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Materials Chemistry and Crystal Growth

Dedicated to Prof. Emanuel Kaldis and Dr. Fritz Hulliger

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'Molecular Designing of Materials. Science, guided by molecular understanding, takes up the challenge to create materials for the future.'

A.R. von Hippel, 1962 [1]

Abstract. Materials chemistry and crystal growth are seen as closely related activities because the assessment and implementation of numerous physical properties are based on single crystals and epitaxial layers. The idea of a materials synthesis directed toward the investigation and application of physical solid-state properties is outlined by three examples: *i*) the supramolecular synthesis of polar molecular crystals, *ii*) a quest for optical materials for short wavelength generation, and *iii*) crystal growth and epitaxy of fluoride laser materials.

1. Introduction

A number of new research journals [2] of the last decade give a significant account on a common interest of chemists, physicists, crystallographers, and people from other fields of research, called *the chemistry of materials*. Taking advantage of the excellence of synthetic chemistry in making all kinds of molecules and solids, the chemistry of materials is an endeavor producing compounds providing *designed physical or chemical properties*.

Along with other forms of condensed matter, *single crystalline* materials are basic to a fundamental investigation of numerous properties of newly obtained compounds as well as they are the key to many real-world applications. Therefore, R&D of materials showing particular solid-state properties often comprise a chemical synthesis along with a procedure yielding single crystals or epitaxial layers of a tailored real structure and an appropriate size.

Briefly said, this is the working philosophy we have been following for several years now [3]. In practice, we begin by whatever a physical phenomenon of inter-

est, searching then for a synthetic approach which at the end should result in an optimized physical performance of crystals or epitaxial layers. Because the group's activity is rather widespread, we shall focus here on examples originating from only three fields. The common issue of these subjects is the focus on *optical properties*.

The overview covers work performed at Bern during the last five years.

2. Tuning the Polarity of Supramolecular Materials

'We consider this to be an important achievement that points to new methodology, a paradigm of guest-host induced dipolar alignment, that can be used by chemists to engineer solid-state materials with specific properties.'

Tam & Eaton et al. [4]

There is a long tradition in the synthesis and crystal growth of dielectric materials showing *polar* properties called, e.g., the pyroelectric, the piezoelectric, and the nonlinear optical effect [5]. Real-world applications resulted from ABO_3 compounds where pronounced polar properties originate from ferroelectric ordering. It turned out to be unlikely that further improvement in this area of ca. 200 inorganic compounds will result from a rational design. This because of the cooperative nature of polar properties in ferroelec-

tric materials. However, engineering of *solid solutions* led to a broad class of materials applied in capacitors, piezoelectric steppers and motors, optical amplitude modulation devices, frequency filters and converters, and holographic storage materials [6].

On the contrary, the synthesis of electrically *hyper-polarizable* molecules has prompted alternative solutions given by inorganic [7] and organic [8] compounds: The nonlinear electrical susceptibility of *molecular crystals* is to a very good approximation proportional to the density and the hyperpolarizability of molecular entities in the solid state. The electronic and the packing properties of molecular bricks are hence the key targets of a synthesis aimed to produce materials with optimized polar properties. Whereas molecular design worked out to be straightforward, the task of packing dipoles in the solid state encounters again difficulties due to effects of cooperativity. Nevertheless, several approaches in crystal engineering succeeded in packing molecules suitable for frequency conversion or the electro-optic effect [8][9]. However, these concepts show a lack of generality, because they may apply only to a small number of particular molecular structures, packing just in the appropriate way.

Recently, we have elaborated a more general concept to *generate polar solids showing a parallel alignment of dipoles* [10]. We could demonstrate that an application of supramolecular chemistry is providing a necessary frame for the spontaneous generation of *tunable polarity* [11]. From the pioneering work of Tam, Eaton, and Ramamurty et al. [4][12] it is known that channel-type inclusion compounds may yield an unexpectedly high percentage of polar crystal structures.

