Hexagonal microlasers based on organic dyes in nanoporous crystals

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Abstract Molecular sieves, such as nanoporous AlPO₄-5, can host a wide variety of laser active dyes. We embedded pyridine 2 molecules as a representative of a commercially available dye which fits into the channel pores of the host matrix. Many efficient dye molecules, such as rhodamines, do not fit into the pores. But modifying the structure of the dyes to appear like the used templates allows to increase the amount of encapsulated dyes. The properties of resulting microlasers depend on size and shape of the microresonators, and we discuss a model for microscopic hexagonal ring resonators. In terms of pump needed to reach lasing threshold molecular sieve microlasers are comparable to VCSELs. For dyes which fit into the pores we observed a partial regeneration of photo-induced damage.

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1 Introduction

In recent years dye laser emission from from crystalline materials attracted considerable interest [1,2]. At the same time in solid state dye lasers based on polymer matrices single mode operation at high peak powers was demonstrated [3], and photodegradation processes were identified [4]. Recently, we reported on microscopic dye lasers, in which the active molecules were embedded in crystallographically defined nanometer size pores of molecular sieves [5]. In the past, such nanoporous materials, e.g. zeolites, proved to be pertinent especially to the catalysis in oil refining and petrochemistry, where they are used in huge amounts. It is only recently that applications of this class of porous crystalline material are discussed in an optical context. In fact, molecular sieves can be used to host a wide variety of optically relevant guests, such as atoms, ions, or molecules [6]. Sieves with tubular or channel pores, in particular, can act as an ordering framework for guest molecules [7]. For optical applications it is possible to exploit thus distinct spatial symmetries in the arrangement of organic molecules, enhancing so, for example, the second order nonlinear susceptibility of the compound [8], or admitting anisotropic Förster energy migration [9]. Nanoporous crystals were also studied as hosts for luminophores [10], pigments [11], optical switches [12] or dye lasers [13]. In the following we report about the novel emission properties of hexagonal monolithic microresonators realized with dyes intercalated in molecular sieve microcrystals, and the photostability of these systems.

2 Material
Molecular sieve materials are characterized by a crystallographically defined framework of regularly arranged pores. In Table 1 we list some sieves, which, owing to their large diameters of channel pores, are suitable for hosting optically effectual organic molecules. Among the listed materials especially the aluminophosphate AlPO₄-5 (molecular mass 1463.4 g/mol) can be synthesized with good optical transparency and low internal scattering losses. Its channel pores exhibit a diameter of 0.73 nm, which is large enough to accommodate suitable organic dye molecules.

AlPO₄-5 crystals are crystallized from aqueous or alcoholic solutions under hydrothermal conditions, with the addition of an organic structurizing agent, called template. The template, tri-n-propylamine in our case, is necessary to direct the synthesis towards the desired structure. The preferred pH range for the synthesis is mildly acidic to mildly basic. The most utilized source of phosphorus is orthophosphoric acid, and the most studied sources of aluminum are pseudoboehmite and alkoxides. Single crystals with nearly perfect morphology were grown using hydrofluoric acid. With a specially prepared and aged aluminum hydroxide gel crystal sizes around 1 mm in c-axis direction were obtained [16], whereas microwave heating below 400 nm to above 800 nm (

 Pure AlPO₄-5 crystals are optically transparent from below 400 nm to above 800 nm (n_{500 nm} = 1.466), and after removing the template (usually by heating/calcinating) they exhibit practically no birefringent properties. X-ray patterns revealed systematic absences which are consistent with space group P\textsuperscript{\text{6\text{cc}}} as well as P6\text{cc}, whereby, however, the latter implies a polar nature of AlPO₄-5 single crystals: In fact, the 4 in the formula is the result of the strict alternation of Al and P in the tetrahedral nodes of the framework, which prevents the corner-sharing oxygen tetrahedra to occur with odd numbers, and which leads to an alternating stacking of Al and P in the direction of the channels (c-axis). This is assumed to cause the crystallographic polar nature of the framework [18]. The macroscopic polar nature of AlPO₄-5 single crystals has been proven recently in scanning pyroelectric microscopy investigations [20]. There it was also observed that AlPO₄-5 crystals are usually twinned. The murky stripes inside the pyridine 2-loaded crystals shown in Fig. 1 and their slightly bowed side faces could well be a result of this kind of twinning. It is not clear, however, to what extent such twinning should affect the optical properties relevant for the effects discussed here.

