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Optical materials for short wavelength generation

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Abstract

This review reports on recent achievements in the synthesis and crystal growth of materials for efficient generation of short wavelength light. Materials exhibiting harmonic generation, stimulated Raman scattering or upconversion are discussed. Early and recent work has confirmed that ferroelectric oxide and borate crystals are most feasible for harmonic generation, while structures containing molecular-like entities seem to be able to generate multiple stimulated Raman scattering responses. In the field of upconversion, halide materials turned out to be more efficient than e.g. oxides. Low-phonon materials such as chlorides or bromides yielded efficient luminescences down to the near UV region. However, chloride and bromide crystals containing rare earth ions generally are not stable in air. The search for stable host crystals may be considered a major challenge in the synthesis of new materials for upconversion. Independent of the nonlinear optical mechanisms of short wavelength generation, formation of waveguides gained considerable importance, because production for real world applications most evidently will follow a waver type technology.

Keywords: Harmonic generation; Upconversion; Stimulated Raman scattering; Crystal growth; Waveguides

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1. Introduction

Owing to the breakthrough in semiconductor materials research, i.e. the synthesis and demonstration of an epitaxial GaN:In room temperature waveguide laser at a wavelength down to 417 nm [1,2], there is a great potential for the real world application of compact blue and green laser light sources. In general, applications will be wide spread: data storage, laser TV and ophthalmology are based on continuous wave laser power below one watt (typically some hundreds of mW); applications in spectroscopy, materials treatment and surgery often require higher intensities and pulsed sources.

From the point of view of laser engineering, there exist approaches of different conceptual complexity:

- Direct electrical generation of light in a semiconductor waveguide laser structure at long term will probably represent the most efficient and commercially valuable solution for low power were beam quality is not critical.
- Hybrid (laser diode pumped) systems comprise a number of demonstrated and proposed solutions which may relay on bulk or waveguide media.

In a hybrid system short wavelengths are generated either through the use of, e.g. a semiconductor laser diode operating in the near IR (NIR) range pumping (i) a dielectric solid state laser being frequency converted or Raman shifted (stimulated Raman scattering) due to a nonlinear optical material, or (ii) an upconversion material. Implementation of an 1-D device is of great interest in both cases. Basic aspects of mechanisms allowing for optical frequency transformation are shown in Fig. 1.

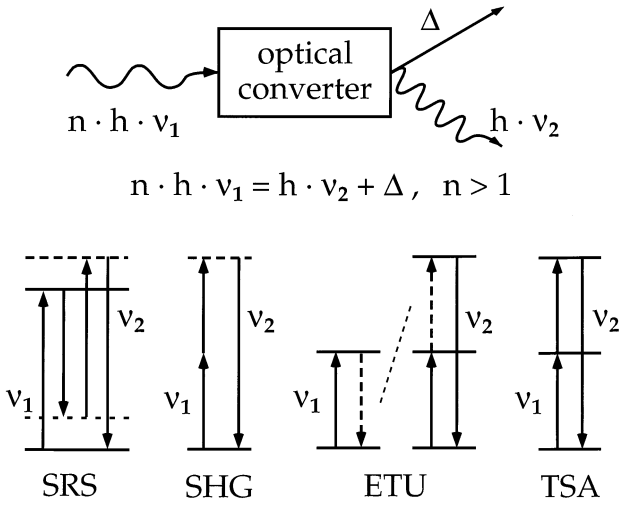

Fig. 1. Some basic mechanisms for short wavelength generation in a optical converter (v_1: long-wave radiation; v_2: short-wave radiation; Δ: fraction of absorbed energy which is not upconverted): stimulated (first anti-Stokes) Raman scattering (SRS), second harmonic generation (SHG), energy transfer upconversion (ETU), two-step absorption (TSA) (adapted from Ref. [81]).

As we will outline below, further development of optical converters is both chemically challenging and technologically demanding.

In the following two chapters we shall recall some of the basic physical constraints in order to yield most efficient and chemically/mechanically stable materials of an appropriate form (3-D, 2-D, 1-D devices). To be close to the chemical audience we shall emphasise how chemical syntheses and crystal growth can contribute to make various classes of compounds feasible materials.

2. Materials for harmonic generation

Since the basic work by Bloembergen [3], harmonic generation by nonlinear optical materials has gained technical importance over the years.

