Then the range of angles where the stack has the same color is not so narrow.

4.2 Color sensing of vapors

The changes in the refractive index of zeolite films are much smaller when exposed to vapors of the analyte. Therefore, there is no overall displacement of reflectance band, only the short wavelength edge shifts towards longer wavelengths. Color sensing of vapors is also possible, but in order to obtain detectable change of color the sensing material has to change its thickness upon exposure to vapors, not only its refractive index. Considering this we have studied Bragg stacks consisting of Poly(methyl methacrylate) (PMMA) as sensitive layers and sol-gel V_2O_5 layers providing high optical contrast [9].

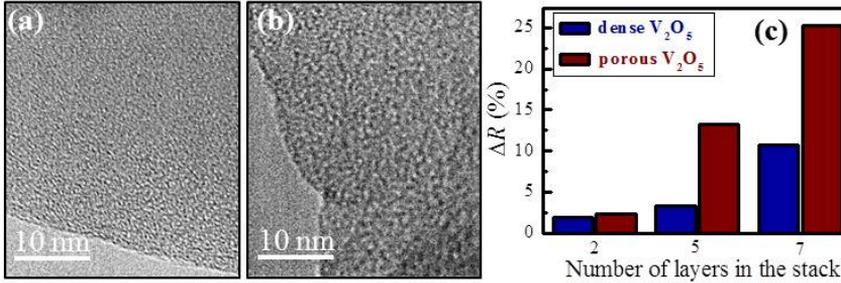


Figure 5. TEM images of dense (a) and porous (b) V_2O_5 films; Reflectance change of stacks consisting of alternating dense or porous V_2O_5 and PMMA films due to exposure to chloroform vapors as a function of number of the layers in the stack (c) (color online).

In order to increase the sensitivity an artificial porosity was introduced in V_2O_5 using organic template (Pluronic, BASF). After annealing at $320^\circ C$, the template burns out leaving empty pores in the film. The comparison between dense and porous films morphology is presented in Figure 5. An increase of pores size with addition of Pluronic is clearly seen. The optical response of stacks consisting of different number of alternating V_2O_5 (porous or dense) and PMMA films when exposed to chloroform vapors is shown in Figure 5(c). In the case of porous V_2O_5 films the response is 2 to 3 times stronger as compared to stacks comprising dense V_2O_5 films because the bigger pores facilitate the penetration of analyte vapors.

When the porous stack is exposed to chloroform vapors there is a red shift of reflectance band that is as stronger as the exposure time is longer. Concerning the selectivity, the optical response of the stack is 4 times higher for chloroform vapors as compared to acetone vapors (Figure 6(b)). There is no change for

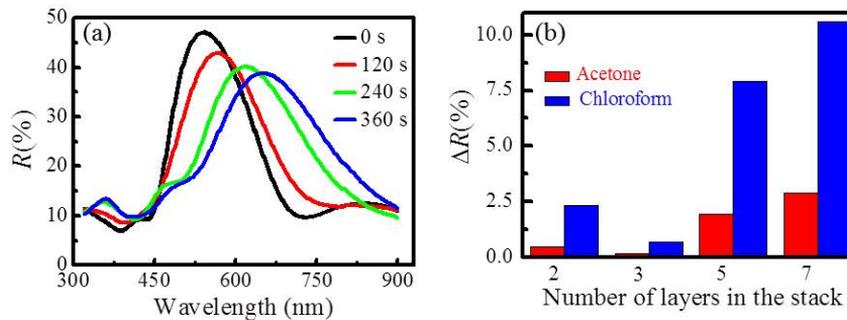


Figure 6. Reflectance band of 7-layers stack consisting of porous V_2O_5 and PMMA films exposed to chloroform vapors for different time (a); Reflectance change of the stack when exposed to acetone and chloroform vapors for 120 s (b) (color online).

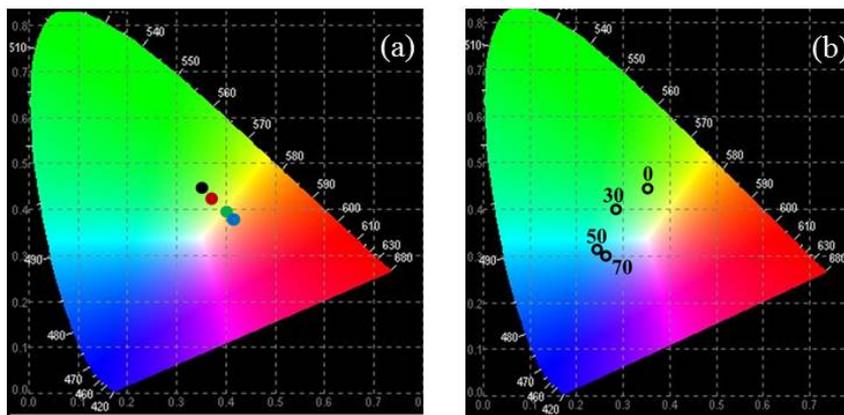


Figure 7. Calculated CIE coordinates using reflectance spectra of 7-layers stack consisting of alternating porous V_2O_5 and PMMA films (a) exposed to chloroform for 120 s (red circle), 240 s (green circle) and 360 s (blue circle) and (b) for unpolarized light incident at different angles denoted on the plot (color online).

ethanol, methanol and water vapors.