2.2 AlPO₄-5/pyridine 2 compound

The compounds were synthesized following a procedure in which the dye 1-ethyl-4-(4-(p-dimethylaminophenyl)-1,3-butadienyl)-pyridinium perchlorate (pyridine 2 [21]; molecular mass 378.9 g/mol) is added to the template or to the aluminum hydroxide suspension [22,23,24]. After 1 h of hydrothermal synthesis dark red crystals with a length of up to 100 \( \mu \)m were obtained. The crystals were refluxed in ethanol for 4 h without any detectable extraction of dye. The slim, linear dye molecules fit snugly into the 0.73 nm wide channel pores of the nanoporous AlPO₄-5 host, resulting so in an ordered compound material, in which the dye molecules are all aligned along the crystal c-axis. As a consequence the compound exhibits strong dichroism, and the emitted fluorescence light is polarized parallel to the optical transition moment of the molecules is absorbed. In the rod-shaped crystal the pyridine 2 dyes are completely aligned, whereas with the rhodamine BE50 dye in the barrel-shaped crystals we observe only a weak dependence of the color upon the incident polarization. Left: incident light horizontally polarized; Right: incident light vertically polarized.

Figure 1. Transmission micrographs of the dichroism in dye-loaded AlPO₄-5 crystals; the rod-shaped crystals contain ca. 0.1 wt-% or 260 pyridine 2 molecules per unit cell, while the barrel-shaped ones (shown in the inset) enclose rhodamine BE50 (ca. 0.5 wt-% or 75 molecules per unit cell). Only the polarization component parallel to the optical transition moment of the molecules is absorbed. In the rod-shaped crystal the pyridine 2 dyes are completely aligned, whereas with the rhodamine BE50 dye in the barrel-shaped crystals we observe only a weak dependence of the color upon the incident polarization. Left: incident light horizontally polarized; Right: incident light vertically polarized.

Figure 2. Structure formula of the dye 1-ethyl-4-(4-(p-dimethylaminophenyl)-1,3-butyadienyl)-pyridinium perchlorate (pyridine 2 [21]); molecular mass 378.9 g/mol.

Figure 3. Morphology of typical pyridine 2/AlPO₄-5 crystals with lasing properties.
the inclusion of pyridine 2 the entire compound acquired pyroelectric properties and an optical second order susceptibility.

Depending on the dye content different morphologies of crystals are observed. Regular hexagonal crystals with a rodlike form, as e.g. the ones shown in Fig. 1, were obtained when the dye content was low, around 0.1 wt% or 260 molecules per unit cell. At higher concentrations the dye accumulated in the middle of the crystal, and the morphology was severely disturbed. At dye content \( \gtrsim 0.2 \) wt% crystals with a characteristic fascicular shape resulted; cf. Fig. 3. Given the small size of the crystals we had to determine the dye content by chemically dissolving them. With this method, however, it was not possible to accurately determine the spatial distribution of the dye. We therefore evaluated the content qualitatively by comparing the depth of the color. It was only with these fascicled pyridine 2-loaded crystals that we observed laser emission. Apparently the low concentration of dye in the undisturbed rod-shaped crystals did not spoil the growth but on the one hand was not sufficient to provide the necessary optical gain for compensating all losses.

### 2.3 AlPO\(_4\)-5/rhodamine BE50 compound

The synthesis gel was prepared according to recipes [28]. To a suspension of 61.6 mmol Al\(_2\)O\(_3\) (8.44 g; Pural SB, Condea Chemie) as aluminum source and 75 g deionized water, 61.6 mmol P\(_2\)O\(_5\) (14.20 g phosphoric acid; 85 wt%, p.a. Merck) in 11.3 g deionized water was added under mechanical stirring. After 5 min a uniform gel formed and then 92.4 mmol tripropylamine (13.25 g Prop\(_3\)N, Merck) was added slowly. Subsequently, the appropriate amount (0.1–10 mmol) of the dye powder was mixed with the gel. The new derivative rhodamine BE50 (ethanaminium, \( N\)-6-(diethylamino)-9-[2-(\( N\), \( N\)-dimethyl-3-aminol-1-propoxycarbonyl)phenyl]-3H-xanthen-3-ylidene]-\( N\)-ethyl-chloride) molecular mass 564 g/mol [27].

