2006

Up-conversion In Rare-earth Doped Micro-particles Applied To New Emissive 2d Dislays

Anne Milliez
University of Central Florida

Part of the Electromagnetics and Photonics Commons, and the Optics Commons

Find similar works at: https://stars.library.ucf.edu/etd
University of Central Florida Libraries http://library.ucf.edu

This Doctoral Dissertation (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations, 2004-2019 by an authorized administrator of STARS. For more information, please contact STARS@ucf.edu.

STARS Citation
https://stars.library.ucf.edu/etd/755
UP-CONVERSION IN RARE-EARTH DOPED MICRO-PARTICLES
APPLIED TO NEW EMISSIVE 2D DISPLAYS

by

ANNE JANET MILLIEZ
M.S. Optics, Université Louis Pasteur, Strasbourg, France 2000

A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the College of Optics and Photonics: CREOL & FPCE
at the University of Central Florida
Orlando, Florida

Spring Term
2006

Major Professor: Dr. Michael Bass
ABSTRACT

Up-conversion (UC) in rare-earth co-doped fluorides to convert diode laser light in the near infrared to red, green and blue visible light is applied to make possible high performance emissive displays. The infrared-to-visible UC in the materials we study is a sequential form of non-linear two photon absorption in which a strong absorbing constituent absorbs two low energy photons and transfers this energy to another constituent which emits visible light. Some of the UC emitters’ most appealing characteristics for displays are: a wide color gamut with very saturated colors, very high brightness operation without damage to the emitters, long lifetimes and efficiencies comparable to those of existing technologies. Other advantages include simplicity of fabrication, versatility of operating modes, and the potential for greatly reduced display weight and depth. Thanks to recent advances in material science and diode laser technology at the excitation wavelength, UC selected materials can be very efficient visible emitters. However, optimal UC efficiencies strongly depend on choosing proper operating conditions. In this thesis, we studied the conditions required for optimization. We demonstrated that high efficiency UC depends on high pump irradiance, low temperature and low scattering. With this understanding we can predict how to optimally use UC emitters in a wide range of applications. In particular, we showed how our very efficient UC emitters can be applied to make full color displays and very efficient white light sources.
In memory of Tata Malika and Mima.
ACKNOWLEDGMENTS

I acknowledge Dr. Michael Bass for his advice, guidance and mentorship throughout my work as a student of his group at College of Optics and Photonics at the University of Central Florida.

I acknowledge my advisory committee, Dr. Kevin Belfield, Dr. Jannick Rolland, Dr. Shin-Tson Wu and Dr. Michael Canva for their help and guidance on my research, and the all teachers at CREOL who helped me further my education in the field of optics.

During my research I was fortunate to work with Dr. Alexandra Rapaport who taught me a lot about rigorous lab work and pushed me to challenge myself in my work, while being a great friend during leisure times. I’m also grateful to Dr. Hans Jenssen and Arlette Cassanho for their collaboration throughout this research. I acknowledge Dr. Frederic Chaput for his assistance on the sol-gels and Dr. Erik Reinhard for his beautiful photos of our displays. I acknowledge Richard Zotti for his patience with the machining work, especially the drilling of the cabochons, and all the students of CREOL/UCF who helped me in my research, including Katherine Shaeffer and Erwan Baleine. I also had the best colleagues within Dr. Bass’s group especially those with whom I got to share our lovely office at some point, Ferenc Szipocs, Jung-Hyunn Cho and Te-Yuan Chung, who not only are great friends but also helped me in the lab for the demonstrations and when I needed assistance with diodes, all this while sharing many laughs.
I would like to thank my dear friend Brian for helping me go through with this, so patiently supporting me and being here for me, and for all the good eats we had too. Thank you to my friends from France, Julie and Amelie (helping me deal since 1994!), Denise, Armelle and Sari for being my home away from home through cyberspace and visits.

I would have never been able to go so far without the support and trust of my family, particularly my parents, my sisters Maya and Hinda, my aunts (les tatas) and uncles.
# TABLE OF CONTENTS

**ABSTRACT** ........................................................................................................ iii

**ACKNOWLEDGMENTS** .......................................................................................... v

**TABLE OF CONTENTS** ......................................................................................... vii

**LIST OF FIGURES** ................................................................................................ xii

**LIST OF TABLES** ................................................................................................ xxii

**LIST OF ACRONYMS** ............................................................................................ xxiv

**CHAPTER ONE: INTRODUCTION** ........................................................................ 1

1.1 Infrared to visible up-conversion applied to displays ............................. 1

1.2 Concept of novel emissive 2D display based on up-conversion .......... 7

1.3 Thesis ................................................................................................................. 12

**CHAPTER TWO: UP-CONVERSION IN RARE-EARTH DOPED MATERIALS AND TOOLS TO CHARACTERIZE THEIR PERFORMANCES** .......... 13

2.1 Useful notions on radiometry, colorimetry and energy transfer basics__ 13

2.1.1 Radiometry ...................................................................................................... 13

2.1.1.1 Definitions and units .................................................................................. 13

2.1.1.2 The human eye .......................................................................................... 16

2.1.1.3 Radiometric considerations for displays ................................................. 18

2.1.2 Colorimetry .................................................................................................... 19

2.1.2.1 Human color vision .................................................................................. 19
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.2.2</td>
<td>Color mixing by addition</td>
<td>20</td>
</tr>
<tr>
<td>2.1.2.3</td>
<td>CIE Chromaticity diagram</td>
<td>22</td>
</tr>
<tr>
<td>2.1.2.4</td>
<td>Example: TV colors</td>
<td>26</td>
</tr>
<tr>
<td>2.1.3</td>
<td>Basics on energy transfers</td>
<td>31</td>
</tr>
<tr>
<td>2.1.3.1</td>
<td>Radiative resonant transitions</td>
<td>31</td>
</tr>
<tr>
<td>2.1.3.2</td>
<td>Phonon assisted transitions</td>
<td>32</td>
</tr>
<tr>
<td>2.1.3.3</td>
<td>Cross relaxation and up-conversion</td>
<td>33</td>
</tr>
<tr>
<td>2.1.3.4</td>
<td>Energy transfer between two rare earths elements</td>
<td>36</td>
</tr>
<tr>
<td>2.1.3.5</td>
<td>Two-photon up-conversion processes</td>
<td>38</td>
</tr>
<tr>
<td>2.2</td>
<td>Up-conversion in rare-earth co-doped fluorides</td>
<td>40</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Rare-earth elements</td>
<td>40</td>
</tr>
<tr>
<td>2.2.1.1</td>
<td>Electronic configuration</td>
<td>40</td>
</tr>
<tr>
<td>2.2.1.2</td>
<td>Energy levels</td>
<td>41</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Up-conversion mechanisms</td>
<td>45</td>
</tr>
<tr>
<td>2.2.2.1</td>
<td>Up-conversion mechanisms in Er(^{3+})-Yb(^{3+}) co-doped systems</td>
<td>45</td>
</tr>
<tr>
<td>2.2.2.2</td>
<td>Up-conversion mechanisms in Tm(^{3+})-Yb(^{3+}) codoped systems</td>
<td>49</td>
</tr>
<tr>
<td>2.2.2.3</td>
<td>Transfer function of UC process</td>
<td>50</td>
</tr>
<tr>
<td>2.2.3</td>
<td>Specifics of the UC emitters</td>
<td>53</td>
</tr>
<tr>
<td>2.2.3.1</td>
<td>Selection of doping concentrations</td>
<td>53</td>
</tr>
<tr>
<td>2.2.3.2</td>
<td>Selection of host crystals</td>
<td>54</td>
</tr>
<tr>
<td>2.2.3.3</td>
<td>Excitation spectra</td>
<td>61</td>
</tr>
<tr>
<td>2.2.3.4</td>
<td>Emission spectra and chromaticity</td>
<td>62</td>
</tr>
<tr>
<td>2.2.3.5</td>
<td>Emission lifetimes</td>
<td>64</td>
</tr>
<tr>
<td>2.3</td>
<td>Efficiency of UC materials</td>
<td>66</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Definitions and experimental setup</td>
<td>66</td>
</tr>
</tbody>
</table>
2.3.1.1 Definition of raw efficiency and maximum efficiency 66
2.3.1.2 Note on intrinsic efficiency and scattering 71
2.3.1.3 Raw efficiency experimental measurement setup 72
2.3.2 Maximum raw efficiencies of powders 77
2.3.3 Irradiance dependence of UC efficiency 79
2.3.4 Pump duration dependence of UC efficiency 82
2.3.5 Irradiance dependence of power spectral density 85
2.3.5.1 Irradiance dependence of red to green emission power ratio in Er,Yb 85
2.3.5.2 Irradiance dependence of power spectral density of the blue emitter 90

2.4 Chapter Two summary 91

CHAPTER THREE: KEY STEPS TOWARDS OPTIMIZATION OF UC DISPLAYS

3.1 Temperature dependence of UC efficiency 92
3.1.1 Thermal effects in non-resonant rare earth co-doped systems 93
3.1.2 Temperature probing by FIR in UC emitters 100
3.1.3 Thermal management for UC emitters 104

