

can be independently adjusted. Shown in Figure 3e is one example of using a size-reduced nanopillar for nanoimprinting. In this case, the size of nanopillars was reduced using a chromium etchant. The lateral dimension of the imprinted holes was less than 30 nm. Other approaches to size reduction are currently under investigation in our group.

In summary, we have developed a low-cost, high-throughput fabrication process for producing large-area, well-ordered periodic nanopillars for nanoimprinting with feature size less than 50 nm that would allow the nanoimprinting technique to be easily accessed without the need for e-beam lithography. When these stamps are used in nanoimprint lithography, large-area periodic nanostructures with lateral dimensions less than 30 nm can be obtained. The size and separation of the fabricated periodic nanostructures can be independently adjusted by selecting different diameters of polystyrene beads in the nanosphere lithography step and by trimming the nanopillars using various size reduction techniques, respectively. The shape of the nanostructures can also be modified by using different combinations of metal masks and etching recipes.

Experimental

Nanopillars: To fabricate silicon nanopillars, $1 \times 1 \text{ cm}^2$ substrates cut from n-doped silicon (100) wafers (Gredmann) were used. These silicon substrates were cleaned by immersion in piranha solution (3:1 concentrated $\text{H}_2\text{SO}_4/30\% \text{ H}_2\text{O}_2$) and sonication for 30 min. After sonication the substrates were rinsed repeatedly with ultrapure water (18.2 M Ω , Millipore Simplicity), acetone, and methanol and used immediately. To produce metal masks for the nanopillar array, nanosphere lithography was employed. Details of the nanosphere lithography procedure can be found in the literature [21,22]. In short, monodispersed polystyrene beads of various diameter purchased from Bangs Laboratories, Inc. (Fishers, IN) were diluted in a solution of surfactant Triton X-100 (Aldrich) and methanol (1:400 by volume). This solution was then spin-cast onto substrates to form hexagonally closed-packed 2D colloidal crystals. Depending on the experimental requirements (single or double layer), the speed of spin-coater was varied between 800 and 3600 rpm (~ 1500 rpm for a double layer), and the dilution ratio of the polystyrene solution was also changed. It was found that the formation of self-assembled 2D colloidal crystals strongly depended on the speed of spin-coater. These 2D colloidal crystals were then used as the deposition templates. A 50 nm thick Cr film was deposited over the polystyrene masks at a rate of 15 nm min^{-1} in an ULVAC vapor deposition system at a pressure of 1×10^{-3} Pa. After Cr deposition, the polystyrene beads were removed by sonicating the substrates in CH_2Cl_2 solution for 3–5 min. To fabricate silicon nanopillar arrays, substrates with metallic masks were placed in a reactive ion etcher (Oxford Plasmalab 80 Plus, 80 W) with a gas mixture of CHF_3 (20 sccm) and O_2 (2 sccm) at a total pressure of 25 mtorr. The nanopillars used for nanoimprinting were fabricated using the procedure mentioned above and were etched for 12 min. The height of the nanopillars was measured to be 150 nm. To remove the chromium, the nanopillar arrays were dipped into a chromium etchant (CR-7, Transene) for 15 s.

Scanning Electron Microscopy: All SEM images were taken in a LEO 1154 scanning electron microscope at 5–20 kV. All samples were coated with a thin layer of metal (~ 10 nm) prior to imaging.

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Up-conversion Luminescence in Dye-Doped Crystals of Potassium Hydrogen Phthalate**

By Jason B. Benedict, Paul M. Wallace, Philip J. Reid, Sei-Hum Jang,* and Bart Kahr*

Solid-state photonic devices containing dyes are typically fabricated as doped polymers and glasses. Single crystals would be an attractive alternative. Here, we report that rhodamine 110, among many other two-photon absorbing laser dyes, can be oriented within particular growth sectors of large, single, second harmonic generation- (SHG)-active crystals of potassium hydrogen phthalate.