![Structure formula of the new dye rhodamine BE50](image)

**Figure 4.** Structure formula of the new dye rhodamine BE50 (ethanaminium, \( N\)-6-(diethylamino)-9-[2-(\( N\), \( N\)-dimethyl-3-aminol-1-propoxycarbonyl)phenyl]-3H-xanthen-3-ylidene]-\( N\)-ethyl-chloride) molecular mass 564 g/mol [27].

As is visible in Fig. 1 – and as the polarization of the emitted fluorescence of the compounds indicates – the absorption, as well as the emission dipole moment of the included dyes are oriented preferentially along the crystal

![Morphology of typical rhodamine BE50/AlPO\(_4\)-5 crystals with lasing properties](image)

**Figure 5.** Morphology of typical rhodamine BE50/AlPO\(_4\)-5 crystals with lasing properties; dye content ca. 0.5 wt-% or 75 dye molecules per unit cell.

![Naïve ray picture interpretation of a whispering gallery laser mode inside a hexagonal prism](image)

**Figure 6.** Naïve ray picture interpretation of a whispering gallery laser mode inside a hexagonal prism.
c-axis (Complete orientation in the pyridine 2/AlPO_4-5 compound). As dipole emission along the dipole-axis is not possible, the emission parallel to a plane perpendicular to the prevailing dipole orientation (i.e. the hexagonal axis) is enhanced. Here a bundle of emission directions meets the condition for total internal reflection (TIR) at the hexagonal side faces inside the crystal. In a whispering-gallery-mode-like way the corresponding emission can circulate sufficiently often to accumulate the gain required to overcome the lasing threshold; cf. Fig. 7 in which this intuitive model is illustrated for a particular ray bundle of high symmetry. However, with resonator sizes in the order of a few wavelengths, as discussed here, the ray picture does not represent the field modes even in a qualitatively correct way. E.g. the ray picture insinuates a mode concentration in the center of the faces and field-free corners. However, this is not consistent with the experimental evidence, which clearly shows that the emission occurs at the corners; cf. Fig. 4. In fact, for dielectric resonator structures a few wavelengths large with TIR field confinement a wave model has to be worked out.

3.1 Ray picture

The main feature that distinguishes the hexagonal resonator from other common whispering-gallery type cavities such as microdroplets [31] or semiconductor disk lasers [32,33], 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, but the straight sides of a hexagon are neither one nor the other. The hexagon in fact constitutes a self-assembled realization of a pseudointegrable resonator [33]: For a polygon with precisely 120° angles between adjacent sides, any ray launched at some angle to the surface will go through only a finite number of different orientations [3], just as in the more familiar rectangular resonator where there are at most two non-parallel orientations for any ray path. In the hexagon, a ray encounters the interface with at most three different angles of incidence. Despite this apparent simplicity, there exists no orthogonal coordinate system in which the wave equation for the hexagonal cavity can be solved by separation of variables. This property of non-integrability is shared by wave equations whose classical (short-wavelength) limit exhibits chaos. However, ray paths in the hexagon display a degree of complexity that cannot be classified as chaotic, and hence the term pseudointegrability has been coined for these systems. The ray-wave duality in “billiards” of this type has to be addressed in order to explain how they can support whispering-gallery modes that emit at the corners.

In order to characterize the sample size, one can specify either the radius R of the hexagon at the corner points or – more conveniently – the width over flats (WoF) satisfying the relation R = WoF/√3. The closed ray path underlying Fig. 4 is only one member of an infinite family of periodic orbits of the hexagon billiard that all have the same length, L = 3 × WoF, as shown in Fig. 4. Long-lived cavity modes should be expected only if the corresponding rays satisfy the condition of TIR at the interface, sin χ > 1/n, where χ is the angle of incidence with respect to the surface normal. This is true for the orbits of Fig. 4. In a naive ray approach one would furthermore obtain the spectrum of modes by requiring an integer number of half wavelengths to fit into L, leading to constructive interference on a round-trip. As we shall see shortly, this estimate is justified, even though a proper treatment of the ray-wave connection has to take into account that any given mode is in fact made up of a whole family of different ray paths. The ultimate breakdown of the ray model, however, is illustrated in Fig. 3 by the degenerate ray orbit hitting the corners where the classical laws of refraction and reflection become undefined.