3.2 Scattering effects on UC efficiency 108
3.2.1 Definitions, theory and experimental method 109
3.2.1.1 Definitions 109
3.2.1.2 Light propagation in a scattering medium 111
3.2.1.3 Experimental methods 114
3.2.2 Minimizing backscattering in UC powders 115
3.2.3 Internal scattering effect on efficiency 116
3.2.4 Maximum raw efficiencies of red, green and blue UC emitters 118
CHAPTER FOUR: APPLICATION TO THREE COLOR DISPLAYS AND WHITE BACKLIGHT

4.1 Three color displays

4.1.1 Monochromatic emissive screens optically written in reflection

4.1.1.1 Preparation of powders

4.1.1.2 Polymeric binder

4.1.1.3 Casting of screens

4.1.1.4 Performances of UC reflective screens

4.1.2 Transparent screens and pixilated screens

4.1.2.1 Transparent screens

4.1.2.2 Pixilated screens

4.1.3 Display considerations

4.1.3.1 Importance of contrast

4.1.3.2 Examples of scanning methods

4.2 White backlight

4.2.1 Engineering of a white emitter: methods

4.2.1.1 White light by partitive mixing

4.2.1.2 Tailoring of a white light emitter operating at predetermined efficiency

4.2.2 Simple demonstration of a white light back-panel

4.2.3 High brightness, high efficiency white light source

4.3 Chapter summary

CHAPTER FIVE: CONCLUSIONS AND FUTURE WORK

5.1 UC display
APPENDIX A: RATE EQUATION WITH TEMPERATURE DEPENDENT COEFFICIENTS IN ER,YB SYSTEMS. 168
LIST OF REFERENCES 175
LIST OF FIGURES

Figure 1.1: UC-display concept: scheme of scanned full color display with screen optically written in transmission and photos of red, green and blue UC-displays made in our lab (true colors). The Lissajous patterns were obtained by vector scanning a 200 mW, 975 nm diode laser beam across an area 25mm on the side. For the red emitting screen, rhodamine B dye was added to the polymer mix to absorb the extra green emission. Photos by Erik Reinhard©. ____________________________________________ 7

Figure 1.2: Example of display optically written in reflection (top view of setup). Two silver coated mirrors driven by galvanometers deflect the infrared beam to form a 2D moving image on the screen (vector scan). The green UC powder was dispersed in p-PMMA and coated on an aluminum substrate about 5 mm on the side. Photo by Erik Reinhard©. ________________ 8

Figure 1.3: Versatility of UC screens. (a) Photo of a green UC reflective screen taken outdoors during a sunny Florida day at noon. This screen is about 50 mm on a side on an aluminum substrate. (b) Transparent green UC display off (top) and on (bottom). The black dashed line was drawn on the pictures to show the area of where the mix of particle and binder was coated. Here the substrate is a standard glass microscope slide. In both (a) and (b) cases, the excitation source was a 500 mW, 975 nm diode laser scanned with two galvanometer mirrors. ________________________________ 9
Figure 1.4: Wedge technology developed by Adrian Travis at Cambridge Flat Projection Display Ltd.  

Figure 2.1: The electromagnetic spectrum [33].  

Figure 2.2: Response of the human eye: absolute spectral luminous efficiency functions for photopic and scotopic vision [34].  

Figure 2.3: Normalized color sensitivity of the red-, green- and blue-sensitive cones of the human eye [34].  

Figure 2.4: (a) The historical RGB color matching functions and (b) the CIE RGB color matching functions [34]. In both case the vertical axis is the tristimulus value (no units, see Footnote 1).  

Figure 2.5: The 1931 CIE chromaticity diagram [34].  

Figure 2.6: Emission spectra of a typical set of CRT phosphors [39]. The vertical scale is the spectral power distribution given here in arbitrary units.  

Figure 2.7: Gamut of media colors [37]. The dotted triangle is the TV color gamut, with the color of the three phosphors marked by x’s. Inside the thick boundary are the print colors, with the color of the full strength inks indicated by y=yellow, m=magenta and c=cyan. The dashed triangle delimits the photographic slides colors with the colors of the three dyes marked by small circles.  

Figure 2.8: Blackbody locus with the color of standard white sources: A: tungsten filament, B: noon sunlight and C: tungsten filament filtered to approximate daylight. Temperatures in °K [37].
Figure 2.9: Energy scheme for different phonon-assisted transitions in ions, for $\Delta E \geq \hbar \omega_m$:

(a) Anti-Stokes vibronic transition (absorption of phonon), (b) Stokes vibronic transition (emission of phonon) and (c) non-radiative transition. Transfer probabilities are noted $W_{AS}$, $W_S$ and $W_{NA}$ respectively[40].

Figure 2.10: (a) Cross relaxation and (b) up-conversion. The thin arrow represents photon absorption, the fat arrows schematize ion-ion energy transfer.

Figure 2.11: Energy transfer from a sensitizer (S) to an activator (A) in its ground state:

(a) resonant radiative transfer, (b) resonant energy transfer, (c) energy transfer assisted by phonons and (d) energy transfer with the activator in an excited state, provided $W_{SA} \geq 1/\tau_e$, where $W_{SA}$ is the transfer probability from (S) to (A) and $\tau_e$ is the lifetime of the excited state. In (d) the transfer from the excited state can be either resonant ($\beta - \alpha = 0$) or phonon-assisted ($\beta - \alpha = \epsilon_0$).

Figure 2.12: Energy schemes for different 2-photon up-conversion processes [41]: (a) up-conversion by energy transfer (APTE effect), (b) 2-steps absorption, (c) cooperative sensitization, (d) 2-photon absorption excitation, (e) cooperative luminescence and (d) second Harmonic Generation (SHG).

Figure 2.13: Dieke diagram for Ho$^{3+}$, Er$^{3+}$, Tm$^{3+}$ and Yb$^{3+}$ [4].

Figure 2.14: Up-conversion in Er$^{3+}$-Yb$^{3+}$ co-doped systems.

Figure 2.15: Up-conversion in Tm$^{3+}$-Yb$^{3+}$ co-doped systems.

Figure 2.16: Calculated transfer function of green UC in Er, Yb systems.

Figure 2.17: Excitation spectra of UC emitters.
Figure 2.18: Emission spectra of the green, red and blue emitters operating at maximum efficiency and each has been normalized to its highest peak.

Figure 2.19: (a) 1931 CIE chromaticity diagram with RGB colors of UC phosphors. The long dashes enclose the region accessed by our UC emitters while the dotted region is that of present day televisions. (b) Unfiltered “red” emitter appears yellow to the eye because of the presence of some green emission.

Figure 2.20: Normalized emission response time of emitters excited at 975 nm with a low energy 4-ns pulse. The samples were tested at 21 C: (a) 1% Er, 18% Yb:NYF. Yb$^{3+}$ emission at 1 micron (thin line) and Er$^{3+}$ green emission at 543 nm (thick line); (b) 0.4%, Tm 30%, Yb:YLF. Yb$^{3+}$ emission at 1 micron (thin line) and Tm$^{3+}$ blue emission at 480 nm (thick line).

Figure 2.21: Calculated transfer function and UC efficiency vs. input irradiance.

Figure 2.22: Experimental setup for efficiency measurements showing the integrating sphere, CAS and cabochon. In the photo the silver mirror is not in place and the green emission of the sample is visible at the upper entrance of the sphere. (Chopper and OD filters not in photo).

Figure 2.23: Screen shot of the IS-SpecWin software output showing an example of the spectro-radiometric measurement of green emission.

Figure 2.24: Beam profile of Unique-mode infrared diode laser superimposed on the emitters excitation spectra.
Figure 2.25: Green raw efficiency of 2%Er, 15% Yb:KY$_3$F$_{10}$ for different pump beam sizes. The excitation was a 975 nm beam modulated at 30 Hz into 2ms duration pulses. 80

Figure 2.26: Example of screen performances for the green, red and blue emitters mixed in a p-PMMA binder and deposited on a glass slide: (a) Ratio of brightness to incident infrared input powers versus average incident power at 975 nm and (b) brightness versus average incident power at 975 nm. Note that the spectral width of the diode light source used was quite wide (see Figure 2.24). 81

Figure 2.27: Experimentally measured green (a) raw efficiency and (b) brightness versus incident irradiance in 1% Er, 18% Yb:NYF for different types of excitation: continuous and pulsed at 30 Hz with various pump durations. 83

Figure 2.28: (a) Blue raw efficiency in 0.4% Tm, 30% Yb:YLF and (b) red raw efficiency in 1% Er, 18% Yb:YF$_3$ for different types of excitation: continuous and pulsed at 30 Hz with various pump durations. 83

Figure 2.29: Emission spectra of 1%Er, 18%Yb:NYF at low and high irradiance normalized to the green emission peak. 86

Figure 2.30: Experimental emission ratio analysis in 1% Er, 18% Yb:NYF. Green, red and blue are the 545, 660 and 410 nm emission peaks of erbium, respectively. (a) Fluorescence and (b) various ratios of emission powers. 87
Figure 2.31: Effect of pump irradian ce on red to green emission ratio in 2% Er, 15% Yb:KY3F10 for a beam focus of various diameters plotted (a) with respect to input power, and (b) scaled to input irradiance. 89

Figure 2.32: Red to blue emission intensity ratios with respect to input irradiance 90

Figure 3.1: Effect of temperature on red, green and blue UC efficiency in our most efficient emitters. 92

Figure 3.2: UC in Tm,Yb:YLF: energy transfers and transitions. 94

Figure 3.3: (a) Calculated and (b) experimental raw efficiencies for 0.4% Tm, 25% Yb:YLF for different types of excitation: continuous, and pulsed at 30 Hz with pump duration of 5 ms (circles), 2.6 ms (up-triangles), 630 μs (down-triangles), and 350 μs (diamonds). 99

Figure 3.4: Emission spectra of 0.4 % Tm, 20 % Yb:KY3F10 for two conditions of excitation: continuous and modulated at 30 Hz with a 2ms pulse duration. The output power in the blue was the same in both excitation conditions (54 μW). The sample holder was made of acrylic. 102

Figure 3.5: FIR of 0.4%Tm, 20%Yb:KY3F10. 103

Figure 3.6: (a) UC emitter temperature and (b) relative raw efficiency of a sample of 0.4 % Tm, 20 % Yb:KY3F10 in acrylic and copper sample holders for different excitations: continuous and modulated at 30 Hz and various pulse durations. 104

Figure 3.7: FEMLAB simulation of heat dissipation in (a) 500 μm and (b) 50 μm pixels for the same amount of heat deposited. 106
Figure 3.8: Scattering of a 611 nm HeNe laser beam through a collection of UC particles.