In the recent past, we have studied the processes of dyeing crystals^[1] and have designed single crystals of simple sulfate, phosphate, and carboxylate salts that have oriented and overgrown organic dyes during growth from solution. During the course of this work we demonstrated that simple single crystals doped with luminescent dyes could be fashioned into lasers.^[2] Dye-doped zeolites were also shown to function as single-crystal micro-lasers.^[3] This work extended the range of solid-state dye laser (SSDL) gain media that had been restricted exclusively to polymers and glasses. Single crystals are an attractive alternative because of their higher thermal conductivity, reduced scattering, and intrinsic polarization. More importantly, the photostability of the fluorophore may be enhanced due to the restriction of both intra and intermolecular dynamic processes within the lattice.

[*] Dr. S.-H. Jang, Prof. B. Kahr, J. B. Benedict, P. M. Wallace, Prof. P. J. Reid
Department of Chemistry, University of Washington
Box 351 700, Seattle, Washington, DC 98195-1700 (USA)
E-mail: kahr@chem.washington.edu

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Here, we describe materials that we propose as gain media for practical up-conversion^[4] SSDLs. Such lasers will be based upon an efficient SHG host crystal, potassium hydrogen phthalate, commonly known as KAP (an acronym for potassium acid phthalate), that can be doped with luminescent, two-photon-absorbing dyes.^[5] By pumping the crystal at 800 nm we aim to excite dye dopants at the second harmonic frequency (400 nm) in phase-matching direction. In addition to two-photon absorption in directions where the SHG is minimal. While this paper focuses on the up-conversion luminescence in KAP crystals doped with rhodamine 110, this is just one of 80 dyes we have oriented in KAP crystals, an extraordinarily general host for a wide variety of multifunctional guest molecules. Selected crystals demonstrating up-conversion luminescence across the visible spectrum are illustrated in Figure 1.

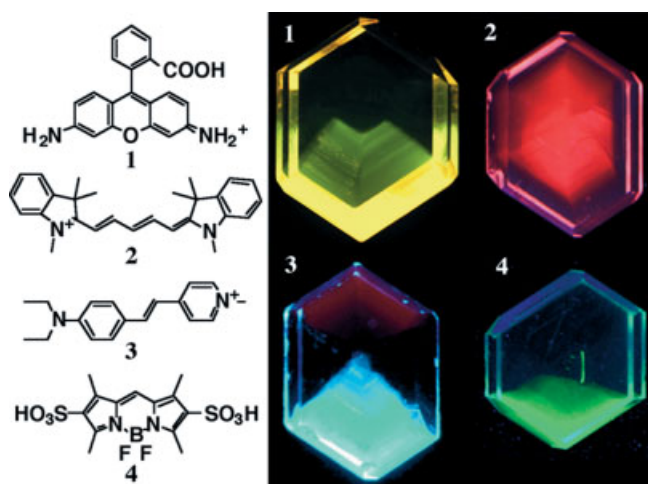


Fig. 1. Photoluminescence of laser dyes doped in KAP. (1) Rhodamine 110 chloride; (2) 1,1',3,3,3',3'-hexamethyl indodicarbocyanine iodide (HIDCI); (3) *trans*-4-(4-(diethylamino)-styryl)-1-methylpyridinium iodide (DEDASI); (4) 4-sulfonato-3,3',5,5'-tetramethyl-2,2'-pyromethene-1,1'-BF₂. Counter ions are not drawn. In many cases (e.g., 3) the solid-state photophysical properties differ markedly from solution and show great variability within different growth sectors of a single crystal, indicating variable conformations, states of protonation, and aggregation. These systems are subject to ongoing investigation.

KAP crystals (space group *Pca*2₁, $a = 9.614(4)$ Å, $b = 13.330(1)$ Å, $c = 6.479(2)$ Å)^[6] are built of layers of potassium and hydrogen phthalate ions stacked along [010] (Fig. 2). The absolute configuration of the polar [001] axis, to which all *hkl* indices refer, was determined by the anomalous dispersion of X-rays and is consistent with the assignment made previously.^[6] Observed phase-matching directions approximately perpendicular to the {111} faces are consistent with the values reported by Belyaev et al.^[7] KAP was chosen for this study because it is easily grown from aqueous solution as large (>10 cm³) {010} plates and has perfect (010) cleavage. This system has been used to model crystal growth kinetics^[8] and it has also been well studied for its optoelectric, piezoelectric, pyroelectric, and elastic properties.^[9]