As a guideline for materials synthesis and crystal growth technologies let us recall basic aspect to be met: (i) by point symmetry, second, forth,… (even Fourier components) harmonic generation occurs only in 20 point groups of crystals without a center of symmetry [4]. (ii) Generation of intense convertion requires true or quasi phase matching. In the case of a homogeneously poled crystal, linear optical and nonlinear optical properties will have to match [5,6], in the case of inhomogeneously poled material, a superimposed structuring, e.g. a periodic change of the sign of a nonlinear tensor coefficient, can lead to constructive interference of light converted along the optical path [7,8]. (iii) High efficiencies under phase matched conditions are obtained for materials exhibiting a nonlinear electrical polarisation due to rather soft lattice modes. The largest class of feasible materials is represented by the ferroelectric oxides ($KNbO_3$, $LiNbO_3$, $KTiOPO_4$, $BaTiO_3$ [9]) and related compounds (β-BaB_2O_4, LiB_3O_5, KH_2PO_4 [10]).

Concerning the probability of obtaining an acentric inorganic material, the perowskite structure type, mainly ABO_3 oxides, worked out to be the most promising class [9,11], showing the classical sequence of phase transitions [12], producing ferroelectric phases. However, these materials are grown at high temperatures in their centric phase [13]. Bulk crystals of acentric phases are thus obtained by cooling procedures to bring large crystals safely through one or two phase transitions. This major drawback render non-perowskite materials technologically even more reliable: Structures such as $LiNbO_3$ showing a transition close to melting or materials being grown below a temperature of a phase change including those performing no transition (β-BaB_2O_4, LiB_3O_5, $Li_2B_4O_7$) down to room temperature.

There is another remarkable class of materials, the various borates, which on the average yield a higher incidence of acentric structures (36%) than general materials [14,15]. Typical examples are β-BaB_2O_4 [16], LiB_3O_5 [17], $Li_2B_4O_7$ [18], $LaBGeO_5$ [19], $Ca_4GdO(BO_3)_3$ [20], $RbNbB_2O_6$ [21], $K_3Nb_3B_2O_{12}$ [22], and $MBe_2BO_3F_2$ (M = Na, K) [23]. It was found particularly efficient to combine the idea of a high polarisability of the [Nb(Ta)O_6] octahedra and structural elements given by introducing B_2O_3 in order to from acentric ternary phases [14].

It is important to notice that new developments comprise the synthesis of crystals creating both the NIR and frequency converted light (self-doubling materials). Promising results have been reported recently for $Ca_4GdO(BO_3)_3$ [20].

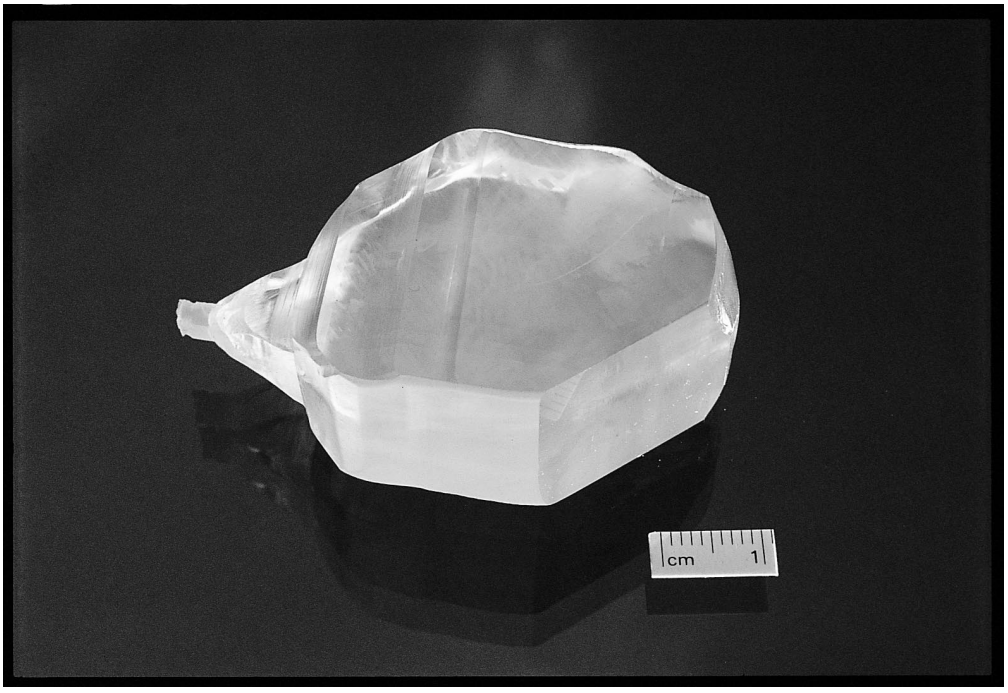

Fig. 2. $KNbO_3$ single crystal as obtained by the top-seeded solution growth procedure [27].