Figure 3.9: Light propagation in scattering and clear media[87].

Figure 3.10: Backscattering of the pump light for different matching fluid indices of refraction for 2% Er, 15% Yb:KY3F10 excited at 975 nm. The thin solid line spectrum corresponds to 100% backscattering from dry alumina powder.

Figure 3.11: Visible emission spectra for 2% Er, 15% Yb:KY3F10 excited at 975 nm under 12.5 mW average input power for a scattering sample and an index-matched sample.

Figure 3.12: (a) Raw efficiency and (b) brightness of 2% Er, 15% Yb:KY3F10 for a high scattering sample and an index-matched sample.

Figure 4.1: Green, red and blue emissive UC screens optically written in reflection via vector-scan (top) in the shade and (bottom) in the sun. For the red screen rhodamine B was incorporated in the binder to absorb the green emission of erbium. The substrate is aluminum. The screens are 5 cm on a side.

Figure 4.2: Particles of Er,Yb:NYF. 1 graduation on the scale is 2.5µm.

Figure 4.3: Particles in binder for (a) regular PMMA, (b)p-PMMA with no surfactant and (c) p-PMMA with surfactant. Powder density in polymer was 30% for these samples. 1 graduation is 0.5 mm.

Figure 4.4: “Scraper".
Figure 4.5: (a) Brightness efficiency and (b) brightness of our hand-made green reflective UC screen for different types of pump modulation. The focus spot was 1 mm in diameter.  

Figure 4.6: Example of blue UC screen written in transmission. The substrate is 5 cm on a side. A 975 nm, 500 mW diode laser beam was scanned by galvanometer mirrors on the screen (average power on one pixel was less than 10 mW).  

Figure 4.7: Tunable index of refraction in sol-gels. The proportions are in dry wt%.  

Figure 4.8: Er,Yb:NYF in sol-gels of index of refraction (a)1.42, (b)1.46, (c)1.48 and (d)1.57.  

Figure 4.9: Green raw efficiency of Er,Yb:NYF in sol-gels of various refractive indices. The 975 nm excitation beam was modulated at 30Hz with a 2ms pulse duration and focused to 900 μm.  

Figure 4.10: Three color pixels of a CRT screen[94].  

Figure 4.11: Example of structure of CRT transfer film[95].  

Figure 4.12: Pixel patterns by micro-lithography in silicon wafers. In all cases the total area of the pattern was 1 mm on the side. The depths of the pixels are, from left to right, 50 μm, 50 μm and 100 μm.  

Figure 4.13: High and low contrast red, green and blue screens (top) indoors and (bottom) outdoors.  

Figure 4.14: Raster scan of excitation beam.  

Figure 4.15: Single lens imaging system: variation of image size with two different focal lengths. The solid ray is the image of the marginal ray through a lens of
short focal length $f_1$, and the thick dashed ray, its image if this lens had a longer focal length $f_2$. The focal planes in each case are marked $f_1$ and $f_2$ respectively. 

Figure 4.16: Image size magnification with telescope. Planes $f_i$ and $f'_i$ are respectively object and image focal planes of lens $L_i$.

Figure 4.17: 40x40 point images formed by raster scan at 60 Hz on emissive red, green and blue UC screens. The total power of the scanned beam was 500mW at the screen. It was focused to ~0.5 mm diameter on the screens. The image displayed was ~20mm on a side.

Figure 4.18: Measured colors of 0.4% Tm, 20% Yb:KY$_3$F$_{10}$ (“Blue emitter”) and 1% Er, 18% Yb:YF$_3$ (“Red emitter”) excited with a 110 mW average power, 976 nm diode laser beam focused to a spot 900 µm in diameter. The diode was modulated at 30 Hz and produced light in 2 ms duration pulses. Standard D65 white is also indicated on this 1931 CIE chromaticity diagram.

Figure 4.19: Measured emission spectrum of the tailored UC D65 white-light emitter operating at 7lm/W efficiency.

Figure 4.20: Color of the “white emitter” as the efficiency of individual powders was modified. Points A, B and C were obtained by varying the average input power in the setup used to tailor the white emitter: 110 mW (Point A), 50 mW (Point B) and 20 mW (Point C). Point D is the white obtained in a white light diffuser demonstration: the pump was modulated at 60 Hz instead of 30 Hz as for point A and the scattering properties of the powder...
in a p-PMMA binder were different from the dry powder used in case A. For this emitter, the proportions of blue and red powders were \( \sim 3:2 \).

Figure 4.21: Demonstration of a simple white backlight using a painted standard glass microscope slide as a diffuser. The white-light emitter mixed in a polymeric binder was cast on the left edge of the slide and excited over 1 cm with a 1.2 W average power, 970 nm diode bar modulated at 60 Hz, 12% duty cycle. Photo in true color.

Figure 4.22: Mixing of blue and red UC emitter in 1.488 oil to make a white UC emitter.

Figure 4.23: White light emitter in high and low scattering conditions.

Figure A.1: Er, Yb energy transfers and transitions (in YLF). For clarity, not all radiative decays are represented.

Figure A.2: FIR in 1% Er, 18% Yb:NYF. 525 and 545 nm peaks are respectively the integrated powers between 511 and 535 nm and between 535 and 575 nm.

Figure A.3: FIR in 1% Er, 18% Yb:YF<sub>3</sub>. 525 and 545 nm peaks are respectively the integrated powers between 511 and 535 nm and between 535 and 575 nm.
LIST OF TABLES

Table 2.1: Radiometric and Photometric Quantities and Units 15
Table 2.2: Electronic configuration of rare earths of interest 40
Table 2.3: Structure parameters of host crystals 57
Table 2.4: Optical properties of host crystals 58
Table 2.5: Maximum raw efficiencies of emitting powders with no binder or thermal management 77
Table 3.1: Room-temperature values of the parameters used in the system of Equation 3.1 96
Table 3.2: Maximum raw efficiencies of UC emitters in index-matched oil 119
Table 4.1: Mass density of UC emitters and of polymer 126
Table 4.2: UC screens specifics for operation at maximum brightness efficiency for a 1 mm diameter pixel and focus spot 130
Table 4.3: Output of the green screen for different pulse durations at 60 Hz for one pixel, 1 mm diameter, obtained by focusing the pump light on the screen surface to a spot of the same diameter as the pixel 133
Table 4.4: Output of the green screen for different pixel diameters for a 1 ms, 60 Hz excitation obtained by focusing the pump light on the screen surface to a spot of the same diameter as the pixel. The target peak irradiance is 70 W/cm² to operate at maximum efficiency 133
Table 4.5: Application to a large 1 x 1 m monochrome green screen (if made the same way as this screen), for a target brightness of 1 kcd/m², refreshed at 60 Hz.

Table 4.6: Application to large display obtained by tiling 122 5 W diode lasers to excite 100% of the pixels

Table 5.1: Measured maximum raw efficiencies of UC emitters

Table A.1: Coefficients in Er, Yb rate equations. The number of phonons is given for YLF as the host crystal
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>at%</td>
<td>atomic percent</td>
</tr>
<tr>
<td>2D</td>
<td>two dimensional</td>
</tr>
<tr>
<td>CAS</td>
<td>Compact Array Spectrometer</td>
</tr>
<tr>
<td>CRT</td>
<td>cathode ray tube</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>CW</td>
<td>continuous wave</td>
</tr>
<tr>
<td>FIR</td>
<td>fluorescence intensity ratio</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>LCD</td>
<td>liquid crystal display</td>
</tr>
<tr>
<td>NRC</td>
<td>National Research Council (Canada)</td>
</tr>
<tr>
<td>p-PMMA</td>
<td>phosphorylated polymethylmethacrylate</td>
</tr>
<tr>
<td>TOP</td>
<td>telescope optical probe</td>
</tr>
<tr>
<td>UC</td>
<td>up-conversion</td>
</tr>
<tr>
<td>UCF</td>
<td>University of Central Florida</td>
</tr>
<tr>
<td>UV</td>
<td>ultra-violet</td>
</tr>
<tr>
<td>vol%</td>
<td>volumic percent</td>
</tr>
<tr>
<td>wt%</td>
<td>weight percent</td>
</tr>
</tbody>
</table>

xxiv
CHAPTER ONE: INTRODUCTION

1.1 Infrared to visible up-conversion applied to displays

The infrared-to-visible up-conversion (UC) considered in this thesis is a sequential form of non-linear two photon absorption in which a strong absorbing constituent absorbs two low energy photons and transfers this energy to another constituent which emits visible light. This thesis concerns applying UC to convert diode laser light in the near infrared to red, green and blue visible light to make displays.