3.2 Wave picture: spectral properties

Because the hexagonal faces are neither focussing nor defocussing, there is no obvious way of determining the weight that should be given to individual members of a ray family as depicted in Fig. 4 in order to predict the spatial structure of the resulting mode. Full solutions of Maxwell’s equations have therefore been carried out for the TM polarized modes of a dielectric hexagonal prism, using methods previously applied in [31,32]. In anticipation of the experimental spectra to be discussed in section 4, attention here is focused on three different sample sizes, with WoF 4.5 µm, 7.5 µm and 22 µm. The aim is to understand the observed laser line spacings and the emission directionality. Comparison of the calculated and observed linewidths will not be attempted because the simulations do not take gain-narrowing into account.

In order first to verify that orbits of the type shown in Fig. 4 determine the characteristic mode spacing of these cavities, Fig. 5 shows light scattering spectra for different sample sizes in the vicinity of the experimental wavelengths. Intensity is plotted versus dimensionless wavenumber kR, where k = 2π/λ. This is the natural scale for comparison with semiclassical predictions because modes differing by one node along a closed path should then be equally spaced, with a characteristic separation Δ(kR)_c = 2π R/(n L) = 2π/(3√3n) = 0.825 independent of the sample size. The expected wavelength spacing of the modes (free spectral range FSR) is Δλ = λ^2 × Δ(kR)_c/(2πR) ≈ 23 nm in (a) and Δλ ≈ 11 nm in (b). For WoF = 22 µm, we obtain Δλ ≈ 4.9 nm. Figure 6 indeed shows a corresponding...
Figure 8. Calculated scattering intensity spectra of a hexagonal cylinder for plane-wave incidence at $15^\circ$ to a side face and detection at $60^\circ$ from incidence. (a) corresponds to a spectral interval $\lambda \approx 653 \ldots 816$ nm for width over flats (WoF) 4.5 $\mu$m; (b) covers the interval $\lambda \approx 605 \ldots 680$ nm for WoF 7.5 $\mu$m. Vertical lines are guides to the eye, indicating narrow resonances. The spacing between resonances is $\Delta(kR) \approx 0.84$ in (a) and $\Delta(kR) \approx 0.83$ in (b), in good agreement with the characteristic mode spacing $\Delta(kR)_c \approx 0.83$ of a closed hexagonal orbit. Expected resonances not clearly seen in the above spectra are marked by dashed lines; they appear at other detection angles.

Figure 9. Calculated scattering intensity spectra for slightly rounded hexagonal cavities (shapes depicted as insets). The incoming plane wave is at an angle of $15^\circ$ to a facet in (a) and $30^\circ$ in (b); detection occurs at $60^\circ$ from incidence. Spacings between modes of the same color agree well with $\Delta(kR)_c \approx 0.83$, cf. Fig. 8. All resonances in (a) appear as doublets. At $kR \approx 42.5$ the doublet structure is seen most clearly. In (b), stronger deviation from hexagonal shape leads to further lifting of degeneracies. Dashed lines mark expected resonances not seen at this observation angle.

Each of the peaks marked in Fig. 8 (b) is in fact a multiplet, which is not resolved because the splittings of the individual modes comprising the multiplet are smaller than their passive linewidths. There is evidence for this because several of the peaks are very asymmetric and in particular exhibit a steep slope on one side. For an isolated resonance, the most general lineshape that could arise is the Fano function (of which the Lorentzian is a special case), which however does not yield satisfactory fits here.

To further expose the multiplet structure, we modeled deviations from the ideal hexagonal shape which could lead to narrower individual linewidths and increase the multiplet splitting. Shape perturbations were chosen that preserve the $D_{6h}$ point group symmetry and hence remove only “accidental” quasi-degeneracies. The actual perturbation that is present in the samples of Figs. 11 and 12 excluded experimental characterization, so that a model calculation can reproduce only generic features which are insensitive to the precise type of perturbation. One such feature is the average mode spacing after degeneracies have been lifted sufficiently.