Since the conversion efficiency depends on the square of the optical path length, a certain interaction length is required. This is demanding with respect to the optical quality of bulk crystals. Advanced crystal growth of KH_2PO_4 (linear size up to ~ 0.5 m), $KNbO_3$ (volume up to ~ 22 cm^3; Fig. 2), $KTiOPO_4$, β-BaB_2O_4, and others has led to commercially available converters, being implemented in today's hybrid lasers yielding ~ 530 nm. For spectroscopic applications, optical parametric oscillators (OPO) [24,25] are of particular interest. In such devices difference frequencies can be generated, which is extending the frequency range of simple harmonic generation.

Because of the miniaturisation of most real world applications in opto-electronics, waveguiding structures are of great importance. Recent progress was achieved with respect to three different technologies: (i) epitaxial growth [26–31] of ABO_3 ferroelectrics on paraelectric substrates, (ii) waveguiding structures of ferroelectric bulk crystals by high energy ion implantations [32], and (iii) periodic poling on the surface of a $LiNbO_3$ waver in order to achieve quasi phase matching [8].

These latest improvements tell us that devices for large scale production most evidently will come from a wavertechnology. Crystal growth of appropriate substrate materials and corresponding surface modifying technologies are hence considered to be most relevant for the near future.

From the point of view of new materials, we can say that it is not likely that many new inorganic compounds will be found which would substantially exceed the nonlinear optical coefficients of, e.g. classical ferroelectrics. However, the search for new materials is of great relevance, with respect to their integral properties, featuring a good performance in (i) nonlinear efficiency, (ii) true or quasi phase matching, (iii) self-doubling, (iv) waveguide formation, and last but not least (v) their availability by crystal growth techniques.

So far, we have considered only effects due to acentric structures. However, materials providing uneven Fourier components in the anharmonicity are of interest for the conversion into the UV. An example is β-BaB_2O_4, being used up to fifth harmonic generation.

Other physical effects such as stimulated Raman scattering [25,33], allowing the generation of multiple Stokes and anti-Stokes responses, have gained new interest. Recent work seems to demonstrate that inorganic materials containing molecular units ($KY(WO_4)_2$ [34], $LaBGeO_5$ [35], $NaClO_3$ [36]) can, in principle, shift NIR pump light up to the blue. However, for practical application only the first Stokes and may be anti-Stokes lines are intense enough.

Up to here, we have focused the discussion on inorganic materials. Extensive research and technology devoted to molecular crystals [37–41] has demonstrated that organic crystals (from the point of view of nonlinearity) can surpass the efficiency of inorganic materials by orders of magnitude. However, from the point of view of engineering, organic crystals bring in the drawback of a lower mechanical and photochemical stability. Nevertheless, recent work has shown, that in the case of highly pure and perfect crystals, the damage threshold can be considerably high.

Coming back to the direct generation of light by semiconductors, we shall mention here, that electroluminescent [42] polymers bear a potential of laser applications in the visible.

3. Upconversion materials

Since the proposition of the quantum counter by Bloembergen in 1959 [43], different authors obtained visible fluorescence as a result of the sequential absorption of two photons (pump and signal) by rare earth (RE) ions [44]. In the mid 1960s, non-coherent processes between RE ions in the excited state attracted the interest of the scientists. Auzel [45] found an energy transfer between a sensitiser ion Yb^{3+} and an acceptor ion Er^{3+} in $WO_4Na_{0.5}Yb_{0.5}$:Er^{3+} to result in an efficient production of short wavelength light (540 nm) at irradiation around 970 nm. In the late 1960s and early 1970s such phenomena were studied extensively, culminating in the presentation of the first upconversion (UC) laser by Johnson and Guggenheim 1971, operating on BaY_2F_8:Yb^{3+}, Ho^{3+} and BaY_2F_8:Yb^{3+}, Er^{3+}, respectively [46]. Subsequently, interest in UC levelled out, until 1987 and 1990, when first room temperature UC laser actions were reported in $BaYb_2F_8$:Er^{3+} [47], $YLiF_4$:Tm^{3+} [48] and in a Ho^{3+}-doped glass fiber [49]. Additionally, efficient NIR laser diodes

Table 1
Selection of blue–green upconversion crystal lasers (adapted from Ref. [50])