Large dyed KAP crystals were grown from seeds in aqueous solutions containing 10⁻⁶ to 10⁻³ M concentrations of **1** (Fig. 1) during programmed 5 °C temperature-reduction sequences (0.5 °C day⁻¹) near 30 °C. The resulting crystals

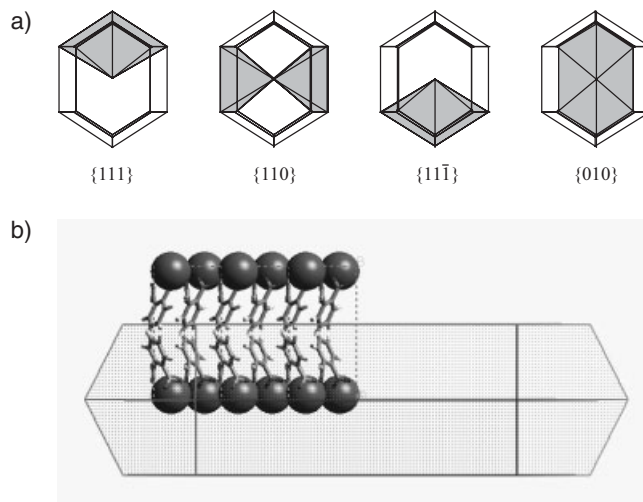


Fig. 2. a) Schematic representation of KAP habit showing growth-sector-specific inclusions. b) Crystal structure of KAP viewed down the *a*-axis. The horizontal axis is *c* and the vertical axis is *b*.

showed patterns of color that were consistent with the fact that different crystallographic faces have different affinities for the dyes. Dyes are thus contained in polyhedral sub-volumes of the crystals, i.e., growth sectors, volumes of the crystals that have grown through particular faces in particular directions. **1** was primarily contained in the four {111} growth sectors with faint inclusions in the {010} and {110} growth sectors as shown in Figure 2. Absorbance measurements of a dissolved crystal grown from 4.9 × 10⁻⁴ m dye solutions, where *m* = moles of dye kg⁻¹ of host, indicated that the concentration of **1** in the {111} sector of the crystal was 3.6 × 10⁻⁶ m.

The rhodamine 110 cation is incorporated in the negative direction of the polar [001] axis, by adsorbing to the {111} faces in preference to {111}. This selectivity is presumably an electrostatic consequence of the fact that {111} faces are OH-rich, whereas the {111} faces display the negatively charged carboxylate groups.

The absorption maxima of **1** was 498 nm in water, 502 nm in a saturated KAP solution, and 505 nm in the crystal. The luminescence maxima were 523, 532, and 532 nm, respectively (Fig. 3).

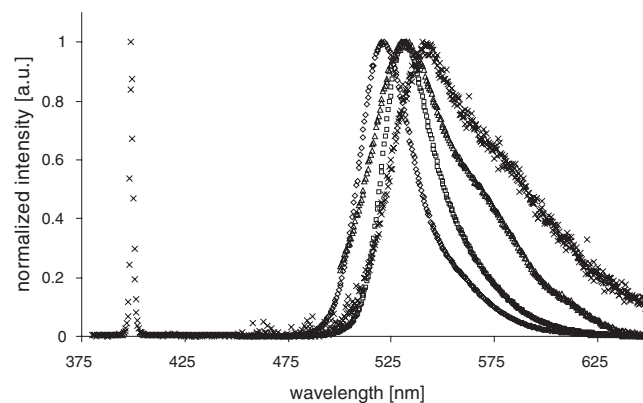


Fig. 3. Normalized one-photon luminescence spectra of **1** ($\lambda_{\text{ex}} = 400$ nm) in water (\diamond), KAP solution (\square), KAP crystal (\triangle), and up-conversion ($\lambda_{\text{ex}} = 800$ nm) of **1** in KAP crystal (\times). The sharp peak at 400 nm is the doubling of the fundamental.

Upon irradiation close to the phase-matching direction with 800 nm light, a sharp 400 nm band was observed (SH) in addition to the dye luminescence maximum at 544 nm. The included dyes are oriented within the lattice as is evident when considering the fluorescence anisotropy where I_d/I_c (I : intensity; the subscripts refer to the a - and c -axes, respectively) = 0.62. **1** was less anisotropic than most other KAP dye-inclusion crystals, many of which shown near-complete absorption and luminescence anisotropy.