In the course of the co-crystallization of rod-shaped nonlinear optically active molecules (A- π -D: acceptor (A) and donor (D) disubstituted π -conjugated guest molecules) with perhydrotriphenylene (PHTP) we have worked out [10] syntheses yielding polar crystals in close to 100% of more than the 40 cases we have investigated. Followed by the discovery [11][13][14] that spontaneous polarity formation in channel-type inclusion compounds is due to a first-order Markov process [15], we gained a *synthetic tool for a valid prediction and production of polarity in particular molecular crystals*. According to the Markov model, the alignment of dipoles when entering growing channels is driven by the intermolecular interaction energies of the terminal groups A and D (Fig. 1). Because of the mathe-

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mathematical equivalence of equations describing different processes such as dipole alignment in growing PHTP inclusion crystals and, e.g., the educt-product ratio of an isomerization reaction, we can say, that for the first time, we have a tunable synthetic procedure which is not primarily producing a compound as usual, but is producing a physical property such as *polarity*. This is the real advantage of a *supramolecular approach* over the use of other types of synthetic strategies. If we ask for most simple requirements in order to obtain a polar molecular crystal, one may proceed as follows: *i*) Formation of a channel-type inclusion crystal preferably by use of a nonpolar host molecule, and *ii*) an X- π -D-R-type guest molecule (X: functional group providing a destabilizing (repulsive) collinear interaction -X...X-; D: electronic donor functionality; R: unit terminated by a less polarizable group). According to Fig. 2, there is also polarity generation for stabilizing (attractive) -X...X- interactions.

Tunability of polarity is given by the fact that D- π -D or A- π -A co-guest molecules can interfere with the alignment of A- π -D entities by cancelling or enhancing the resultant polarity of an inclusion crystal (Fig. 3). Experimental confirmation of the stochastic model derived from the theory of *Markov* became possible due to a newly developed technique called scanning pyroelectric microscopy [16].

Extended work on these nanotube crystals is now being directed toward the growth of epitaxial layers, with the aim of investigating photoinduced charge transport along the channels [17]. Other ongoing work is concerned with the structural disorder and the probing of functional group interactions -X...Y- (two different or equal groups) at a collinear geometry.

3. Optical Materials for Short Wavelength Generation

'On montre qu'on peut utiliser le transfer d'énergie entre deux ions de terre rares pour réaliser l'absorption successive de deux photons dans un compteur quantique infrarouge'.

F. Auzel [18]

Owing to the breakthrough in semiconductor materials, i.e., the demonstration of an epitaxial GaN:In waveguide laser at 300 K operating at a wavelength down to 417 nm [19], there is a great potential for real-world applications of compact blue and green laser light sources. In general, applications will need dif-