The transfer of energy from one ion to another has been studied for many years [1]. Pioneering work on understanding the basic physics of these interactions was conducted by Foerster in 1949 and Dexter in 1953. They found that the electric dipole-dipole, the higher multipolar, and for short interaction distances, the exchange interaction were responsible for ion-ion energy transfer. In 1959 Bloembergen described a process in which a rare-earth ion is excited to a state giving rise to visible luminescence by the absorption of an infrared photon and another pump photon [2]. This concept has been broadened since by the consideration of other rare-earth ions as sensitizers. Part of the required absorption is accomplished by these sensitizer ions, which may or may not be identical to the emitting or acceptor ions. A portion of the absorbed energy is transferred by either a resonant or a phonon-assisted process to the acceptor. Self-sensitized systems have been known for some time, however systems in which the sensitizer is different from the acceptor are considered here because, though they may be more complicated they can be more efficient up converters.
Auzel was apparently the first to discover the sensitization of erbium (Er$^{3+}$) and thulium (Tm$^{3+}$) by ytterbium (Yb$^{3+}$): in 1966, he observed the conversion of 960 nm to blue light by Yb$^{3+}$-Tm$^{3+}$ ions in a tungstate host and proposed a sequential transfer mechanism to explain the process [3]. Hewes and Sarver demonstrated in their 1969 paper [4] that Auzel’s model was correct for Yb$^{3+}$-Tm$^{3+}$ ions in YF$_3$. Esterowitz et al. discovered the sensitization of holmium (Ho$^{3+}$) by Yb$^{3+}$ in CaF$_2$ in 1967 [5] which they attributed to a single transfer from the Yb$^{3+}$ ion to the Ho$^{3+}$. Then Hewes and Sarver proved that the double-transfer mechanism of Auzel was operative in the excitation of Ho$^{3+}$ or Er$^{3+}$ acceptors [4]. They concluded that infrared-to-visible up-conversion is accomplished by absorption of energy in the Yb$^{3+}$ ions followed by two (for Er$^{3+}$ and Ho$^{3+}$) or three (for Tm$^{3+}$) transfers to the acceptor, resulting in production of strong visible luminescence (green and red for Er$^{3+}$ and Ho$^{3+}$ and blue and red for Tm$^{3+}$). They also specified the importance of not neglecting back transfer in which the acceptor transfers its energy back to the sensitizer in a non-radiative process. Further explorations of erbium, thulium and holmium sensitized by ytterbium confirmed that infrared to visible conversion efficiencies were improved by one to two orders of magnitude over singly-doped materials [5-9].

The next important step was taken by Golubov and Konobeev (1972) and Sakun (1973) who took into account the geometry of the sites where the randomly distributed acceptor ions can sit, showing that the host crystal has a strong influence on the process of interest [10, 11]. Sommerdijk reported in his 1971 paper that fluoride crystals were much more
effective than oxidic lattices [12]. The reason of the great efficiency of the fluorides is that they have especially weak ion-lattice interactions and thus a low non-radiative relaxation probability, whereas in oxidic lattices the non-radiative decays are much stronger due to the enhanced ion-lattice interactions, making them less efficient.

At that time there was an effort to study up-conversion in these more efficient materials in order to better characterize their efficiency. These studies tackled the dependence of up-conversion efficiency on dopant concentrations and host crystals, temperature, pulse duration of excitation and infrared input power [3, 4, 13-16]. Indeed up-conversion is a nonlinear process and its efficiency varies with infrared excitation: in a two-photon process, at low input power, this dependence is quadratic. Departure from this behavior was observed at higher input power, and was incorrectly attributed by Johnson et al. to heating of the diode and/or the materials in [3]. Rich and Pinnow understood it was due to saturation of the up-conversion process and attempted to predict and measure maximum efficiencies but no quantitative data were obtained for lack of powerful enough sources [13]. Indeed, the most practical source at that time was the GaAs:Si diode which has a peak output at $\lambda = 940$ nm that we now know is far from the optimum pump wavelength. At this point, further studies and practical applications were made difficult by this lack of infrared sources that could take advantage of the efficiencies ultimately attainable in these co-doped crystals.

The work resumed in the 90’s with the development and commercialization of high power InGaAs diode lasers able to pump the Yb$^{3+}$ absorption band near 970 nm. The
most notable photonic application so far is solid-state laser engineering, e.g. UC lasers, which are visible lasers that are pumped with infrared diodes [17-22]. Indeed, recently, there have been increasing demands for compact visible laser sources in a variety of applications, including color displays, optical recording, reprographics, biomedical diagnostics and underwater optical communication. Up-conversion lasers can potentially provide practical all-solid-state sources with output at wavelengths from the ultraviolet to the red[17, 23]. However, red, green and blue visible laser sources are complex and expensive and produce light that an observer sees as speckled.

The idea of UC displays was also revisited at that time. In the early 90’s, two patents were issued on UC displays [24, 25]. S. A. Pollack of Hughes Aircraft Company received a 1991 patent entitled “Full Color Up-Conversion Display”[24]. He claimed a full up-conversion display, comprising an up-conversion screen and means to excite pixels in a spatially selective manner, the wavelength of excitation, and the screen comprising a transparent substrate on which is deposited a layer of host material doped with rare earth ions. Grinding the doped crystals into powder and mixing it in a binder is stated as a preferred technique but is not claimed, neither is the nature of the binder nor the size of the particles, and Pollack doesn’t claim any other host crystals than CaF$_2$, nor any other rare-earth dopants than Er$^{3+}$ and Tm$^{3+}$ possibly sensitized by Yb$^{3+}$. The other patent was by R. A. McFarlane also of Hughes Aircraft Company[25]. It was issued in 1993 and is entitled “Infrared-To-Visible Up-Conversion Display System and Method Operable at Room Temperature”. He mentions a dispersion of particles but not in what, the particles are polycrystalline phosphors and no mention of fluorides is made.
However no real product came out of these patents, and by 1998, there was still a scarcity of quantitative data on UC efficiencies. It prompted Payne et al. to re-investigate red, green, and blue emitting UC materials, with the goal of systematizing their characterization by defining proper efficiency measurements for the first time [26]. However these efficiency measurements were still not fully adequate for display applications and didn’t outline the potential of the technology. As a result, when Cockroft et al. tried to make a UC display prototype in 2000, the technology didn’t seem to live up to its potentials, and they acknowledged that the performances of UC-phosphors were application-dependant [27]. Still they emphasized that other good properties of UC materials, e.g. their chromaticity, absorption length, refractive index, saturation behavior and stability might compensate the short-comings in efficiency.

In 2000, AC Materials provided Dr Bass’s group with high quality co-doped fluorides which appeared more efficient than any other materials studied in the past, and Dr Bass decided to revisit the idea of using UC for display applications. Still UC crystals are very hard and very expensive to grow as large single crystals, thus they can not be prepared in sizes as large as needed for most display applications. The simple innovative concept proposed by Dr Bass relied on using these efficient UC materials in powder form to be dispersed in a passive matrix, e.g. a polymeric binder. Such inexpensive way of making UC screens would also allow applications to conformable displays. Depending on the crystal selection, mixture, size of the crystallites, binder and substrate used, this new technology allows one to make red, green or blue displays, full color displays and white
on black displays that are transparent, black or reflective when not emitting light
representative of the displayed information. As we investigated fluorides co-doped with
$\text{Yb}^{3+}$ and $\text{Er}^{3+}$ or $\text{Tm}^{3+}$ ground into a specific size and dispersed in a specific index
matching passive matrix specially elaborated at UCF, a patent was submitted for the new
display. No matter how efficient the new materials were, we still needed to overcome the
caveat brought up by Cockroft: that UC-performances seemed application dependant. It
was, therefore, essential to fully understand the fundamental mechanisms of UC in
crystallites in order to predict their performances whatever the application. As our work
on UC displays progressed, we identified additional concepts that were key to making
this technology competitive, and they were added to the initial patent. Such concepts are
developed in this dissertation where for the first time up-conversion displays are
investigated and developed in an integrated manner with the aim of eventual
commercialization.
1.2 Concept of novel emissive 2D display based on up-conversion

![Diagram of UC-display concept: scheme of scanned full color display with screen optically written in transmission and photos of red, green and blue UC-displays made in our lab (true colors).](image)

Figure 1.1: UC-display concept: scheme of scanned full color display with screen optically written in transmission and photos of red, green and blue UC-displays made in our lab (true colors). The Lissajous patterns were obtained by vector scanning a 200 mW, 975 nm diode laser beam across an area 25mm on the side. For the red emitting screen, rhodamine B dye was added to the polymer mix to absorb the extra green emission. Photos by Erik Reinhard©.

