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Optical Materials Based on Nanoscaled Guest/Host Composites

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Ordered periodic microporous and mesoporous materials allow the construction of composites with many guest types, e.g. organic molecules, inorganic ions, semiconductor clusters or polymers. These guest/host materials combine high stability of the inorganic host system, new structure forming mechanisms due to the confinement of guests in well defined pores, and a modular composition. This could lead to new optical materials which are described in this paper by examples in switches, nonlinear optics and lasers.

Keywords: optical switch; nonlinear optics; mesoporous; laser material

INTRODUCTION

Is it possible to construct desired materials on a molecular level? Or is, what we call material design, more or less an optimization of already existing materials found occasionally? Of course, materials scientists try to realize a molecular design of materials, but the practical success has, so far, been restricted to a few examples only. However, these examples are a strong motivation for new research directions, especially in the area of nanoscience.

A material is made to fulfill certain functions. It is, therefore, important to understand the relationship between function and structure. Based on that, a particular structure can be tried to realize. Nonetheless, this task becomes extremely complex since one function alone generates a whole number of requirements. In order to design new materials, it is not sufficient to synthesize new solids, determine their properties and to find out whether or not these are superior to already existing materials. One decisive question is, whether the new material will be adequate to fulfill all of the requirements simultaneously. In case there is such a material, a practical demonstration for testing the desired

function must be possible. This test is the only convincing proof that truly a new, useful material has been synthesized.

A strategy to achieve the simultaneous meeting of different requirements is to focus on systems which allow a nearly independent tuning of different material properties. From this point of view, guest/host composites are very promising because the guest and the host are mostly connected with different material properties which can then be influenced independently. In the following, three examples are given for the demonstration of this approach.

MATERIALS FOR OPTICAL SWITCHES

An optical switch is made for changing the electromagnetic radiation under the influence of a control signal. The change can happen in the intensity, phase or polarization. The control can be realized optically or electronically. The material used for a switch must change its optical properties strongly to be suited for an effective switch. However, there are a number of additional requirements for a useful switch: low damping in at least one state (ON), high stability, high sensitivity and a short switching time. There are several solutions to this bunch of requirements but neither of them are fully satisfactory. For example, classical photorefractive crystals are stable and fast, but their switching effect (dynamical range of the refractive index) is very low: $\Delta n = 10^{-5} \ldots 10^{-4}$. Optical orientation of chromophores in polymers have much larger switching effects but this process is very slow. Since all the existing solutions have drawbacks, it is worth trying to find appropriate alternatives.

Our approach[1,2] to construct a switch, is based on the well-known photochemical trans-cis reaction of azobenzene. Azobenzene has been incorporated into the channels of the molecular sieve $AlPO_4$-5 by a gas-phase loading process. The 7.3 Å-wide channels of $AlPO_4$-5 can host the trans form as well as the cis form of the molecule. The composites have been irradiated with light of 360 nm and 436 nm, respectively. It can easily be proven that the

photoisomerization occurs in this composite by applying absorption spectroscopy on individual microcrystals.

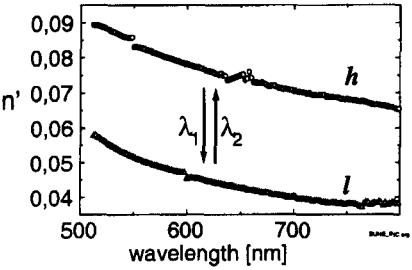

FIGURE 1 The change of the birefringence $n'=n_e-n_o$ of an azobenzene/$AlPO_4$-5 composite after irradiation with light of 360 nm or 436 nm, respectively.

Furthermore, the polarization-depending spectra reveal that the isomerization is accompanied by orientational changes of the guest in the host channels. The trans form of the molecule turns out to be much better aliened than the cis form. This may result from the different shape of the isomers or from the dipole moment of the cis-azobenzene. The orientational changes are very important because they can be used for changing optical properties. For example, big changes must be expected in the refractive index as a result of the orientation effects. By measuring the transmission of the crystal between two polarizers, the birefringence can be determined. Fig. 1 gives a typical result revealing the birefringence change to be 0.03. This value depends on the preparation and on the individual crystal chosen. The maximum value found so far, reached 0.046. Furthermore, the other parameters of this material also look very promising. The sensitivity of the material (S_{n2}) is in the order of 10 cm^2/kW, resulting in a similar energy consumption for the switching process as photorefractive crystals or switchable polymers. The switching time could reach nanoseconds, although this has not yet been demonstrated.