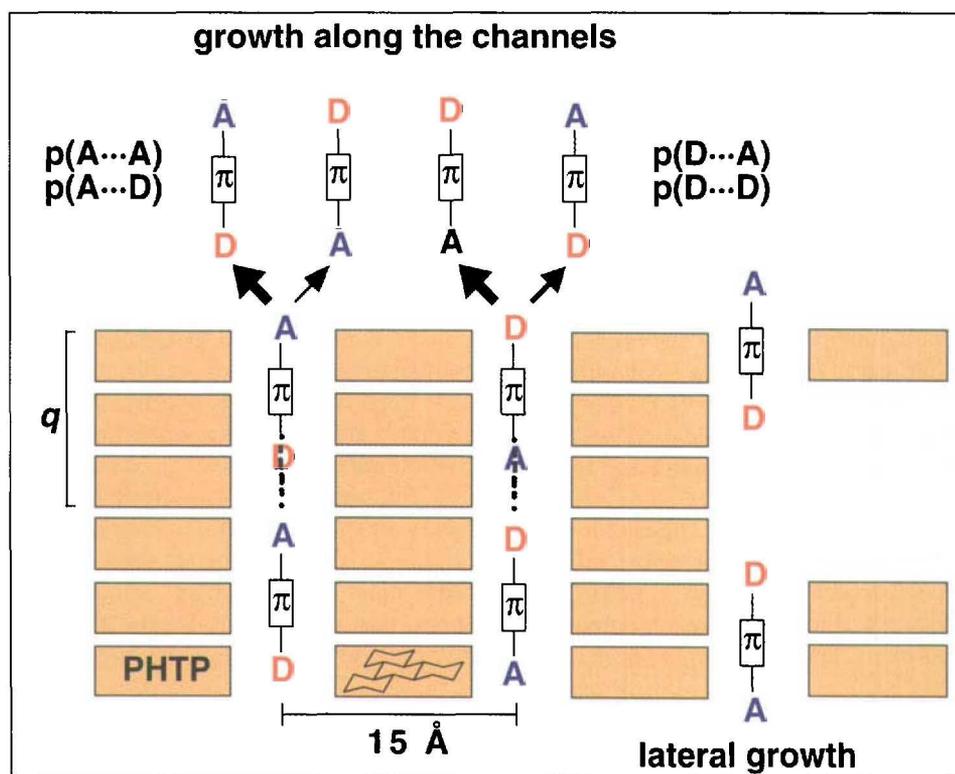


Fig. 1. Schematic representation of the channel-type structure of perhydrotriphenylene (PHTP) inclusion compounds and the two mechanisms operating (along the channel axis and perpendicular to it) for guest-molecule attachments (for details see [11][16]). The polycyclic hydrocarbon structure of all-*trans*-PHTP ($C_{18}H_{30}$) is illustrated. The probabilities $p(X...Y)$ of the various possible attachments are identified by arrows. The growth step q in this case corresponds to a new layer whose depth is ca. 3 PHTP molecules per guest molecule.

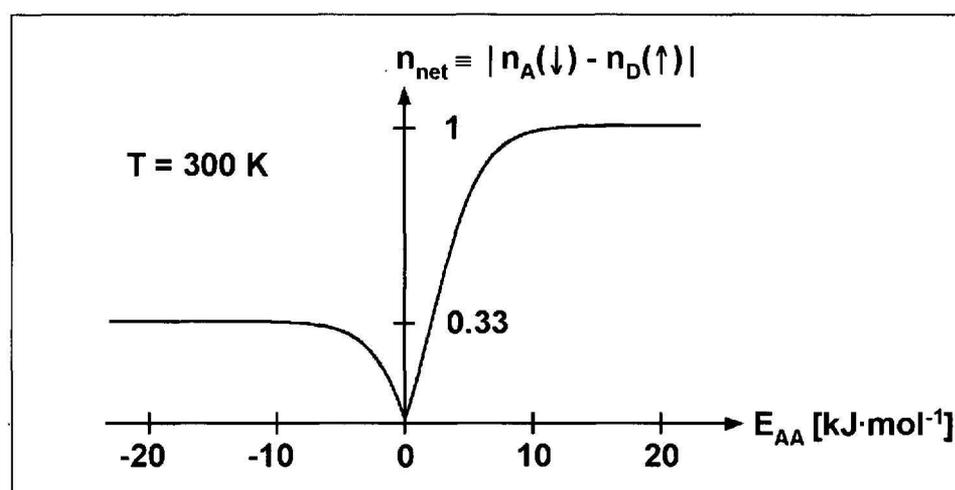


Fig. 2. Polarity evolution as a function of the interaction E_{XX} . The curve was calculated using *Markov's* theory on stochastic processes (for details see [11]). $n(\downarrow)$, $n(\uparrow)$ correspond to the two different orientations for aligned molecular dipoles in the channels of perhydrotriphenylene (PHTP). n_{net} corresponds to the resultant polarity (vector sum). Use of an A functionality providing a stabilizing (attractive) interaction energy would produce only one third of the theoretically possible polarity, if the molecules A- π -D-R are terminated by a nonpolarizable group R.

ferent levels of output power and beam quality. Data storage, laser TV, and ophthalmology are based on continuous wave lasers below one Watt, whereas applications in spectroscopy, materials treatment, and surgery often require higher intensities and pulsed sources. From the viewpoint of laser engineering, there exist approaches based on different materials and

conceptual complexity: *i*) Direct *electrical* generation of light in semiconductor waveguide lasers will probably represent the most efficient and commercially valuable solution in long term for low power where beam quality is not critical. *ii*) *Hybrid* systems comprise a number of demonstrated and proposed solutions which may rely on *bulk* or *waveguide* media.

In hybrid systems, we generate short wavelengths either through the use of, e.g., a semiconductor laser diode operating at the near infrared (NIR) range pumping *i*) a dielectric solid-state laser being frequency-converted or *Raman*-shifted due to a nonlinear optical material, or *ii*) an upconversion material. Implementation of epitaxial waveguide lasers is of great interest in both cases. Basic aspects of mechanisms allowing for frequency conversion are shown in Fig. 4. As we will outline in the case of *upconversion* (UC) materials, the development of optical converters is both chemically challenging and technologically demanding [6].