Figure 9 (a) shows the spectrum of a rounded hexagon where the radius of curvature at the corners is $\rho \approx 0.9 \lambda$ (assuming $\lambda \approx 610$ nm for definiteness). No qualitative difference to Fig. 8 (b) is seen, except that the resonant features have become somewhat narrower, thus enabling us to identify two distinct series of modes with characteristic spacing $\Delta(kR)_c$. This indicates that departures from sharp corners are not resolved in the wave equation when their scale is smaller than $\lambda$. A qualitatively different spectrum is observed in Fig. 9 (b) where $\rho \approx 3.7 \lambda$. Here, the perturbation reveals three well-separated, interpenetrating combs of modes, again with period $\Delta(kR)_c$. There are 21 distinct resonances in the wavelength interval of Fig. 9 (b), which translates to an average mode spacing of $\Delta\lambda \approx 3.6$ nm for a WoF = 7.5 $\mu$m resonator, well in agreement with the experiment; cf. Fig. 12.

In order to verify that no further modes will be revealed by other choices of deformation, an independent
estimate of the average density of modes can be made based on semiclassical considerations [35]:

$$\langle \frac{dN}{d(kR)} \rangle = \frac{n^2 k R}{4} \times \left[ 1 - \frac{2}{\pi} \left( \arcsin \frac{1}{n} + \frac{1}{n} \sqrt{1 - \frac{1}{n^2}} \right) \right]$$

(1)

Here, \( dN \) is the number of modes in the interval \( d(kR) \). The result is \( \langle \frac{dN}{d(kR)} \rangle \approx 4.6 \), and hence we expect \( \approx 22 \) modes in the interval of Fig. 9 (b), again in good agreement with the actual count.

### 3.3 Wave picture: intensity profile

There is one class of quasi-degeneracies that is not removed by any of the perturbations in Fig. 9, their physical origin is time-reversal symmetry for the ray motion inside the cavity. Any of the periodic orbits in Fig. 7 can be traversed either clockwise or counterclockwise, and the same holds for more general ray paths. The different propagation directions can be linearly combined in various ways to obtain nearly-degenerate standing-wave patterns that differ only in their parity with respect to some of the crystal’s reflection axes. A minute splitting does exist because the non-integrability of the ray motion implies that the propagation direction itself is not a “good quantum number”, i.e. reversals of the sense of rotation are unlikely but not impossible in the wave equation. This is analogous to quantum tunneling and hence leads only to exponentially small splittings that can be neglected on the scale of the individual resonance linewidths [36]. These multiplets have been counted as one resonance in Eq. (1).

Following this reasoning, in Fig. 10 the traveling-wave patterns belonging to one of the resonances in Fig. 8 (a) and (b), respectively, is plotted. High-intensity ridges inside the resonator form a whispering-gallery-like pattern that decays from the interface into the cavity center. The number of ridges in the radial direction (perpendicular to a side face) provides an approximate analogue of a transverse mode order, however 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. The modes can therefore not be properly labeled by “good quantum numbers” characterizing the number of radial and azimuthal nodes – this is a direct consequence of the nonintegrability of the problem. The most significant difference to the whispering-gallery modes of a circular cavity is clearly the anisotropic emission. High intensity is seen to emanate predominantly from the corners and is directed almost parallel to an adjacent crystal facet. The overall emission pattern is very similar in both modes despite the large difference in size (or \( kR \)) between the two hexagons.

![Figure 10. False-color representation of the cross-sectional intensity in the ideal hexagon for a mode with (a) \( kR = 22.89 \) [cf. Fig. 8 (a)] and (b) \( kR = 42.78 \) [cf. Fig. 8 (b)]. The resonance width is \( \delta(kR) = 0.10 \) in (a) and \( \delta(kR) = 0.04 \) in (b).](image)

## 4 Laser properties

The microcrystals were pumped with 10 ns pulses from the 532 nm second harmonic of a Nd:YAG-laser delivered to the sample with an optical fiber. The emitted luminescence was collected with a 20×-microscope objective (collecting aperture 42°) relaying the microlaser emission simultaneously to the spectrometer (cooled CCD-detector...
Figure 11. Emission and lasing spectra of different pyridine 2-loaded compounds with from a to c increasing amounts of included dye. The dye concentration was estimated empirically based on the sample color depth. The width over flats of sample b is 4.5 µm. The free spectral range of this resonator is so large (ca. 24 nm) that one emission mode acquires the available gain resulting in single line emission.