Host crystal:dopant	Laser λ (nm)	Pump mechanism (λ [nm])	T (max.) (K)
BaY_2F_8:Yb^{3+}, Ho^{3+}	551.5	ETU (IR flashlamp)	77
$YAlO_3$:Er^{3+}	549.6	TSA (792+840)	77
$YLiF_4$:Er^{3+}	551.1	ETU (797, 969)	90
	551.1	ETU (1500)	70
	469.7	ETU (1500)	40
	551	TSA (810)	300
BaY_2F_8:Er^{3+}	470.3	ETU ($\sim$790, $\sim$970)	30
$YLiF_4$:Tm^{3+}	453	TSA (781+648; pulsed)	300

became available as pumping sources and people began to think of UC as a possible operating scheme for compact and efficient visible lasers. An overview on UC lasers implemented so far is given in Tables 1 and 2.

There are three principal mechanisms for UC excitation (cf. Fig. 1): two-step absorption (TSA), energy transfer (ETU) UC and avalanche absorption [50]. All of these mechanisms take advantage of the electronic characteristics of RE ions (especially Er, Ho, Tm, Pr), featuring ladder-like arranged electronic states, some of them with long lifetimes, thus facilitating excited state absorptions and energy transfers between neighbouring ions.

Taking a look at the application form of UC laser media, fibers have got increased attention. Their waveguiding properties guarantee for a high density of the exciting radiation along the entire absorption medium. This is of distinct advantage for laser operating schemes such as UC, where the need for high pump intensity comes together with a low activator concentration and hence long absorption lengths. As a further advantage, the fiber geometry facilitates heat removal. Based on the advantages of the fiber geometry over other laser technologies, most progress in UC lasers, especially concerning slope efficiency and threshold power, has been achieved using UC fluoride glass fibers [49,51–53].

In our research, we approach the UC issue by four different routes: (i) improvement of the bulk crystal growth of known UC materials, (ii) search for new, air-stable and efficient crystalline UC host materials, (iii) growth of epitaxial layers to obtain UC waveguides and (iv) synthesis of UC glasses and cladded fibers thereof. Concerning activator ions, we so far concentrated on Er^{3+}.

Table 2
Selection of blue–green upconversion glass fiber lasers (adapted from Ref. [50])

Host glass:dopant	Laser λ (nm)	Pump mechanism (λ [nm])	T (max.) (K)
ZBLAN:Ho^{3+}	540–553	TSA (647.1)	300
ZBLAN:Tm^{3+}	455	TSA (645+1064)	300
ZBLAN:Tm^{3+}	480	TSA (1112+1116+1123)	300
ZBLAN:Pr^{3+}	491	TSA (1010+835)	300
ZBLAN:Er^{3+}	546	TSA (801)	300

Table 3
Highest phonon energies *hv* (max.) in inorganic dielectric hosts

Host	*hv* (max.) (cm^{-1})	Ref.
Y_2O_3	550	[57]
LaF_3	350	[57]
$LaCl_3$	260	[57]
$LaBr_3$	175	[57]
$Cs_3Er_2I_9$	160	[60]

(i) Bulk crystals of the laser host material $LiYF_4$ (YLF) are now being grown routinely in our laboratory by the vertical gradient freezing (VGF) technique [54]. To obtain oriented single crystals of high quality from this technologically simple method, a controlled seeding of the growth process turned out to be essential. This in turn requires precise temperature control as well as the addition of a considerable amount of excess LiF to the melt. Furthermore, the growth and cooling rates have to be slow (0.5–1.5°C h^{-1}) and the growth direction has to be chosen perpendicular to the *c*-axis. For Nd^{3+}-doping, its low effective distribution coefficient of 0.3 complicates the growth of homogeneously doped crystals by the Czochralski technique. However, in our work only a small variation of the Nd^{3+} concentration along the growth direction could be detected. This is probably driven by a stable temperature distribution (absence of thermal convection), leaving diffusion as the dominant mechanism of mixing. Rather high effective distribution coefficients for Nd^{3+} seem to be a positive side-effect of the present approach. Altogether, these conditions allowed to grow single crystals of high optical quality, of a usable length up to 60 mm and a diameter of 15 mm. Besides YLF:Nd^{3+}, also Er^{3+} (20%) doped crystals were used successfully as laser crystals emitting at 2.8 μm (threshold, 42 mW; slope efficiency, 46% [55]). Current work is dedicated to the optimisation of the seeding procedure in order to improve both the optical homogeneity for the growth along the *c*-axis and the crystal size. This is being addressed by the introduction of forced convection in the conditioning phase.