For UC to take place, solid solutions of appropriate host lattices with lanthanide ions such as Er^{3+} , Pr^{3+} , Tm^{3+} and Ho^{3+} , are necessary. First and recent demonstrations of UC lasers used *fluoride* and *oxide*

host lattices as well as fluoride glasses [20]. As the reduction of the phonon energies of host materials significantly slows down the non-radiative multiphonon relaxation and thus increases the UC luminescence efficiency, there is considerable interest in so-called *low-phonon* UC materials [21]. Because lowering phonon energies can be achieved by introducing ligands of larger molecular weight and weaker bonding than to O^{2-} and F^- , a number of *chloride* and *bromide* materials have been found to show efficient luminescence in the visible when excited at NIR frequencies. However, compounds of a thermodynamic stability lower than binary and ternary metal oxides and fluorides are expected to be air-sensitive. Indeed, most of the binary, ternary, and quarternary metal chlorides and bromides investigated in the past are highly air-

sensitive materials [22] and are therefore technologically demanding with respect to laser applications.

Based on this groundwork, we concentrated on a quest for materials which form solid solutions with, e.g., Er^{3+} and are *air-stable*. At first we had to recognize that all the binary chlorides of the 3rd to the 6th row metals being stable in air show a very low distribution coefficient for Er^{3+} , even when attempting charge compensation by co-dopands. The testing of a large number of known and new metal chlorides and bromides finally yielded two different materials: $\text{Cs}_3\text{Tl}_2\text{Cl}_9$ [23] and Ba_2YCl_7 [24], both forming solid solutions with Er^{3+} .

$\text{Cs}_3\text{Tl}_2\text{Cl}_9$ is featuring unique properties among most other compounds containing an M^{3+} site to accommodate Er^{3+} . This compound is one of the few low-phonon lattices being completely stable in air. However, difficulties arose in growing large single crystals of solid solutions with Er^{3+} , because the compound segregates before melting at 310° [23]. The transition to an yet unknown phase is reversible in Cl_2 atmosphere. This implies that bulk and epitaxial growth of $\text{Cs}_3\text{Tl}_{2-x}\text{Er}_x\text{Cl}_9$ will have to be carried out at $T < 300^\circ$ and under Cl_2 atmosphere. Preliminary results show that ZnCl_2 can be used as a solvent. The luminescent properties are such that $\text{Cs}_3\text{Tl}_{2-x}\text{Er}_x\text{Cl}_9$ bears a potential for a yellowish-green light source.

Ba_2YCl_7 is a member of a new isotopic series of $\text{Ba}_2\text{M(III)Cl}_7$ ($\text{M} = \text{Gd}-\text{Yb}$, Y) compounds forming isolated polyhedrons of seven-coordinated M^{3+} lanthanide ions, which may be described as a trigonal prism monocapped on a rectangular prismatic face [24]. Large single crystals of solid solutions of $\text{Ba}_2\text{Y}_{1-x}\text{Er}_x\text{Cl}_7$ can be obtained by the *Czochralski* method. Single crystals are relatively air-stable when compared to similar ternary and quarternary chlorides, although protection is necessary for all types of optical investigations. Ba_2ErCl_7 and $\text{Ba}_2\text{Y}_{1-x}\text{Er}_x\text{Cl}_7$ show promising NIR to near UV and VIS upconversion luminescence properties. Upon excitation at either 803 nm or 980 nm, an intense yellowish-green (ca. 550 nm) transition from $^4\text{S}_{3/2}$ to $^4\text{I}_{15/2}$ and an unusually strong $^4\text{G}_{11/2}$ to $^4\text{I}_{15/2}$ (385–390 nm) luminescence are observed. A detailed spectroscopic analysis revealed [25] that the excited-state absorption UC process (see Fig. 4) may be strongly enhanced by a two-color excitation, i.e., by tuning two pump laser lines to the first and second absorption step, respectively [26].