The red shift of the reflectance band results in gradual change of the color of the stack from green before exposure to red after 360 s of exposure to chloroform vapors. Unfortunately, because of the low optical contrast (0.47 in the case of porous V_2O_5 film) both the reflectance of the stack at oblique incidence and the color are sensitive to incident / viewing angles (Figure 7(b)). Our calculations of CIE coordinates using measured reflectance spectra at oblique incidence show that the color changes from green to blue when the viewing angle increase from 0 to 70 degrees. However, if we increase the optical contrast by using dense V_2O_5 films, then weaker sensitivity of color to the viewing angle will be achieved, but the sensor sensitivity will drop by 2 to 3 times. Therefore, a compromise between the porosity level and omnidirectional reflectivity has to be done in order the optical indicator to be more sensitive.

5 Conclusions

It is shown that one dimensional photonic crystals comprising sensitive materials such as zeolites and polymers that change their optical parameters and / or thicknesses could be utilized for selective color sensing of liquids and vapors of volatile organic compounds. Depending on the optical contrast between the constituent blocks of the stack, the color is more or less sensitive on the viewing angle. As the porosity of high refractive index layer increases, its refractive index decreases and the sensitivity of the color on viewing angle becomes stronger. A compromise between porosity and omnidirectional reflectivity should be found.

Acknowledgments

The author thanks to all collaborators and co-authors from IOMT and LCS, Caen, France. The partial financial support of National Science Find – Bulgaria under the project DRILA-D01/13 from PHC RILA 2015 program and project DFNP-199/14.05.2016 of the Program for career development of young scientists, BAS is highly appreciated.

References

- [1] S.H. Kim, C.K. Hwangbo (2002) *Appl. Opt.* **41** 3187.
- [2] T.J. Clement, N. Ponnampalam, H.T. Nguyen, R.G. DeCorby (2006) *Opt. Express* **14** 1789.
- [3] S.Y Choi, M. Mamak, G. Freymann, N. Chopra, G. Ozin (2006) *Nano Letters* **6** 2456.
- [4] M. Anaya, A. Rubino, M.E. Calvo, H. Miguez (2016) *Mater. Chem. C* **4** 4532.
- [5] D. Lee, M. Rubner, R. Cohen (2006) *Nano Letters* **6** 2305.
- [6] T. Babeva, R. Todorov, B. Gospodinov, N. Malinowski, J. El Fallah, S. Mintova (2012) *J. Mater. Chem.* **22** 18136.
- [7] B. Gospodinov, J. Dikova, S. Mintova, T. Babeva (2012) *J. Phys.: Conference series* **398** 012026.
- [8] T. Babeva, K. Lazarova, M. Vasileva, B. Gospodinov, J. Dikova (2013) *Bulg. J. Phys.* **40** 253.
- [9] K. Lazarova, R. Georgiev, M. Vasileva, B. Georgieva, M. Spassova, N. Malinowski, T. Babeva (2016) *Opt. Quant. Electron.* **48** 310.
- [10] K. Petkov, G. Vassilev, R. Todorov, J. Tasseva, V. Vassilev (2011) *J. Non-Cryst. Solids* **357**, 26692.
- [11] R.M. Barrer (1982) *Hydrothermal Chemistry of Zeolites*, Academic Press, London.
- [12] T. Babeva, H. Awala, M. Vasileva, J. El Fallah, K. Lazarova, S. Thomas, S. Mintova (2014) *Dalton Trans.* **43** 8868.
- [13] T. Bein, S. Mintova (2005) *Stud. Surf. Sci. Catal.* **157** 263.
- [14] S. Mintova, N.H. Olson, J. Senker, T. Bein (2002) *Angew. Chem.* **41** 2558.
- [15] S. Mintova, N. Petkov, K. Karaghiosoff, T. Bein (2001) *Micropor. Mesopor. Mater.* **50** 121.
- [16] K. Lazarova, H. Awala, S. Thomas, M. Vasileva, S. Mintova, T. Babeva (2014) *Sensors* **14** 12207.
- [17] CIE Technical Report: Colorimetry (2004), third ed., Commission Internationale De l'Eclairage, Vienna, Austria.
- [18] R.J. Mortimer, T.S. Varley (2011) *Displays* **32** 35.
- [19] O. Dalstein, D. Ceratti, C. Boissière, D. Grosso, A. Cattoni, M. Faustini (2016) *Adv. Funct. Mater.* **26** 81.