The base materials we use are fluoride crystals doped with Yb$^{3+}$ and an active ion (Er$^{3+}$ or Tm$^{3+}$). In particular, we have found 1 % Er, 18 % Yb:YF$_3$, 1 % Er, 18 % Yb:NaYF$_4$ (NYF), and 0.4 % Tm, 20 % Yb:KY$_3$F$_{10}$ to be desirable red, green and blue up-conversion emitters, respectively. To make the technology scalable, we grind these materials into powder and disperse the powdered material in a polymeric host. The mixture is then coated on a substrate to form a screen. Common polymethylmethacrylate (PMMA) was used at first but samples quickly flaked off as the different thermal expansion coefficients of the crystallites and the polymer caused stresses and separation. A phosphorylated version of PMMA (p-PMMA) that was developed in collaboration with Prof. Kevin Belfield [28] has shown much improved properties with sample screens in use for over 4 years showing no sign of deterioration. An infrared laser beam is
scanned (direct writing) or projected (projection display) onto the UC screen to form an image. This can be done in transmission where the infrared excitation is incident on one side and the visible emission is viewed on the other side of the screen (similar to a cathode ray tube (CRT) emissive display) as schematized in Figure 1.1 or in reflection where the infrared is incident on the same side of the screen from which the visible light is viewed. An example of direct-writing on a reflective screen is shown in Figure 1.2.

Figure 1.2: Example of display optically written in reflection (top view of setup). Two silver coated mirrors driven by galvanometers deflect the infrared beam to form a 2D moving image on the screen (vector scan). The green UC powder was dispersed in p-PMMA and coated on an aluminum substrate about 5 mm on the side. Photo by Erik Reinhard©.

It is important to underline that because the up-conversion excitation source is in the infrared the low energy pump photons do not produce damage in the UC materials. Hence, in addition to the stability of the emitters, the screens do not suffer performance deterioration as do down-conversion displays (such as in plasma display technology) after many hours of operation or after use at high brightness levels. As a result, we have been able to operate our screens at tens of kcd/m² without degrading their properties.
One major consequence is that such displays can be operated in high ambient lighting environment and still be visible, without degradation.

Figure 1.3: Versatility of UC screens. (a) Photo of a green UC reflective screen taken outdoors during a sunny Florida day at noon. This screen is about 50 mm on a side on an aluminum substrate. (b) Transparent green UC display off (top) and on (bottom). The black dashed line was drawn on the pictures to show the area of where the mix of particle and binder was coated. Here the substrate is a standard glass microscope slide. In both (a) and (b) cases, the excitation source was a 500 mW, 975 nm diode laser scanned with two galvanometer mirrors.

The photo in Figure 1.3 (a) was taken of a green emitting UC screen on a sunny Florida day at noon. Similar easy visibility was obtained with our red and blue emitting screens. The UC screens were the only displays visible in the high ambient lighting conditions despite the unfavorable contrast of the UC screens used. We will discuss scattering issues later in this paper, but it can be observed from the picture that the screen appears white. This is because the visible sun-light is backscattered by the UC powder in suspension in the plastic. In Figure 1.3 (b) we show that it is possible to use polymers that are index-matched to the UC materials to suppress scattering and form transparent
display screens. Similarly, one could think of designing not only conformable, but also flexible displays using the same UC concept.

Figure 1.4: Wedge technology developed by Adrian Travis at Cambridge Flat Projection Display Ltd.

UC display technology offer many other advantages. The UC materials absorb the infrared excitation light and re-emit the energy through fluorescence in the visible region. The visible fluorescence radiates in a Lambertian pattern so that a UC display does not have the restricted viewing angles that is found in Liquid Crystal displays (LCD). This is illustrated in Figure 1.2 where the photo of the UC display was taken from the top yet the display is still visible despite the steep angle of view. Because the viewer does not see visible laser light, there is no speckle as in a laser display. Other advantages over laser displays include the facts that there is no demand for laser grade optics, nonlinear crystals, alignment and fixturing. UC displays can use the super efficient diodes developed in the SHEDS program which emit at 975 nm where our UC emitters are efficiently excited [29]. It is also a benefit for safety reasons: the infrared excitation
light, being spectrally narrow and well separated from the visible emission, can easily be filtered out in order to completely shield the viewer from any laser radiation. Additionally, UC technology requires no high voltage or vacuum tube, hence reducing weight and safety concerns over CRT displays. Another advantage is that the optical excitation path can be folded in order to reduce the depth of the display to just a few centimeters. An example of such a folded optical system for an up-conversion display is shown in Figure 1.4 where a wedge technology developed by Adrian Travis[30, 31] at Cambridge Flat Projection Displays Limited is used to project the infrared image onto the screen face, forming the visible image.
1.3 Thesis

This dissertation is organized as follows. Chapter Two presents the tools necessary to understand how UC materials can be suitable emitters for display technology. It includes basics on radiometry, colorimetry, energy transfer, a review of the physics of up-conversion in the rare-earth doped crystals of interest in this thesis, and the definition and experimental measurement techniques of UC efficiency, which is the quantity that we seek to maximize. In Chapter Three the key fundamental methods to optimize UC efficiencies in micro-particles in UC-based display technology are demonstrated. These are thermal and scattering management in our emitters. The dependence of UC efficiencies on temperature is revealed by studying the critical case of non-resonant UC materials. Then simple thermal management of the emitter is shown capable of improving the performance of display. Next, reducing scattering in UC emitters is demonstrated to significantly improve their efficiencies. Chapter Four reports on how these results can be applied to make efficient three color displays and white light sources based on UC emitters. It also present prototypes of UC-displays which showcase the versatility of the technology. Finally, results are summarized and conclusions presented in Chapter Five, before proposing future work on this subject.
CHAPTER TWO: UP-CONVERSION IN RARE-EARTH DOPED MATERIALS AND TOOLS TO CHARACTERIZE THEIR PERFORMANCES

2.1 Useful notions on radiometry, colorimetry and energy transfer basics

2.1.1 Radiometry

Principles of radiometry can be found in Reference [32]. Here are some definitions pertaining to this work.

2.1.1.1 Definitions and units

Electromagnetic radiation is characterized either by its frequency $\nu$ or, equivalently its wavelength $\lambda$, with $\lambda=c/\nu$ where $c$ is the speed of light.

![Electromagnetic spectrum]

Figure 2.1: The electromagnetic spectrum [33].

*Radiometry* is the measurement of optical radiation in the electromagnetic spectrum, namely the radiation within the frequency range from $3\times10^{11}$ to $3\times10^{16}$ Hertz (Hz),
corresponding to wavelengths between 10 nanometers (nm) and 1000 micrometers (microns or µm). As it can be seen in Figure 2.1, this range includes the regions commonly called ultraviolet (UV), visible, and infrared (IR). Radiometric quantities are based on energy in joules (J) or power in watts (W), energy being the integration of power over time. Photon quantities are also common, i.e. the measurement of the number of photon emitted by a source, rather than the energy produced. Photon quantities and radiometric quantities are related by the relationship $E_p = h \cdot c / \lambda$ where $E_p$ is the energy of a photon at wavelength $\lambda$ and $h$ is the Plank constant. Since the energy of a photon is inversely proportional to its wavelength, long wavelength photons are less energetic than short wavelength photons. Also, if the radiation is not monochromatic, i.e. is composed of several wavelengths, the conversion from photon quantities to radiometric quantities is done by integrating the spectral density of the photon energy (J/nm) over the wavelength range.

*Photometry* is the measurement of electromagnetic radiation detectable by the human eye. It is thus restricted to the wavelength range from about 360 to 830 nm. Photometry is identical to radiometry except that everything is weighted by the spectral response of the nominal human eye. The base unit for photometry is the lumen (lm) and is defined by the following standard: at a wavelength of 555 nm, one watt of radiant power is equal to 683 lumens.
Table 2.1: Radiometric and Photometric Quantities and Units

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Radiometry</th>
<th>Photometry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Name</td>
<td>Unit</td>
</tr>
<tr>
<td>Power</td>
<td>Radiant flux</td>
<td>watt (W)</td>
</tr>
<tr>
<td>Power per area</td>
<td>Irradiance</td>
<td>W·m$^{-2}$</td>
</tr>
<tr>
<td>Power per solid angle</td>
<td>Radiant intensity</td>
<td>W·sr$^{-1}$</td>
</tr>
<tr>
<td>Power per area per solid angle</td>
<td>Radiance</td>
<td>W·m$^{-2}$·sr$^{-1}$</td>
</tr>
</tbody>
</table>

The definitions of the relevant quantities and their radiometric and photometric units are given in Table 2.1. We see that most quantities are relative to area or solid angle. The quantity that is most appropriate to characterize a light emitting system will depend on the nature of the source (e.g. point source or radiating surface of a given area) and the geometry of the detection system (e.g. area of detector and angle of detection). When a radiating surface appears equally bright from any viewing direction the surface is called a *Lambertian radiator*. For a Lambertian surface, the radiance (W·m$^{-2}$·sr$^{-1}$) or luminance (lm·m$^{-2}$·sr$^{-1}$ or cd·m$^{-2}$) is independent of direction. We note that the correct term for a point source radiating equally in all direction is *isotropic*. However in this work we will extend the use of Lambertian to small finite size emitters, although each could technically constitute a point source. An example of Lambertian emitters for displays is the surface of a cathode ray tube (CRT) TV screen. A Liquid Crystal Display (LCD) display is one where brightness depends on viewing angle.
2.1.1.2 The human eye

The quantities described in Table 2.1 have a strictly physical basis and have been defined monochromatically at a single wavelength of 555 nm. However the eye does not see all wavelengths equally. For other wavelengths or for band or continuous-source spectral distributions, the spectral response \( V(\lambda) \) of the human eye must be considered. It is a normalized function called spectral luminous efficiency function. It is an empirical curve adopted by the Commission Internationale de l’Eclairage (CIE) which has the shape of a slightly skewed Gaussian depending on the ambient lighting. Indeed the eye has two general classes of photosensors: cones and rods. The cones are responsible for light-adapted (photopic) vision and respond to color with high resolution. The rods are responsible for dark-adapted (scotopic) vision with no color information and lower resolution than the cones.