(ii) Most UC systems investigated so far are oxides and fluorides. Among them, fluorides are most attractive because they combine high UC efficiency with favourable chemical and mechanical properties. This is the reason for intensified research on fluoride based UC lasers (especially fiber lasers) as well as fluoride based UC luminophores (cf. later). However, novel series of host materials open up new UC pumping schemes, including the efficient population of higher lying states and shorter wavelength emissions. This is especially true for so-called low-phonon materials. According to the energy gap law [56,57], lower highest lattice phonon energies of an UC host can reduce the rate, at which a given energy gap is crossed non-radiatively by multiphonon relaxation. Thus, the luminescence yield is increased and/or the are emissions shifted to shorter wavelengths [58–60]. Other than the fluoride and oxide materials, investigated thoroughly so far, heavier halides like chlorides, bromides and iodides feature significantly lower phonon energies (Table

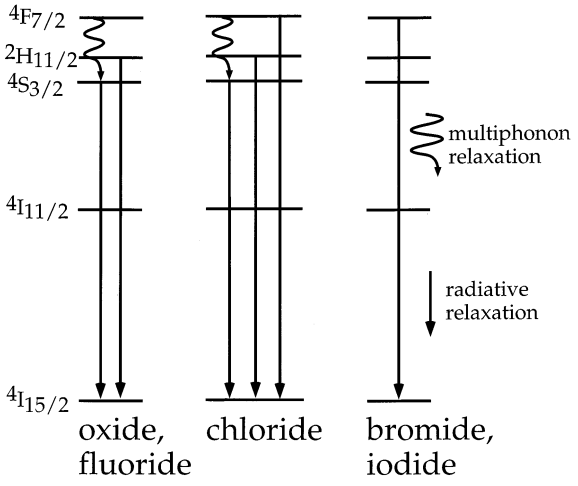

Fig. 3. Relaxation mechanisms in upconversion hosts providing different phonon energies (adapted from Ref. [61]).

3), which allows for interesting luminescence properties (Fig. 3). The influence of phonon energies on the UC behaviour can nicely be observed for the systems $RbGd_2Cl_7$:Er^{3+} and $RbGd_2Br_7$:Er^{3+} (Table 4 and Fig. 4) [61]. However, most RE containing heavier halide UC systems investigated so far (Table 5) suffer from the major drawback of being highly sensitive to moisture. Thus, a set of requirements can be formulated for the target compound of our research to fulfil:

1. Containing heavier halide ions (Cl^-, Br^-, I^-) in order to reduce non-radiative multiphonon relaxation rates.
2. Featuring a structure favourising isolated or paired Er^{3+} in order to create optimum conditions for either two-step absorption or energy transfer UC.
3. Being stable in air and suitable for the polishing of optical surfaces.
4. Congruent (or nearly congruent) melting and no phase transitions or phase segregations during cooling to 300 K. This, because no low temperature solvents ($T < 200$°C) are reported for, e.g. the growth of Er^{3+}-containing chlorides.

Recently, we developed Ba_2ErCl_7 and $Ba_2Y_{1-x}Er_xCl_7$ solid solutions to combine strong UC with a reasonable stability in air [62]. In the case of Ba_2ErCl_7, 803 nm

Table 4
Influence of phonon energies on UC behaviour (Figs. 3 and 4) [61]

Host:dopant	$h\nu$ (max.) (cm^{-1})	k (rad.)[a]: k (mp.)[b]	Main luminescence at excitation ~975 nm
$RbGd_2Cl_7$:1% Er^{3+}	264	1: 40	$^4S_{3/2} \rightarrow {}^4I_{15/2}$ (550 nm; yellowish–green)
$RbGd_2Br_7$:1% Er^{3+}	180	60: 1	$^4F_{7/2} \rightarrow {}^4I_{15/2}$ (490 nm; turquoise)

[a] k (rad.), radiative decay rate of $^4F_{7/2}$.
[b] k (mp.), non-radiative multiphonon decay rate of $^4F_{7/2}$.