Oriel InstaSpecIV), and to the imaging system consisting of a cooled low noise CCD-camera (PCO SensiCam). In Fig. 1 the emission and lasing spectra of different pyridine 2-loaded compounds are shown. With increasing dye content the fluorescence emission maximum of regularly shaped crystals shifted from 645 nm to 665 nm; cf. Fig. 1k. In none of these rod-shaped crystals laser emission was observed. However, narrow laser emission peaks (observed linewidth of 0.3 nm given by spectrometer resolution) occurred in most fascicled samples. Emission maxima in these fascicled samples were observed at wavelengths up to 695 nm, and again, increasing dye concentration correlated with increasing redshift (cf. Figs. 1b and c). As already mentioned, together with increasing dye content we also notice an increasingly disarranged crystal morphology. The observed facts, disturbed morphology and red-shifted emission spectrum are consistent with the hypothesis of a host-guest interaction which increases with dye content. Essentially both, the pyridine 2 molecules and the AlPO₄-5 framework carry a static dipole moment [18,19]. Obviously the buildup of electrostatic energy in the crystal lattice has to be compensated by an increasing amount of stacking faults. On the other side, the mechanism of the redshift is not unequivocally identified, yet, but is probably related to the one discussed in [27,28].

The dye concentration in the rhodamine BE50-loaded AlPO₄-5 samples was around 75 unit cells per dye molecule, corresponding to 0.5 wt%. Also with these samples the same correlation between the emission wavelength and dye concentration was observed; cf. also [27]. In contrast to the pyridine 2-loaded samples, the fluorescence emission was not completely polarized. The observed polarization contrast \( c_p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \) was around 10%, indicating that in the average the Rh BE50 molecules are only weakly aligned parallel to the crystal c-axis.

Figure 12. Lasing spectrum of a rhodamine BE50-loaded AlPO₄-5 microcrystal with a concentration around 75 unit cells per dye molecule and size of 7.5 µm width over flats.

Independent of the type of loading, in most microcrystals with WoF \( \gtrsim 8 \) µm lasing was observed to occur on several sharp lines with instrument resolution limited width. A typical example is represented in Fig. 12. Note that the lines are not equally spaced. In fact, the free spectral range (FSR) of 11 nm corresponding to the resonator size is far above the observed line spacing of 3.2, 4.3 and 3.4 nm. This is in agreement with the theoretical model of paragraph [5] in which the average lasing mode spacing (after lifting the quasi-degeneracies in the ideal hexagon) was estimated to be \( \Delta \lambda = 3.6 \) nm. Also in agreement with the theoretical discussion are the emission regions where the laser light leaves the hexagonal resonators. Figure 13(left) shows the laser emission as bright spots. The emission is concentrated along the crystal edges. The complex emission distribution is compatible with the simultaneously recorded spectrum (cf. Fig. 14) which reveals multimode emission.

On the other hand, samples with smaller resonator (WoF \( \lesssim 4 \) µm), as e.g. the one shown in Fig. 1b emitted one single laser line. Therefore the emission is unaltered by hole burning induced multimode beating and interference, and appears in the simple pattern shown in Fig. 13(right), where two ca. 1 µm-spots (\( \approx \) microscope resolution limit) mark the region of laser emission, which, again, is located on the crystal edges. Compared with larger samples, the ratio of the line peak to the underlying fluorescence shoulder of these small lasers is an order of magnitude higher (cf. Fig. 13).

While, as described above, the average linespacing of 3.6 nm observed in the sample of Fig. 12 is not compatible with the free spectral range of \( \Delta \lambda = 12 \) nm of the corresponding resonator, the 4.2 nm spacing of the 3 dominant peaks in the sample shown in Fig. 11 is in accord with the FSR resulting from the 22-µm-WoF hexagonal resonator. The theoretical model for the 22-µm-WoF sample (cf. Eq. 5) yields an average mode spacing of \( \Delta \lambda \approx 0.5 \) nm which is close to the spectrometer resolution. This high spectral density helps to explain the large background in the lasing spectrum of Fig. 11. It appears likely that not all the individual lasing modes in this sample were

\[ I_{\parallel} - I_{\perp} \]

\[ I_{\parallel} + I_{\perp} \]
solved, and hence part of the shoulder on which the three peaks of curve c sit is probably made up of other lasing modes. Any microcavity effects such as enhanced β factor (spontaneous emission enhancement and suppression) are also suppressed by the larger density of modes in the large sample.