NLO MATERIALS

Nonlinear optical (NLO) materials allow the interaction of light waves with each other or with static fields. One of the simplest processes of this kind is second harmonic generation (SHG). This process is well suited for the examination of the problems connected with the desired construction of NLO materi-

als. Besides realizing high nonlinearities, it is crucial to make the SHG phase-matchable. This means that only certain components of the nonlinear susceptibility tensor can be used for the NLO process and that the refractive indices must fulfill a definite relation. In addition, low absorption, low scattering and a high stability is required for NLO materials. These complex requirements have only been fulfilled by inorganic crystals up to now. These materials, however, have relatively low nonlinearities. Guest/host composites might be an alternative since organic molecules have high molecular hyperpolarizabilities. In 1988, high NLO effects of dye-loaded zeolites were discovered.[3] This pointed to an interesting alignment process in the zeolite channels. To result in high nonlinearities, the dipolar guest molecules must have the same dipole direction. This results in one or two large domains of dipolar direction in the composite crystal as it was found by microscopic pyroelectric scanning experiments.[4] The most probable mechanism explaining the alignment is based on the entering process of the molecules into the molecular sieve channels.[4]

The composite of p-nitroaniline (pNA) and the molecular sieve $AlPO_4$-5 was found to give very large NLO effects. However, it turns out through

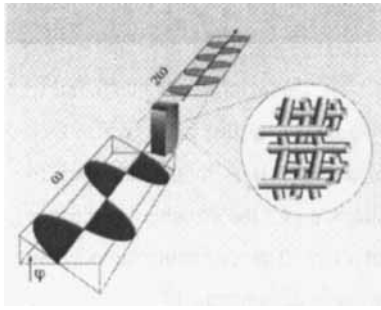

FIGURE 2 Schematic representation of the second harmonic generation of a ZSM-5 crystal loaded with organic molecules. The frequency-doubled radiation can have both polarizations (*parallel and perpendicular* to the channels).

investigating the polarization dependence of the SHG that the nonlinear susceptibility tensor is dominated by one component (χ_{zzz}) only. This means that only waves polarized parallel to the z-axis, which is the channel direction, can interact with each other. According to that it is, however, impossible to fulfill the phase-matching condition. Therefore, changing the material in such a way so that more than the tensor component χ_{zzz} is characterizing the material,

has been a decisive task. Since the electronic states of the guest control the nonlinear susceptibility, a variation of the guest molecule can be used to reach that goal. pNA has only one transition in the visible region generating the tensor component χ_{zzz} only. Many other molecules, e.g. p-nitrodimethylaniline or p-dimethylaminobenzonitrile have more than one electronic transition in the visible region. Using these molecules it has been shown that the other phase-matchable tensor components, e.g. χ_{yzy} can be generated.[5] Furthermore, the refractive indices of these composite materials have been found to fulfill the phase-matching condition.[6]

LASER MATERIALS

The amplification of light is the key function of laser materials. In combination with an optical resonator leading to a feedback, such an amplifying medium can be used to build up a laser. But also without applying a resonator such materials can be very useful as optical amplifiers. Such devices could gather the same or even more importance than lasers do for future photonic devices.

The most crucial requirement for laser materials is a high gain. But also other requirements are important such as low scattering losses, a low thermal sensitivity (avoiding thermal lensing), photochemical stability, and efficiency.

The high gain and the variability of dye lasers have stimulated many efforts in seeking a replacement for the dye solution by doped solids. The utilization of polymers or glasses serving as hosts for dyes are the approaches most commonly known. Nowadays, however, zeolites also are being used.[7] The use of mesoporous materials would offer further prospects because of the many synthesis possibilities and the large pores which can host complicated chromophoric systems. An example that mesoporous materials can really be used for optical purposes has been demonstrated in a recent paper.[8] Here, rhodamine 6G is incorporated into mesoporous silica fibers. When the fiber is pumped with a frequency-doubled YAG laser, a gain-narrowed emission was observed. This emission turned out to be originating from the fiber ends and it

was nearly parallel to the fiber axis. This phenomenon is known as amplified spontaneous emission and demonstrates that the composite could be used as a laser material. It is interesting to note that only some of the waveguide modes are strongly amplified. This results in the beam-like output of the fiber.

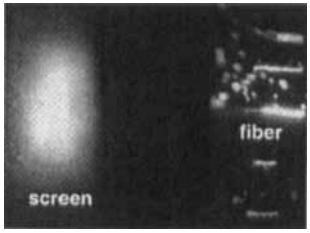

FIGURE 3 Emission of a dye-doped mesoporous silica fiber made visible by a screen placed in about 2 mm distance from the fiber. The fiber is about 0.5 mm long and 0.02 mm thick.[8]

SUMMARY

Examples for guest/host composites have been presented demonstrating efficient opto-optical switching, high optical nonlinearities and stimulated emission. In these composites, a tuning of the composition could be applied to fulfill the complex requirements necessary for practical applications.

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