

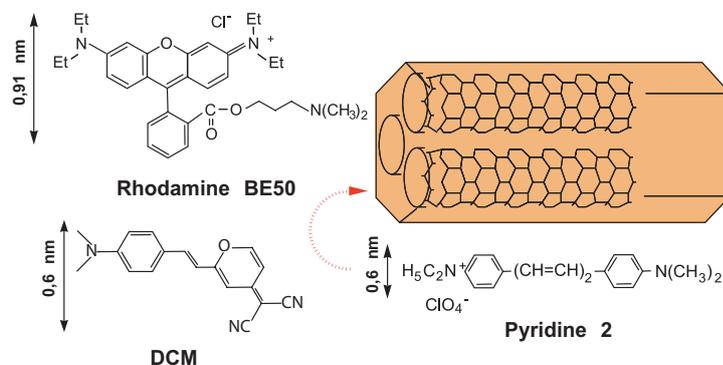
Lasing in hexagonal molecular sieve waveguide resonators

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Introduction

Molecular sieves are crystalline solid state materials with nanometer size pores of well defined diameter. This property enables the material to be used as an ordering framework for arranging optically functional molecules, thus creating a host-guest-system with new optical properties. Its closer examination leads to a better understanding of optical host-guest systems that might be valuable for various optical applications.

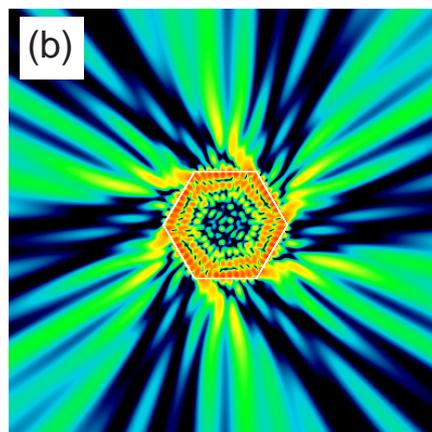
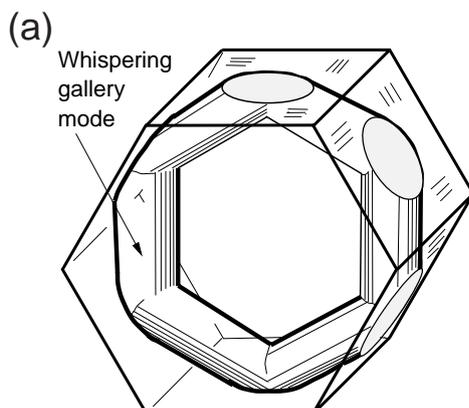


In our case, organic dye molecules have been included into the lattice pores of $\text{AlPO}_4\text{-5}$ crystals. The crystals vary in size and morphology depending on the nature of the included molecules.

Nevertheless, lasing crystals exhibit a regular hexagonal cross section.

Lasing behavior has been observed in four different compound

materials: $\text{AlPO}_4\text{-5}$ containing DCM, pyridine 2, oxazine 1 and rhodamine BE 50. The microlasers are pumped with a Nd:YAG 532nm pulsed laser, which is far off the absorption bands of the host to ensure maximum guest excitation. If the pulse energy exceeds a certain threshold, lasing behavior can be observed. The laser resonator is defined by the light bundle, which is confined by total internal reflection at the natural side walls of the hexagonal prism. In this way a ring resonator is formed allowing whispering gallery modes to oscillate in a resonator of 5 micrometers in size. The threshold power is a direct indicator of the quality and regularity of the inner structure of the crystal, since every inhomogeneity inside the compound increases the losses. The threshold power corresponds to the same number of quantum excitations to achieve threshold in a VCSEL.

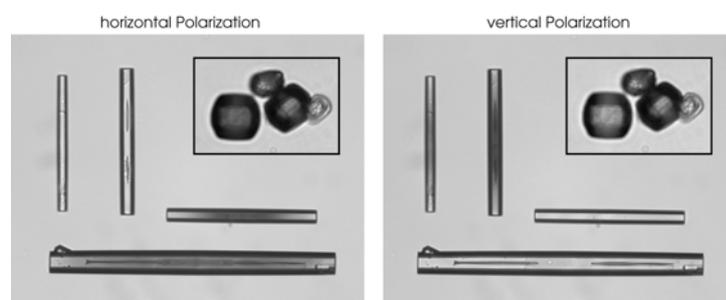


In figure (a) a naive picture of the whispering gallery lasing mode in a hexagonally bounded dielectric prism is portrayed. Contrary to this picture the experiment clearly reveals, that the laser light leaves the prism resonator at the edges. The main feature that distinguishes the hexagonal resonator from other common whispering gallery type cavities, such as microdroplets or semiconductor disk lasers, is that the latter do not exhibit sharp corners and flat sides. Portions of the boundary in convex resonators can act as focussing or defocussing elements.

The straight sides of a hexagon, however, are neither one nor the other. The hexagon in fact constitutes a self-assembled realization of a “pseudointegrable” structure: There exists no orthogonal coordinate system in which the wave equation for the hexagonal cavity can be solved by separation of variables.

In Figure (b) we show the result of a numerical simulation of the field distribution of a counter clock wise propagating mode with a wavelength of 685 nm in a hexagon with a width over flats of 4.5 micrometer. The simulation correctly reproduces the outcoupling location of the field at the corners and the directionality of the outcoupled light. Upon closer examination one sees that the number of ridges and nodal lines is not uniquely defined, in particular along a diameter joining opposite corners (“optical defects”). The modes in a hexagonal resonator can therefore not be properly labeled by “quantum numbers” characterizing the number of radial and azimuthal nodes -- this is a direct consequence of the nonintegrability of the problem.