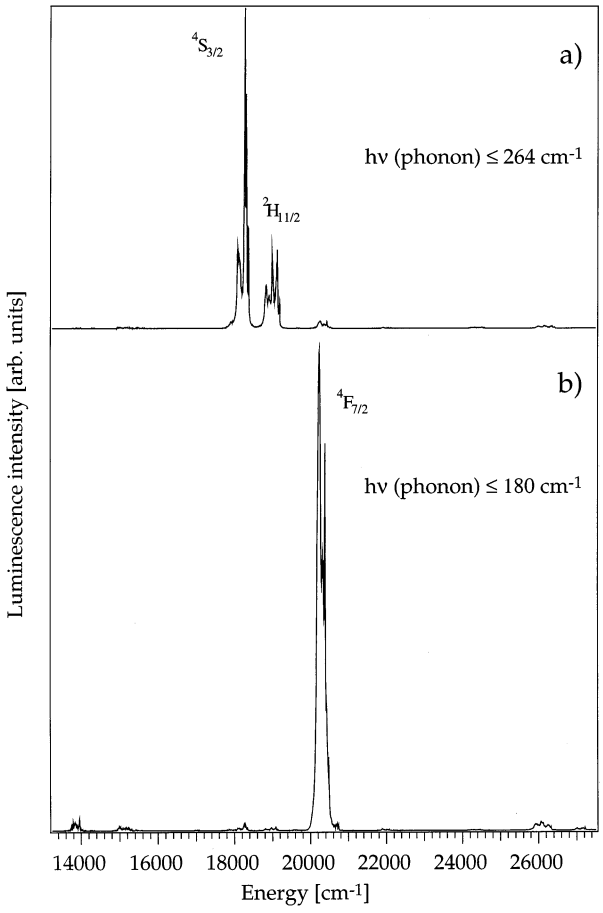

Fig. 4. Room temperature upconversion luminescence spectra of $RbGd_2Cl_7$:1% Er^{3+} (a) and $RbGd_2Br_7$:1% Er^{3+} (b) with $^4I_{15/2} \rightarrow {}^4I_{11/2}$ excitation at 10255 cm^{-1} (975 nm) and 10229 cm^{-1} (978 nm), respectively (reproduced with permission from Ref. [61]).

excitation leads to a bright greenish luminescence (Fig. 5), dominated by an emission at 550 nm. Comparison of the luminescence of powder samples showed, that this emission is one to three orders of magnitude more intense than found for other well characterised UC materials (BaY_2F_8:Er^{3+}, $LiYF_4$:Er^{3+}, $Cs_3Er_2Cl_9$). Upon intensive 803 nm excitation, a strong line appeared in the near UV at 390 nm, which is apparently pumped by a three photon process. At excitation around 980 nm, the emitted light consisted of many lines distributed over the whole visible range. Particularly, the contributions of the blue–green emissions at 490 and 510 nm are stronger than observed for many other materials. Single crystals up to 3 cm in length and 1 cm in diameter have been grown by Czochralski pulling under inert gas atmosphere. Ba_2ErCl_7 crystallizes in the monoclinic space group $P2_1/c$ and belongs to a new ternary halide series Ba_2RECl_7 (RE = Gd–Yb, Y) [63]. A

Table 5
Selection of heavier halide upconversion systems (adapted from Ref. [81]).

Host crystal:dopant	Ref.	Host crystal:dopant	Ref.
$Cs_2NaErCl_6$	[82]	$Cs_2NaYCl_6:Yb^{3+}$, Er^{3+}	[83,84]
$BaCl_2:Er^{3+}$	[70]	Ba_2ErCl_7; $Ba_2YCl_7:Er^{3+}$	[62–64]
$LaCl_3:Pr^{3+}$	[85–87]	$LaCl_3:Nd^{3+}$	[88]
$CsMgCl_3:Er^{3+}$	[89,90]	$CsMgCl_3:Tm^{3+}$	[91]
$Cs_3Er_2Cl_9$	[60]	$Cs_3Er_2Br_9$	[60]
$K_2LaCl_5:Er^{3+}$	[92]	$K_2LaBr_5:Er^{3+}$	[92]
$CsCdBr_3:Er^{3+}$	[59,89,93,94]	$Cs_3Er_2I_9$	[60]

characteristic feature of this new structure type is the polyhedron of a seven-fold coordinated RE^{3+} ion, which may be described by a monocapped and slightly distorted trigonal prism (Fig. 6). Representing the first example, the $[MCl_7]$ polyhedra are isolated from each other at a rather long Er^{3+}–Er^{3+} distance of 6.48 Å. The UC mechanisms in Er^{3+}-doped Ba_2YCl_7 and Ba_2ErCl_7 have been determined [64]. At present, we are building up special Czochralski growth equipment for the growth of high quality crystals of $Ba_2YCl_7:Er^{3+}$ to be tested for down- and upconversion laser action.