Recent work yielded a few compounds

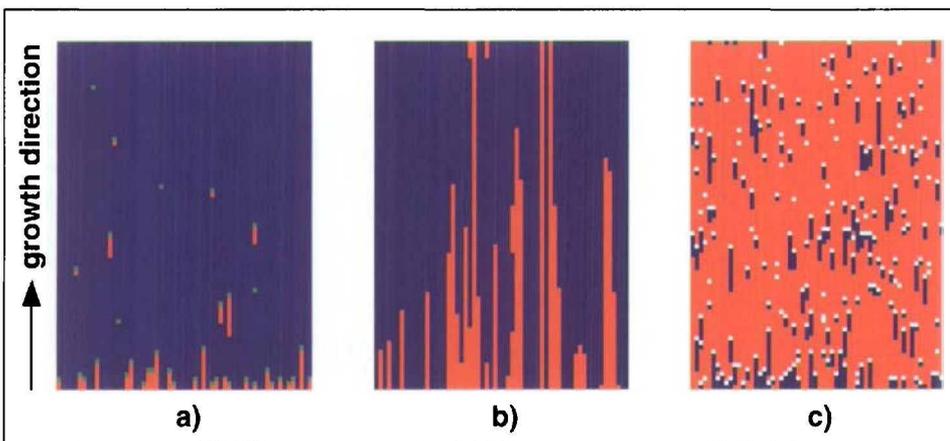


Fig. 3. Polarity evolution within channel-type inclusion crystals along the channel axis. Stochastic simulation according to *Markov*'s theory. Dipoles are represented by square pixels (vertical: channel direction; horizontal: different channels; blue: \downarrow ; red: \uparrow ; green: inclusion of $\text{A}-\pi-\text{A}$; white: inclusion of $\text{D}-\pi-\text{D}$; $\Delta G_{\text{AD}}/RT = -6.9$, $\Delta G_{\text{DD}}/RT = -3.4$, $\Delta G_{\text{AA}}/RT \equiv 0$ (kJ/mol)). a) Influence of $\text{A}-\pi-\text{A}$ when molar fraction $X_{\text{A}-\pi-\text{A}} = 0.18$ (enhancement of convergency and net polarity \downarrow); b) only $\text{A}-\pi-\text{D}$ (more orientational defects close to the nonpolar seed, until the system reaches a thermodynamic equilibrium with respect to processes on the growing interface); c) influence of $\text{D}-\pi-\text{D}$ when molar fraction $X_{\text{D}-\pi-\text{D}} = 0.18$. The effect of $\text{D}-\pi-\text{D}$ is such that polarity is reversed (\uparrow) and n_{net} is reduced.

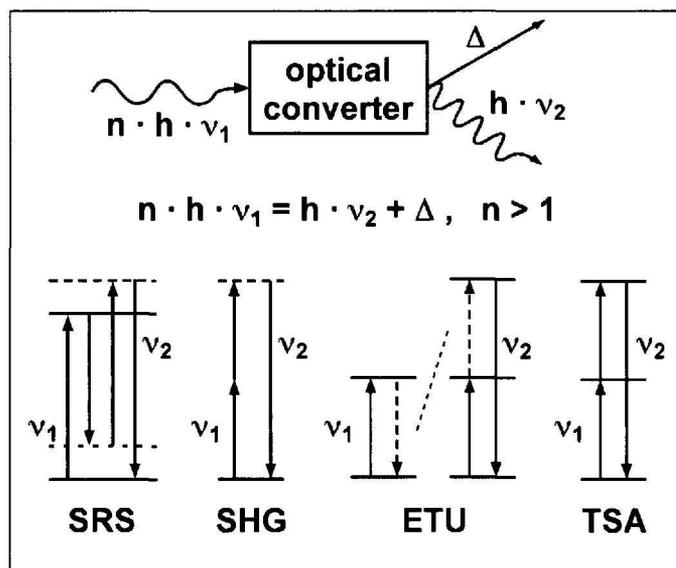


Fig. 4. Some basic mechanisms for short wavelength generation in an optical converter (n_1 : long-wave radiation; n_2 : short-wave radiation; Δ : fraction of absorbed energy which is not upconverted): Stimulated (first anti-Stokes) Raman scattering (SRS), second harmonic generation (SHG), energy-transfer upconversion (ETU), two-step absorption (TSA) (for details see [6]).