For photopic vision, \( V(\lambda) \) peaks at 555 nm and goes to ~ zero beyond 400 and 750 nm. In the scotopic case, \( V(\lambda) \) peaks at 507 nm and goes to ~ zero beyond 360 and 650 nm. The conversion to absolute spectral luminous efficiency is done by multiplying \( V(\lambda) \) by the factor \( K_m=683 \text{ lm/W} \) and the resulting functions are shown in Figure 2.2.
Figure 2.2: Response of the human eye: absolute spectral luminous efficiency functions for photopic and scotopic vision [34].

The conversion from watts to lumens requires that the spectral distribution of the radiation be known over the spectral range where \( V(\lambda) \) is non-zero (typically from 360 to 750 nm). A luminous quantity \( X_\nu \) is then obtained by:

\[
X_\nu = K_m \int_{360}^{750} X_\lambda V(\lambda) d\lambda
\]  

(2.1),

where \( X_\lambda \) is the corresponding radiant quantity spectral distribution and \( V(\lambda) \) the photopic luminous efficiency function.
2.1.1.3 Radiometric considerations for displays

In the present work, we are interested in radiation from ~ 350 nm to 1 µm, i.e. near-UV (~ 350 to 400 nm), visible (~ 400 to 750 nm) and near-IR (~750 to 1 µm). The range definition adopted here for the visible relates to the wavelengths detectable by the human eye: outside of this range the eye sensitivity is ~ zero. From this point on “infrared” or IR will mean “near IR” and “UV” will mean “near-UV”.

A UC-based display is a screen made of emitters that produce light when excited by an infrared beam. We evaluate the performances of our technology by determining the infrared to visible power conversion efficiency of our emitters. For that we measure the optical power of the infrared beam incident on the emitter. It is measured in radiant watts (W). As for the visible emission, good emitters for displays should not only be efficient up-converters, they should be so at wavelengths detectable by the human eye. Therefore we find that a good assessment of their performances is to measure visible emission both in radiometric (watts) and in photometric (lumens) units. Radiometric efficiencies are either given in % or W/W (unit-less), and photometric efficiencies are in lm/W. We point out that these are relative to optical watts, not electrical watts as it is the case for most existing display technologies. The conversion to efficiencies per electrical watt takes into account the efficiency of the infrared diode laser (~ 80% for 975nm diode lasers developed in the SHEDS program). Screen performances are evaluated by measuring brightness’s in nits (cd·m⁻²). To allow for a broad range of applications, display technology performances relate to normal lighting vision: the photometric
quantities given in this work are quantities weighted by the photopic response of the human eye.

2.1.2 Colorimetry

The goal of colorimetry is to incorporate properties of the human color vision system into the measurement and specification of visible light. Colorimetry provides quantitative representations that predict when two lights will appear identical to the human observer, allowing color reproduction (e.g. nature and paint, photography, display, printing, etc.). A good introduction to colorimetry can be found in Reference [35] and a more exhaustive study in Reference [36].

2.1.2.1 Human color vision

Human color vision derives from the response of the cones contained in the retina of the eye. There are three types of cones corresponding roughly to red, green, and blue sensitive detectors. Each of these photoreceptors responds differently to the varying wavelengths of light. The "green" and "red" cones are mostly packed into the fovea centralis. The approximate spectral sensitivities of these photo-receptors are shown in Figure 2.3. The relative heights for the three types are set equal for lack of detailed data.
Figure 2.3: Normalized color sensitivity of the red-, green- and blue-sensitive cones of the human eye [34].

2.1.2.2 Color mixing by addition

The colors we see are usually not monochromatic, but rather are made of a distribution of visible wavelengths characterized by an intensity-distribution curve. Colored lights appear the same to us, no matter what their intensity-distribution curves, provided that three of their properties are the same: their hue, saturation and brightness for colored lights and lightness for colored surfaces [37].

- **Hue** corresponds to the main color: it is what distinguishes one spectral color from another. It is specified by the dominant wavelength in the intensity-distribution curve.

- **Saturation** corresponds to the purity of the color. A very saturated color generally has almost all its intensity fairly close to the dominant wavelength, while an unsaturated color would have contribution from many other wavelengths.
Monochromatic colors have the highest saturation and white light is completely unsaturated. Other colors may be thought as a mixture of white light with a saturated color.

- **Brightness** refers to the sensation of overall intensity of a light, ranging form dark, through dim, to bright, and dazzling. For surface colors, the third property is *lightness* which is related to the percentage of incident light reflected by a surface and refers to the whiteness, grayness or blackness of a color.

Overlapping spots of light on a white screen, i.e. a screen which diffusely reflects all the visible wavelengths equally well, combines their colors by additive mixture. In the 1920’s color matching experiments were conducted showing that, if it were possible to remove some amount of one or more colors (sometimes referred to as negative amounts of color), any color could be matched by an additive mixture of monochromatic red at 700 nm, green at 546.1 nm and blue at 435.8 nm. These three colors are called the RGB *primaries*. Colors that additively combine to produce white are called *complementary* colors. The weights given to the three primaries in order to match a color are called *tristimulus* values\(^1\). The tristimulus values at all wavelengths of the visible spectrum constitute the *color matching functions*, which for the historical RGB primaries are

---

\(^1\) It is always necessary to specify the units in which these tristimulus values are expressed. This can be done by stating in the same units the tristimulus values for some standard or physically defined sample. Such specification is always advisable because the absolute values of radiometric quantities are rarely given or used, and consequently the tristimulus values can only rarely be based on absolute units. For the same reason, the conversion to absolute photometric values is also rarely encountered [36].

21
shown in Figure 2.4 (a). A negative value on a color matching function indicates that some colors cannot be exactly produced by adding up the primaries.

Figure 2.4: (a) The historical RGB color matching functions and (b) the CIE RGB color matching functions [34]. In both case the vertical axis is the tristimulus value (no units, see Footnote 1).

2.1.2.3 CIE Chromaticity diagram

In 1931, the Commission Internationale d'Eclairage (CIE) derived a new set of primaries from the RGB primaries matching functions of Figure 2.4. This new set of primaries, called X, Y, and Z, was derived so that the set always produces positive tristimulus values. It is possible to represent any color in terms of these primaries and equal values of X, Y, and Z produce white. They also were arranged so that a single parameter Y determines the luminance of the color. The CIE defined the Standard Observer to have the color-matching functions shown in Figure 2.4. These tristimulus values specify the
chromaticity, i.e. the amounts of three standard primaries X, Y, Z needed to exactly reproduce any visible color via the following formulas where $E(\lambda)$ is the product of the surface reflectance and the light source distribution [38]:

\[
X = \int E(\lambda) \bar{x}(\lambda) d\lambda \\
Y = \int E(\lambda) \bar{y}(\lambda) d\lambda \\
Z = \int E(\lambda) \bar{z}(\lambda) d\lambda
\] (2.2).

All visible colors are found in a horseshoe shaped cone in the X-Y-Z space. As it is a 3D space it is impractical to work in it directly. It is common to project this space to the X+Y+Z=1 plane. The result is a 2D space known as the CIE chromaticity diagram shown in Figure 2.5. The coordinates in this space are usually called x and y and they are derived from X-Y-Z using the following equations:

\[
x = \frac{X}{X + Y + Z} \\
y = \frac{Y}{X + Y + Z} \\
z = \frac{Z}{X + Y + Z} = 1 - x - y
\] (2.3).

As the z component bears no additional information, it is often omitted. Note that since x-y space is just a projection of the 3D X-Y-Z space, each point in x-y corresponds to several points in the original space. As the missing information is the luminance Y, a
color is usually described by x, y, Y coordinates, where x and y determine the chromaticity and Y the brightness component of the color.

Figure 2.5: The 1931 CIE chromaticity diagram [34].

The horseshoe outline is the locus of the saturated (monochromatic) colors, i.e. the colors produced by one wavelength of the visible spectrum. Inside the horseshoe shaped locus are all the spectral colors, i.e. the colors produced by any combination of the monochromatic colors. We note that the line of purples, the straight line connecting the lowest wavelength blue and the highest wavelength red, does not represent spectral colors.

White is perceived when the colors add to achieve a value in the central part of the CIE diagram. A particular white point is of theoretical interest as it gives certain information about spectral colors. It is the achromatic white point E of Figure 2.5 which is the point...
of coordinates x=1/3, y=1/3, z=1/3, i.e. formed by mixing equal amounts of the three primaries. By drawing a straight line connecting the achromatic point E and any spectral color of coordinate x,y, we can derive important information about this spectral color, namely its dominant wavelength, its degree of saturation and its complementary color. The dominant wavelength of the spectral color (which determines this color’s hue) is determined by the intersection of this line with the horseshoe outline. For instance in Figure 2.5, the dominant wavelength of all the colors lying on the straight line between points E and A (for instance point X) is given by point A. The degree of saturation of color X is given by the ratio of the distances $\frac{XE}{AE}$. If this ratio close to unity, i.e. X is close to the spectral horseshoe outline, its saturation is high. If the ratio is small (X close to the achromatic point) it means the color of point X is unsaturated. The complementary color of any spectral color X is found by extending the straight line between X and E through the achromatic point to the opposite side of the horseshoe outline. For instance, on Figure 2.5 point B is the complement of point A and of any spectral color located on the straight line between A and E.