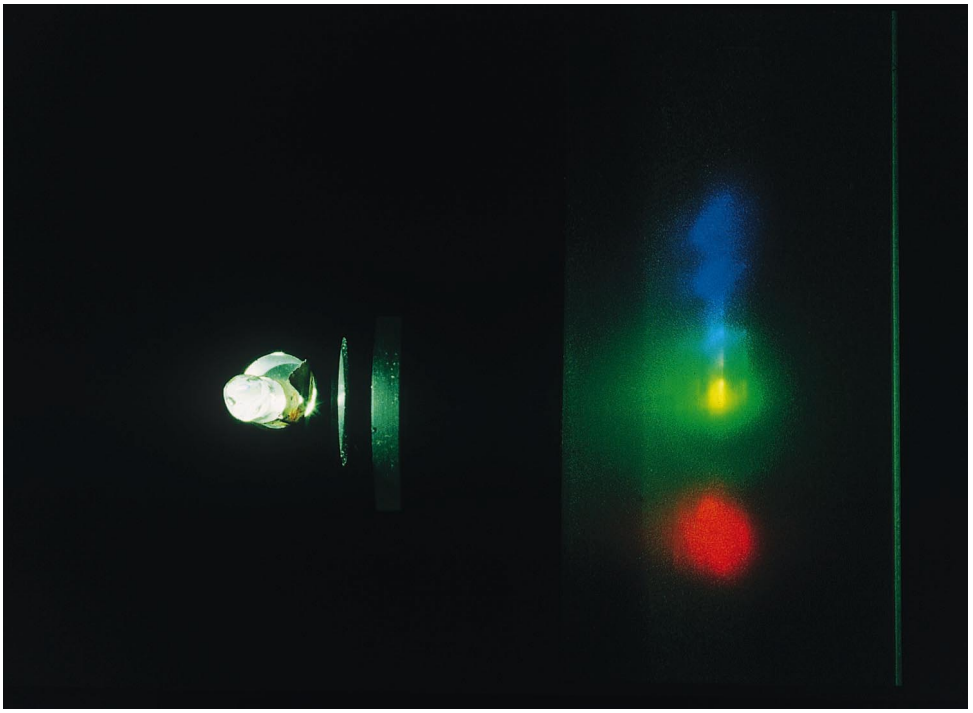

Fig. 5. Room temperature upconversion luminescence as seen by the powder setup (Ba_2ErCl_7; λ(excit.) $\sim$ 800 nm).

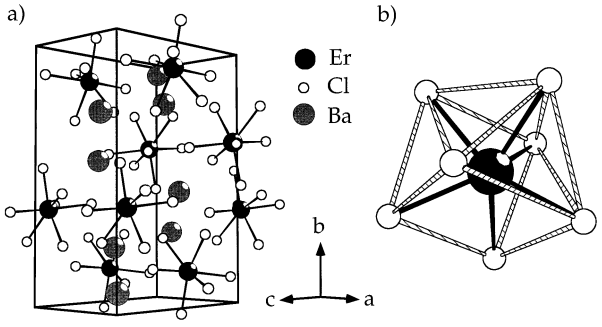

Fig. 6. Crystal structure (a) and coordination polyhedron of Er^{3+} (b) in Ba_2ErCl_7 [63].

A second UC host, $Cs_3Tl_2Cl_9$, emerged to be one of the few low-phonon materials which is completely stable in air. Dopable with Er^{3+} and due to its dimeric structure, $Cs_3Tl_2Cl_9$ favours efficient energy transfer UC. We are currently investigating a phase segregation around 310°C [65] in order to be able to define parameters for gas and liquid phase epitaxy experiments to follow.

Finally, efficient and air stable UC luminophores are of potential interest for different applications, including sensing [66–70]. With requirements on an UC luminophore being different from those posed on a UC laser material, we have built up a setup, using a NIR diode laser (SDL-8630) as the pumping source and working on powder samples (Fig. 5) [71]. This allowed for standardised measurements and comparison between series of newly synthesised compounds. The requirement of complete stability excluded all heavier halide low-phonon materials, leaving behind fluorides as the only materials for potential applications. Among them, $BaY_2F_8:Er^{3+}$, a well known UC laser material, was found to be most efficient.