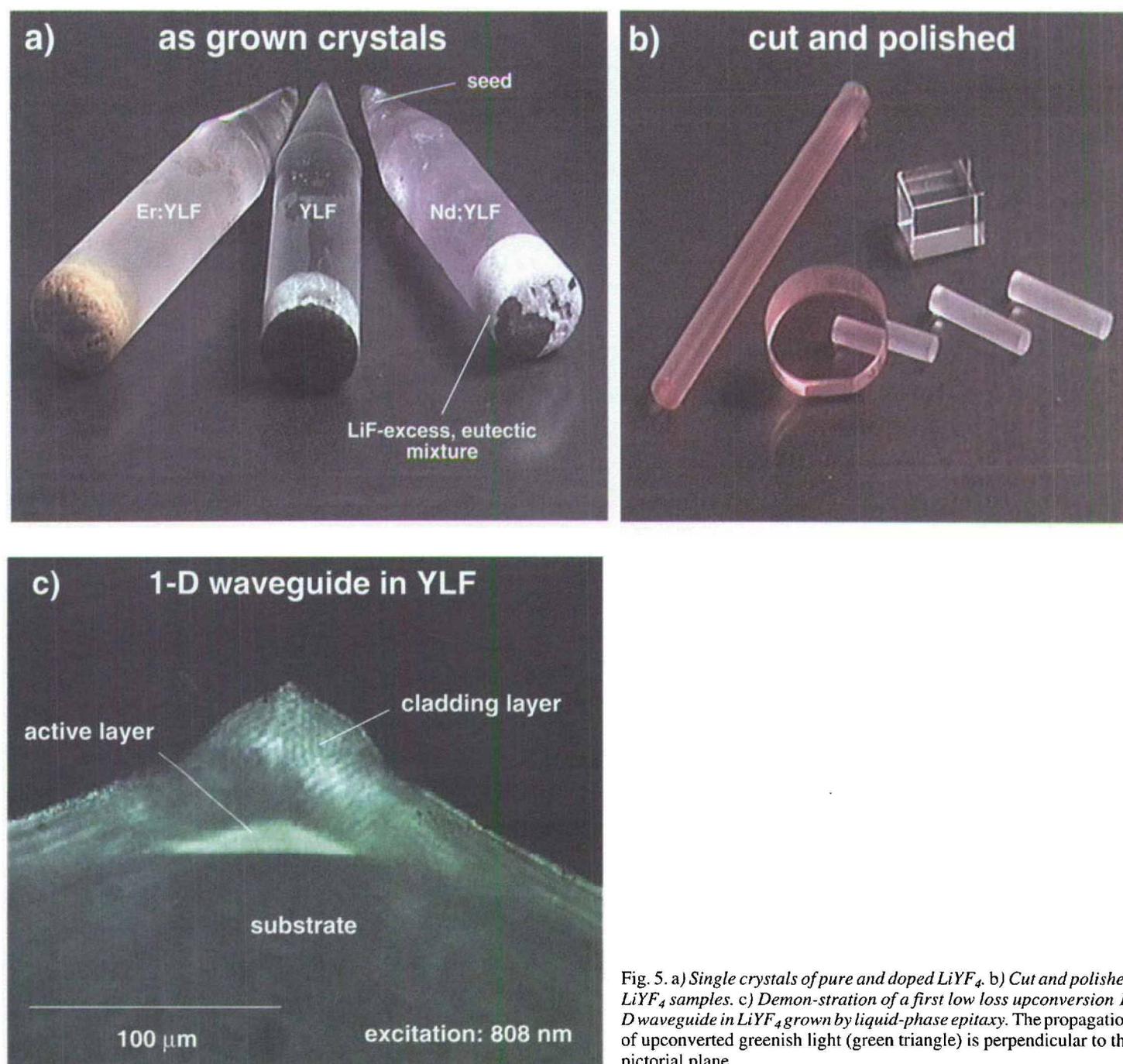


Fig. 5. a) Single crystals of pure and doped LiYF_4 . b) Cut and polished LiYF_4 samples. c) Demonstration of a first low loss upconversion 1-D waveguide in LiYF_4 grown by liquid-phase epitaxy. The propagation of upconverted greenish light (green triangle) is perpendicular to the pictorial plane.

which might become feasible materials for short wavelength generation by an UC mechanism. However, complete air-stable low-phonon crystals which can accommodate Ln^{3+} ions to a few mol-% are hard to obtain. For this reason, we have expanded our quest into the field of stable fluoride compounds [27], accepting that their UC luminescence is generally weaker than reported for chlorides and bromides.

4. Crystal Growth and Epitaxy of Fluoride Laser Materials

'Crystals of the fluoride compounds with ordered structure which are doped with trivalent lanthanide ions occupy a specif-

ic position among almost three hundreds of the famous crystalline laser hosts'.