An interesting property of the x,y chromaticity diagram is that all possible mixtures of two colors $x_1,y_1$ and $x_2,y_2$ are given by the straight line connecting these two points. As a result, all the possible mixtures of three colors $x_1,y_1$, $x_2,y_2$ and $x_3,y_3$ lie inside the triangle determined with those three points. For instance, using 650 nm red, 520 nm green and 460 nm blue as the three primary colors, any color inside the large triangle can be made without using negative contributions of the tristimulus values. The gamut of colors is all colors that can be reproduced using the three primaries. These three colors give about as
big a triangle can fit inside the horseshoe, so they give the biggest gamut without negative contributions, i.e. that can be physically achieved with three lights. That is why blue, green and red are called the additive primary colors. Of course, even by using the primary colors, other spectral colors cannot be produced. However, for most purposes that is not important, because most colors occurring in nature are unsaturated.

In spite of all its useful characteristics, the 1931 CIE x,y chromaticity diagram has one important caveat: if the distance between any arbitrary two points is the same as the distance between another two points, the perceived amount of change in color from one point to the other will not be the same for the two pairs. In order to correct this, researchers are trying to find a perceptually uniform color space. It has, unfortunately, still not been found. CIE proposed two alternatives as improvements compared with the 1931 CIE x,y,Y space. These are CIE LUV and CIE LAB. Although they are referred to as perceptually uniform color spaces by some authors, they are not and additional research is required.

2.1.2.4 Example: TV colors

We saw in Section 2.1.2.2 that a way of mixing colors additively is to illuminate the same region with different color light sources. This technique is used in large-screen color television projection (such as found in sports arenas and home projection systems). Another way of enabling lights of different colors to mix is to place small separate sources close to each other. If the viewer’s eye cannot see them as separate sources, their colors will mix additively. This type of additive mixing is called partitive mixing [37]
and is the way an ordinary color TV picture is produced, for instance in a cathode ray tube (CRT) display [39].

In a CRT display, there is a picture tube with three electron guns in it, each gun directing the electrons to different points on the screen through a mask with many holes. The screen consists of dots of three different phosphors, each of which will produce one of the additive primary RGB colors. The dots are arranged so that each type can be hit through the mask by only one of the guns. Each gun makes a complete TV picture in one of the primary colors, but since the pictures are tightly interlaced on the screen they are not seen individually. As a result there is less light from a given color than by using different projectors since each primary color, at best, comes from one third of the screen. This is the reason most large-screen TV projection systems use three different picture tubes that each produce one of the primary colors.

![Emission spectra of a typical set of CRT phosphors](image)

Figure 2.6: Emission spectra of a typical set of CRT phosphors[39]. The vertical scale is the spectral power distribution given here in arbitrary units.
The emission spectra of a typical set of CRT phosphors are shown in Figure 2.6. Their respective colors are at the tips of the dotted triangle on the 1931 CIE chromaticity diagram of Figure 2.7, and their dominant wavelengths are respectively 610 nm, 545 nm and 463 nm. The gamut of a color CRT monitor coincides with the modern National Television Standard Committee (NTSC) standard, which is the North American standard for the generation, transmission and reception of television signals. We can clearly see on Figure 2.7 that this color gamut is much smaller than the horseshoe indicating that the palette of colors available in color TV is only a subset of all visible colors. Still the trichromatic color mixing system gives an acceptable rendering of the colors of life. Few people, however, notice that the system is extremely weak when it comes to the projection of the turquoise band of colors. Other display technologies such as Light Emitting Diode (LED) displays, LC displays, plasma displays, etc, will have their own color gamut, covering more or less the span of the NTSC standard. We note that gamut standards are not only for moving images. Other areas where gamut standards are defined are monitors, scanners, projectors, printers, etc. The color gamut for typical ink is also shown in Figure 2.7.
Figure 2.7: Gamut of media colors [37]. The dotted triangle is the TV color gamut, with the color of the three phosphors marked by x’s. Inside the thick boundary are the print colors, with the color of the full strength inks indicated by y=yellow, m=magenta and c=cyan. The dashed triangle delimits the photographic slides colors with the colors of the three dyes marked by small circles.
Finally, a source or display usually specifies the x,y coordinates of the white color used, since pure white is not usually captured or reproduced. The white standard for modern TV is the D65 white of x,y coordinates (0.3127, 0.3290). It is a white of the same color as an incandescent source at 6500 °K. Other white standards are located along the blackbody locus of the chromaticity diagram which is shown in Figure 2.8. This locus represents the chromaticity of blackbody radiators at various temperatures. Emitters with a chromaticity in the vicinity of this locus can be characterized by a color temperature i.e. the temperature of the Planckian radiator of similar chromaticity[36].
2.1.3 Basics on energy transfers

2.1.3.1 Radiative resonant transitions

The three main radiative energy exchanges available to electrons in the outer shells of electrons in atoms or ions are the following: absorption, spontaneous emission and stimulated emission. Let us consider an ion having two manifolds of energy $E_1$ and $E_2$ respectively ($E_1 < E_2$). We suppose at first that the initial state of the atom corresponds to the energy $E_1$. When radiation strikes the atom, if the incident beam frequency $\nu_0$ satisfies $h\nu_0 = E_2 - E_1$, and if the selection rules allow it, the transition to the upper level can occur: a photon can be absorbed by the ion. Such transition where $h\nu_0 = E_2 - E_1$ is called resonant. If the frequency doesn’t satisfy $h\nu_0 = E_2 - E_1$, the radiation passes through the atom without interacting with it. For an ion with more than two manifolds, if $E_1$ is the ground state, absorption is called “ground state absorption”. If $E_1$ is an excited energy level, it is called excited state absorption (ESA).

Let’s now suppose that the initial energy of the atom is $E_2$. This atom is in an unstable state. There are two ways to lower its energy. In one the atom might spontaneously emit a photon of energy $h\nu_0 = E_2 - E_1$. Other radiation of frequency $\nu_0$ striking the atom can also stimulate the emission of a photon. In that case, the emitted photon will have the same characteristics (frequency, direction of propagation, polarization and phase) as the incident photon.
2.1.3.2 Phonon assisted transitions

Other energy exchange mechanisms exist. Indeed, energy exchanges can occur in a host lattice doped with impurities through absorption or emission of phonons. Those phonon-assisted transitions can occur via two mechanisms.

The first kind of phonon-assisted transition occurs when the frequency of the photon to be absorbed doesn’t exactly match the energy gap between two states. If the mismatch is not too large (but larger than $\hbar \omega_m$ where $\omega_m$ is the highest phonon frequency of the host), phonons can be absorbed (Anti-Stokes transition) or emitted (Stokes transition) to complete the transition. Such transitions are called vibronic as phonons correspond to a lattice vibration and are represented in Figure 2.9 (a) and (b). Vibronic transitions are commonly referred to as phonon-assisted transitions.

Figure 2.9: Energy scheme for different phonon-assisted transitions in ions, for $\Delta E \geq \hbar \omega_m$: (a) Anti-Stokes vibronic transition (absorption of phonon), (b) Stokes vibronic transition (emission of phonon) and (c) non-radiative transition. Transfer probabilities are noted $W_{AS}$, $W_S$ and $W_{NA}$ respectively[40].
The second kind of phonon-assisted transitions are the *non-radiative transitions*, i.e. transitions without emission or absorption of a photon, often schematized by a wavy arrow as shown in Figure 2.9 (c). Such a process depopulates a level but does not contribute to either the electromagnetic absorption or emission spectrum. These transitions are very important for closely spaced energy levels ($\hbar \omega_m \leq \Delta E \leq 3000 \text{ cm}^{-1}$). In particular, they are responsible for the thermalization of the populations in the energy levels: for levels separated by very small energies (especially within a given state where energy levels are split by the crystal field), the non-radiative transitions are extremely fast.

**2.1.3.3 Cross relaxation and up-conversion**

Not all transitions are radiative, i.e. involve the absorption or emission of a photon. Other types of transitions are energy transfers where energy is exchanged by means of a virtual photon. These can occur in rare-earth doped crystals where nearest-neighbor distance between ions is small and short distance-exchange interactions are allowed. For ions with multiple manifolds of energy, two interesting types of energy transfer are cross relaxation and up-conversion. To define these two processes, let’s consider the general case of a rare-earth singly doped crystal in which the element presents a five level energy diagram as shown in Figure 2.10. We assume that the ground state energy is $E_0 = 0$, and that two sets of levels admit the same energy difference: $E_3 - E_1 = E_4 – E_2$. ($E_1$ can be the ground state and/or $E_2$ can be equal to $E_3$ for a simple 3 level system). We also assume that every transition is allowed by the selection rules.
Cross-relaxation, schematized in Figure 2.10 (a), is the following process. By pumping with a radiation of frequency $\nu_0 = E_4/h$, we populate the level $E_4$. In order to return to the equilibrium state, the ions in this state admit various transitions towards lower energies. In particular, transitions occur from $E_4$ to $E_2$ (1). Normally, if this transition is radiative, a photon of frequency $\nu_1 = (E_4 – E_2)/h$ is emitted. Level $E_1$ might be populated (if it’s the ground state because every single ion in the crystal cannot be excited, or if a transition occur from $E_4$ to $E_1$), and atoms in that state are able to reach the level $E_3$ by absorbing the energy $(E_3 – E_1) = h\nu_1$ (2). Eventually, if two identical ions are close enough, if ion 1 is in the state $E_4$ while ion 2 is in the state $E_1$, ion 1 might reach the state $E_2$, the energy released in that transition might be absorbed by ion 2 which then will reach the state $E_3$. Cross relaxation may take place even if $E_3 - E_1$ doesn’t exactly match $E_4 – E_2$ by being phonon-assisted. Cross relaxation has different effects on observed spectra: it reduces the intensity of the line at the frequency $\nu_1$ (quenching of the emission at frequency $\nu_1$), and increases the observed emission strength coming from $E_2$. 