Figure 14 illustrates the differential efficiency behavior of a typical microcavity with WoF < 10 μm and one with WoF > 10 μm. Lasing threshold for the latter size samples was around 0.5 MW/cm², regardless of the type of dye loading. On the other side, crystals of smaller size (WoF = 4.5 μm) from the same synthesis batch revealed a considerably smaller threshold (0.12 MW/cm²) and a factor of > 7 larger differential gain. Whether this is a consequence of quantum size effects will be clarified in progressing studies.

It is informative to compare the threshold of molecular sieve microlasers with vertical cavity surface emitting lasers (VCSELs). VCSELs with a size comparable to sample b in Fig. 1 exhibit threshold currents of ca. 1 mA, which corresponds to 6.25 × 10¹⁵ s⁻¹ electrons. On the other hand, the threshold power density of 0.12 MW/cm² incident on the molecular sieve laser surface of 1 × 4.5 μm (cf. Fig. 3) corresponds to a current of 1.4 × 10¹⁶ s⁻¹ 532-nm-photons, or a factor of 2.24 over the electron rate. As the pump radiation is not polarized but the molecular ensemble of the considered laser is aligned, only half of the pump photons actually contribute to the inversion. Thus, in terms of elementary (quantum) pump processes needed to reach lasing threshold the molecular sieve lasers are comparable to VCSELs.

5 Photostability

Photostability is a critical issue with dye lasers. We investigated samples exhibiting an undisturbed morphology, similar to the one shown in Fig. 1. The pyridine 2-loaded samples were irradiated with 10 Hz trains of 10 ns pulses of the 532 nm second harmonic of a Nd:YAG-laser and a power density of 5 MW/cm². Figure 15 illustrates the dwindle of fluorescence activity of a pyridine 2-loaded AlPO₄-5 sample under such bleaching irradiation. After a bleaching period of 140 seconds the exposure was interrupted for 18 minutes. Then the bleaching procedure was resumed. Apparently the fluorescence recovers during the intermission. If it is assumed that bleaching consists in breaking bonds of the dye molecules, then bond energies in the eV-range have to be considered. Even if the dye debris might remain encaged in their pores, spontaneous or thermally activated self healing of broken eV-bonds seems not very probable. One can therefore suppose that the recovery is due to diffusion of new, intact dye molecules into the bleached volume. Considering the stereometrically restricted possibilities inside the molecular sieve framework together with diffusion distances of several μm and the observed recovery time in the range of minutes, diffusion is more plausible than self healing.

As bleaching reduces the concentration of dye, a blueshift of the fluorescence is expected with increasing photo-bleaching. However, the 656-nm-fluorescence emission maximum of this sample is already at the shortest observed wavelength (cf. Fig. 1), corresponding to a low dye concentration, and consequently, to weak dipole interactions. Thus, the blueshift under these circumstances must be rather small. This explains the fact that we could not detect a measurable blueshift with these pyridine 2-loaded samples.

On the other hand, the rhodamine BE50-loaded samples under investigation contained dye at a concentration of around one Rh BE50 molecule per 75 unit cells, and therefore bleaching caused a detectable 4 nm shift of the fluorescence towards the blue (bleach irradiance 0.5 MW/cm²). Observing the laser emission spectrum while bleaching the samples, a further consequence of the blueshift was revealed: Blueshift of the fluorescence reduces the
6 Conclusion

We have reported about a new form of microlasers based on nanoporous molecular sieves containing embedded dyes. Size- and shape-dependent laser properties were observed, in agreement with theoretical predictions: Larger hexagonal crystals (WoF ≈ 10 µm) revealed multiline laser emission, while the smaller ones (WoF ≈ 5 µm) oscillate on one single line. The laser threshold power density of these small lasers is approximately a factor of 3 lower than the threshold of WoF ≈ 10 µm–lasers, and their differential efficiency is almost an order of magnitude larger. Although these properties did not depend on the type of embedded dye molecules, the photostability seems to be affected by the size of the molecules. Molecules which fit into the pores, such as pyridine 2, keep the ability to diffuse in the pore framework of the molecular sieve. Therefore photo-bleached molecules can be replaced by intact ones diffusing into the luminescing volume.

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