The luminescence lifetime of rhodamine 110 in KAP ($\lambda_{\text{ex}} = 400$ nm, $\lambda_{\text{em}} = 532$ nm) was measured to be 3.7 ± 0.2 ns. The photoluminescence efficiency (Φ_{PL}) of a 2.36 mm thick slice of **1** in KAP was determined to be 0.081, using the method described by Palsson and Monkman.^[10] This figure can be compared with other rhodamine derivatives in polymer^[11] and sol-gel matrices^[12] that typically show efficiencies of about 50 %; but our value was measured far from resonance, in keeping with the self-doubling theme. Photobleaching experiments were carried out to assess the improvement single-crystal isolation affords when compared to traditional polymer doping. A slice of a KAP crystal and a polyvinylalcohol (PVA) film (80 % hydrolyzed $\bar{M}_w = 9000$ – $10\,000$), both prepared from solutions of equivalent concentration (in m), were mounted on an inverted microscope excited with an 800 nm femtosecond laser excitation source. The up-conversion fluorescence was measured as a function of time. As illustrated in Figure 4, dyed KAP crystals exhibited persistent luminescence compared

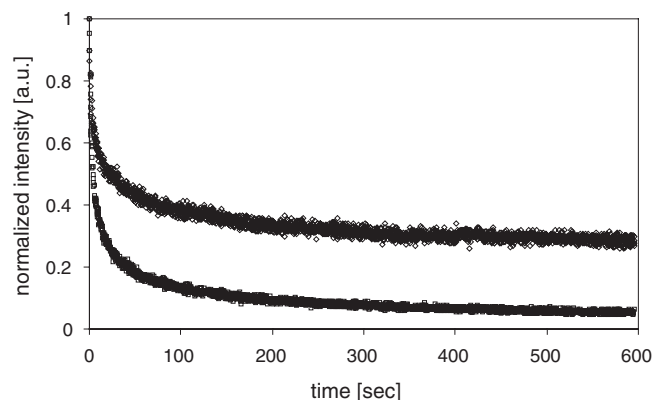


Fig. 4. Normalized up-conversion luminescence of **1** in KAP (upper) and PVA (lower) as a function of time ($\lambda_{\text{ex}} = 800$ nm, $P_{\text{ave}} = 1.0$ mW).

with doped PVA. Scans of the surfaces of the crystal and polymer, for excitations of < 5 mW average power, indicated that the loss of fluorescence intensity was the result of fluorophore degradation, rather than the failure of the host.

Maker fringe experiments are underway in order to separate the competing up-conversion mechanisms.

Experimental

Rhodamine 110 chloride (Aldrich) was used without further purification. The crystal-growing solution was prepared by dissolving A.C.S. grade KAP (Aldrich) in deionized water (Barnsted NANOpure, 18.2 M Ω cm $^{-1}$). The solu-

bility data of Solc et al. were used for the preparation of KAP solutions and in the calculation of supersaturation [13]. Crystals were indexed with a Stoe 2-circle Model J optical goniometer and a Nonius KappaCCD diffractometer. Molar absorptivities were determined with a Hitachi U-2000 spectrophotometer controlled by Spectracale software (Galactic Industries). Crystal absorption spectra were obtained with SpectraCode Multipoint Absorbance Imaging (MAI-20) Microscope. The extinction directions of the crystals were used to orient the sample relative to the input polarization. Lifetime measurements were carried out on a Photon Technology International pulsed nitrogen dye laser fluorescence lifetime spectrometer. Quantum efficiencies were determined using a Jobin-Yvon Fluoromax-2 fluorimeter fiber-optically coupled to a Newport integrating sphere. Solid-state fluorescence measurements were made using the Fluoromax-2 fiber-optically coupled to an IMT-2 inverted Olympus microscope. Two-photon excitation provided by a Millennia pumped, Tsunami Ti:sapphire oscillator operating at 800 nm pulsed at 80 MHz and 120 fs was channeled into a homebuilt inverted microscope [14]. Up-conversion fluorescence was detected utilizing a single-photon-counting photomultiplier tube (Hamamatsu HC135-01). The up-conversion luminescence spectrum was measured using a fiber-optically coupled Ocean Optics photospectrometer.

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