(iii) As mentioned earlier, further progress in UC, especially on the issue of the slope efficiency and laser threshold, are to be expected from the application of approved or new UC materials in the form of waveguides. This is especially true for crystalline waveguides, with their advantage of narrower spectral linewidths and, consequently, higher gain coefficients than found in glassy media. Crystalline dielectric waveguides of low losses have been produced by surface-modifying techniques (diffusion [72], proton exchange [73], ion implantation [74]). However, these waveguides are highly asymmetric and sensitive to surface defects and contamination. Further efforts are focused on gas phase methods like molecular beam epitaxy [75] and laser ablation [76]. Low loss waveguides have been reported for garnet films grown by liquid phase epitaxy (LPE) [77]. In our group, the LPE of YLF was developed to produce planar and ridge-type waveguides, activated with either Er^{3+} or Nd^{3+} [78]. The (101) orientation of the substrate favoured by the growth morphology of YLF is unusual when compared to (100), but not prohibitive for laser design. Neodymium or erbium doped layers of about 10 μm thickness were grown by dipping an undoped YLF substrate into a slightly supercooled melt flux consisting of typically 60 mol% lithium fluoride and 40 mol%

yttrium plus doping RE fluorides. Cover layers could be grown in a second step by the same process, yielding low loss buried waveguides. Preliminary results showed losses below 0.3 dB cm^{-1} for a $\sim$ 30 μm thick waveguide at about 810 nm wavelength, measured by sideband-pumped UC fluorescence of erbium. The numerical aperture of the waveguide, usually being low due to the low dopant concentrations necessary for many important laser operating schemes, could be improved by adding gadolinium as an optically inert co-dopant. A waveguide grown from a melt containing 10% Gd^{3+} and 1% Er^{3+} exhibited a numerical aperture of about 0.1 without loss of optical quality. A ridge-type structure was obtained by mechanical polishing and subsequent growth of a cladding layer. In this way, a first epitaxial YLF:Nd^{3+} waveguide laser could be demonstrated [79]. The observed low threshold power of 8 mW demonstrated the potential of epitaxially grown YLF waveguides for low input power lasers. Currently, we are elaborating etching techniques, including plasma etching, in order to produce waveguides of a considerably smaller cross-section.

(iv) Trying to combine the advantages of low-phonon materials with those of the waveguide geometry, we have produced waveguiding fibers using a new Er^{3+}-doped and $ZnBr_2$-based glass [80]. This low-phonon material exhibits interesting UC properties, including the appearance of a strong turquoise emission (490 nm) at irradiation around 980 nm. Furthermore, its IR transparency being high down to 700 cm^{-1} makes the $ZnBr_2$-glass potentially attractive for IR (CO_2) laser light delivery. However, the high hygroscopicity of the $ZnBr_2$ glass required handling and processing under inert gas atmosphere. First waveguiding fibers of a length of 1–2 cm and a diameter down to 2 μm (and larger) have been obtained by filling silica glass capillaries with the glass melt and subsequent quenching. Present work is concerned with reducing the attenuation of the fibers, being at 2 dB cm^{-1} for first samples. Furthermore, a cladding glass of higher refractive index than silica will have to be found in order to produce single mode fibers for exploiting their laser potential.

Summing up, the exploitation of new UC host materials and the processing of UC materials into waveguides have shown some promising results, challenging both optical scientists and materials chemists.

4. Conclusions

At long term, the horse race between optical dielectric and semiconductor materials will be in the favour of short wavelength generation by semiconductors.

Meanwhile, two other classes of materials can bridge the gap: (i) Classical ferroelectrics and related materials grown as high quality bulk crystals have reached the level of commercial applications. Further progress can be expected from self-doubling crystals and frequency doublers based on crystalline waveguides; (ii) fluoride glasses, processed into fibers, are operated through upconversion processes yielding several 100 mW green and blue.

Beam confinement is essentially important for crystalline upconversion lasers which operate on a rather high intrinsic threshold. Following the concept of low-phonon materials in the synthesis of new upconversion crystals, complete or moderate stability against air is necessary in order to promote fabrication technologies. In this respect, bromide and chloride based glass fibers cladded by an oxide glass of proper refraction index appear attractive.

After all, it seems as if their is not to much left for the synthesis of new compounds. Independent of the fact that new compounds are always of interest, this is true to considerable extent. In the present time some materials chemistry should concentrate on crystals which are known for their performance, but where crystal growth and waveguide formation lags behind. In many cases this is because of the complex chemistry to be known in order to be able to set up appropriate growth techniques and control parameters. In this sense, liquid phase epitaxy, laser ablation or chemical vapour deposition are challenging processes full of unresolved chemical problems for inorganic research, traditionally called coordination chemistry.

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