Properties of the crystals



The channel pores in the $\text{AlPO}_4\text{-5}$ molecular sieve crystal are located perpendicularly to the hexagonal cross section. Given the size of the pyridine 2 and DCM molecules (long prisms in the figure), the pore framework acts as an ordering structure for the dipole moments.

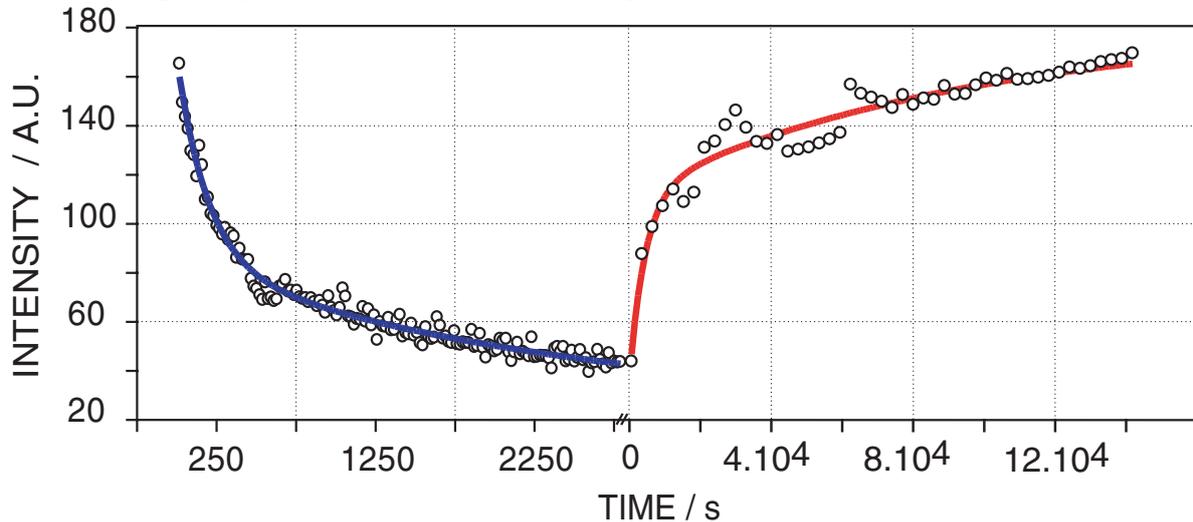
That compounds thus exhibit a pronounced dichroism. On the other side, rhodamine molecules (barrel shaped crystals in the figure) do not fit into the regular structure pores, but they reside in defect pores. This compound exhibits only weak dichroic properties.

By comparing the fluorescence decay of the encapsulated dye to that of the same dye in solution, the decorrelation time of the molecular dipole moment orientation could be revealed. This leads to confirmation of the strict confinement of orientation of the pyridine and DCM. Rhodamine, however, shows less confinement, its dipole moment can rotate inside the larger macropores with a decorrelation time of 400 ps.

Some dyes, e.g. pyridine 2, are polar and may be encapsulated with a distinct orientation resulting in a compound with pyroelectric properties. Pyroelectricity can give a good hint on the internal structure and the lattice-dye interactions inside the crystal. By means of pyroelectric examinations, the pyridine 2 has been found to exhibit a flip of the polarity of dipole moment in the center of the crystal.

Photostability

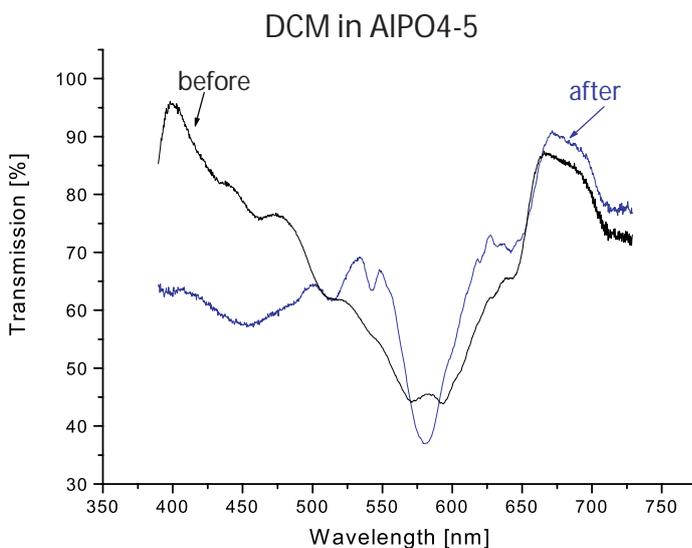
The photostability of organic dyes is a critical issue. Exposure to strong light bleaches dye molecules. In traditional, “liquid”, dye lasers photobleaching is irreversible. However, we observed that the fluorescence of the encaged pyridine 2 shows a partial recovery over time, the DCM-doped crystals even reach their full original fluorescence.



The mechanism behind the recovery is as yet not fully understood. The DCM shows the closest confinement inside the crystal, followed by the pyridine 2 and then the rhodamine, in the same order as their recovery behavior, so a connection between these facts might be present. Oxygen bleaching, one of the most prominent factors of dye bleaching in photochemistry, the oxygen bleaching, can not alone be held responsible for the dye bleaching in the DCM compound, so that the extraordinary behavior of the dye inside the crystal must be directly connected to a matter of dye-lattice interaction.

We observed a strong sensitivity of the fluorescence recovery on the probing light. Even the weak pulses disturb the recovery rates.

A connection between the temperature of the compound and the time scale of the bleaching and recovery process has been established, which strengthens the hypothesis of a strong participation of the host lattice in the bleaching process.



During the process of bleaching, the absorption spectrum of the enclosed dye changes significantly, thus hinting to a change in electronic configuration of the dye resulting in a change of absorption bands.