A. Kaminskii [28]

Regarding the effects of laser action and spectroscopy, an important difference between oxide and fluoride materials is given by the lower phonon energies of fluorides. With regard to synthesis and crystal growth, oxides are generally higher-melting compounds than fluorides. Oxides are prepared simply in air, where as fluorides of transition metals and lanthanides need complete exclusion of O_2 and H_2O , this because of the formation of, e.g., oxyfluoride phases. Fluoride laser materials give access to a broad range of wavelengths: A first demonstration of an UC laser was achieved for

monoclinic $\text{BaY}_{2-x-y}\text{Er}_x\text{Yb}_y\text{F}_8$ (red) and $\text{BaY}_{2-x-y}\text{Ho}_x\text{Yb}_y\text{F}_8$ (green) [29]. Substitution of Y by Lu yields an optically more convenient orthorhombic high-temperature phase, which by fast cooling techniques can be kept metastable at room temperature [30]. Tunable laser sources in the VIS range are obtained by Cr^{3+} -doped LiMAlF_6 ($M = \text{Ca}, \text{Sr}$). A host lattice offering a broad range of transparency is LiYF_4 allowing transitions from the near UV to the IR. Solid solutions of Er^{3+} and LiYF_4 are of particular interest for medical applications [31]. At present, most of the laser applications mentioned above rely on *bulk crystals*. However, the use of *optical waveguides* instead of bulk crystals does not only hold promise for improvements such as lower lasing thresh-

olds of, e.g., UC lasers, it also allows for smaller setups with fewer and possibly integrated optical components. Waveguide lasers are very common in semiconductor materials and some fiber-type glass hosts, but the fabrication of epitaxial waveguides of dielectric laser crystals still presents a challenge. This is the reason why we entered the crystal growth and *liquid-phase epitaxy* of LiYF_4 . This scheelite-type material is melting incongruently. A reinvestigation of the binary phase diagram and the crystal-growth procedure resulted in a gradient-freezing technique producing crystals (Fig. 5), showing an equal IR laser performance [32] as commercially distributed *Czochralski* grown samples of LiYF_4 . Based on this groundwork, we gained epitaxial layers by dipping LiYF_4 substrates into a solution of 40 mol-% YF_3 and 60 mol-% LiF . To account for the small change in the refractive index caused by a low level of the activator ions (Nd^{3+} , Er^{3+}), ca. 10 mol-% of the Y^{3+} were replaced by Gd^{3+} to form $\text{LiY}_{1-x-y}\text{Ln}_x\text{Gd}_y\text{F}_4$ layers on top of a pure LiYF_4 substrate. By growing a cladding layer of LiYF_4 , buried *planar* and *ridge type* (1-D) waveguides were fabricated [33]. For the first time, Nd^{3+} down-conversion laser operation could be demonstrated for a buried $\text{LiY}_{0.89}\text{Nd}_{0.01}\text{Gd}_{0.1}\text{F}_4$ 1-D waveguide end-pumped with a laser diode operating at 806.5 nm [34]. For buried $\text{LiY}_{0.89}\text{Er}_{0.01}\text{Gd}_{0.1}\text{F}_4$ layers, intense UC luminescence was observed [35] in low loss (< 0.3 dB/cm) waveguides. Present investigations concentrate on the preparation of high-temperature solutions being more dilute than possible by the phase diagram of LiYF_4 . This because improvement is directed toward the growth of ca. 5 μm thick layers being laterally structured to 1-D by etching and other techniques. The elaboration of an improved epitaxial growth procedure [36] is considered a key on the way to a first crystalline Er^{3+} or a $\text{Pr}^{3+}/\text{Yb}^{3+}$ 1-D UC waveguide laser.

5. Instead of a Summary

Along the development of materials into real devices chemistry is playing a key role from the first appearance of a compound as well as chemistry stays on and often turns into the bottleneck of an endeavor. This has to do with processing compounds finally into *ceramics*, *glasses*, *polymers*, and *single crystals* designed to show particular properties. However, after the discovery of whatever a new and exciting compound, the way to follow into

a valuable material is much less spectacular, but nevertheless needs attention and funding! Following my own experience in crystal growth, precise knowledge on a *phase diagram*, i.e., the stability conditions for a compound, is an example of critical importance to the development of many materials called at first 'promising'.

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