Figure 2.10: (a) Cross relaxation and (b) up-conversion. The thin arrow represents photon absorption, the fat arrows schematize ion-ion energy transfer.
An interesting configuration arises when the radiation is pumped at the energy $E_3$: the crystal might present emission of higher frequency. This process is called up-conversion and is schematized in Figure 2.10 (b). For this process the assumptions are that $E_2$ is populated; ion 1 is in the state $E_3$ while ion 2 is in the state $E_2$. If so, ion 1 might reach the state $E_1$ (1) and the energy released in that transition might be absorbed by ion 2 which then will reach the state $E_4$ (2). If $E_4$ relaxes radiatively to the ground states, this radiation has greater energy than does the pump that populated $E_3$. This is called up-conversion and is the phenomenon of interest in this present research. Up-conversion enables infrared light to be converted to visible light. If $E_2$ is a metastable state, i.e. ions that decay into that state are trapped for a long time (several milliseconds), high visible output can be expected. More steps can be required to up-convert infrared into visible light depending on the emission wavelength of interest and the complexity of the structure of the active rare earth ion. For simplicity, unless stated otherwise, we will consider the case of a two step process when describing the principles of up-conversion.

In the system described above, since two ions need to be simultaneously in an excited state for up-conversion to happen, two infrared photons are absorbed for one visible photon emitted: it is a nonlinear process. However unlike a nonlinear frequency doubler, the output frequency is not exactly twice the input frequency, as non-radiative or phonon-assisted transitions may occur.
From Figure 2.10 we can see that cross relaxation and up-conversion are competitive processes. Another competitive process to up-conversion is re-absorption of the visible emission. Cross relaxation and visible re-absorption can be minimized by keeping the dopant ion concentration low.

2.1.3.4 Energy transfer between two rare earths elements

The phenomenon of energy transfer can also occur between the two rare-earth elements of a co-doped crystal, whenever four levels are found to satisfy $E_{a2}^a - E_{1}^a = E_{b2}^b - E_{1}^b$. This phenomenon can be detected by exciting an element (the donor or sensitizer): luminescence from the other element (the acceptor or activator) will then be observed. Co-doping is useful when no effective pump is known for the acceptor: if the energy transfer is efficient and the signal obtained can be stronger than when pumping directly.

![Energy transfer diagram](image)

**Figure 2.11:** Energy transfer from a sensitizer (S) to an activator (A) in its ground state: (a) resonant radiative transfer, (b) resonant energy transfer, (c) energy transfer assisted by phonons and (d) energy transfer with the activator in an excited state, provided $W_{SA} \geq 1/\tau_e$, where $W_{SA}$ is the transfer probability from (S) to (A) and $\tau_e$ is the lifetime of the excited state. In (d) the transfer from the excited state can be either resonant ($\beta - \alpha = 0$) or phonon-assisted ($\beta - \alpha = \varepsilon_0$).
Figure 2.11 (a)-(c) summarize the different types of transitions from a sensitizer (S) to an activator (A) in its ground state. Co-doping is particularly interesting if the active ion has several energy manifolds. In this case, illustrated in Figure 2.11 (d), energy transfer can occur when the activator is in an excited state, provided that the energy transfer probability $W_{SA}$ from the sensitizer to the active ion is greater than the inverse lifetime $1/\tau_e$ of the excited state. When these conditions are met up-conversion can happen. Sensitization helps achieve stronger visible output than in a singly doped medium by increasing the effective absorption cross-section of the emitter while keeping the active ion doping low to avoid quenching by cross-relaxation or visible re-absorption.

Once again, in all cases transfer may take place even when there is a slight mismatch between the levels by being phonon-assisted. Still, the smaller the mismatch (i.e. the more resonant the transitions), the more efficient will be the transfer. Also, one has to keep in mind that transfer is allowed both ways, so all transitions of Figure 2.11 can also occur from the acceptor back to the sensitizer. This process is called back transfer. However, forward and back transfers don’t have the same probability and efficiency. In particular, the transfer is usually more efficient from the element which has the highest transition energy $E_2 - E_1$ to the other one. To minimize back transfer the sensitizer concentration mustn’t be too high.
2.1.3.5 Two-photon up-conversion processes

Until now we have described up-conversion by energy transfer. However several up-conversion processes exist involving 2 photons (real or virtual) and the distinction must be made between all these non-linear processes. In Reference [41] Auzel clarifies the terminology of the different processes which are presented in Figure 2.12.

![Energy schemes for different 2-photon up-conversion processes](image)

Figure 2.12: Energy schemes for different 2-photon up-conversion processes [41]: (a) up-conversion by energy transfer (APTE effect), (b) 2-steps absorption, (c) cooperative sensitization, (d) 2-photon absorption excitation, (e) cooperative luminescence and (d) second Harmonic Generation (SHG).

The process of interest in this work is the up-conversion by energy transfer, which Auzel calls *APTE effect* (Addition de Photons par Transferts d’Energie) and is illustrated in Figure 2.12 (a). Up-conversion via 2-step absorption where the active ion absorbs photons directly from the pump (Figure 2.12 (b)) is also possible but less likely than APTE in an efficient rare-earth co-doped system. These two processes are often called “*sequential* two-photon absorption” in distinction from two-photon absorption excitation which is the process where an atom makes a transition from its ground state to an excited state by the *simultaneous* absorption of two photons [42]. It is illustrated in Figure 2.12.
(d) and is commonly called “two-photon absorption”. Two-photon absorption excitation can also be enhanced by sensitization and in this case the process is called cooperative sensitization (Figure 2.12 (c)). Another important non-linear effect is Second Harmonic Generation (SHG) or frequency doubling that takes place in crystals for which the second-order susceptibility $\chi^2$ is non-zero (noncentrosymmetric crystals like KDP, BBO, etc.) [42] (Figure 2.12 (f)). Cooperative luminescence is the process used in order to increase SHG by the partial resonance of cooperative luminescence (Figure 2.12 (e)). In the rest of this work, unless specified otherwise, up-conversion or two-photon absorption refers to APTE or 2-step absorption (Fig. 2.12 (a) and (b)).
2.2 Up-conversion in rare-earth co-doped fluorides

2.2.1 Rare-earth elements

2.2.1.1 Electronic configuration

In the fifth period of the periodic table of elements after the element Lanthanum (La, Z = 57) the filling of the 4f shell takes place, from Cerium (Z = 58) with the outer configuration 5s\(^2\) 5p\(^6\) 4f\(^1\) 5d\(^1\) 6s\(^2\) to Lutetium (Z = 71) with the outer configuration 5s\(^2\) 5p\(^6\) 4f\(^14\) 5d\(^1\) 6s\(^2\). These are the lanthanide or rare-earth elements, which occur as doubly or triply charged ions in ionic solids. In the triply charged rare-earth ions all 5d and 6s electrons are removed and the 4f shell is only partially occupied. The number of electrons in the unfilled 4f shell ranges from \(n = 1\) (Ce\(^{3+}\)) to \(n = 14\) (Lu\(^{3+}\)) [43]. The rare-earth ions that are of interest in this project are the trivalent Erbium (Er\(^{3+}\)), Thulium (Tm\(^{3+}\)) and Ytterbium (Yb\(^{3+}\)). The electron configurations of the atomic and ionic forms of those lanthanides are given in Table 2.2.

Table 2.2: Electronic configuration of rare earths of interest.

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronic configuration</th>
<th>Ionic configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erbium (Z = 68)</td>
<td>[Er] = [Xe] 6s(^2) 4f(^{12})</td>
<td>[Er(^{3+})] = [Xe] 6s(^2) 4f(^{11})</td>
</tr>
<tr>
<td>Thulium (Z = 69):</td>
<td>[Tm] = [Xe] 6s(^2) 4f(^{13})</td>
<td>[Tm(^{3+})] = [Xe] 6s(^2) 4f(^{12})</td>
</tr>
<tr>
<td>Ytterbium (Z = 70):</td>
<td>[Yb] = [Xe] 6s(^2) 4f(^{14})</td>
<td>[Yb(^{3+})] = [Xe] 6s(^2) 4f(^{13})</td>
</tr>
</tbody>
</table>
2.2.1.2 Energy levels

The many energy levels of the unfilled 4f\(^n\) shell between which radiative transitions may occur cover a spread of energies of about 40000 cm\(^{-1}\). The next highest configurations are 4f\(^{(n-1)}\) 5d, 4f\(^{(n-1)}\) 6s and 4f\(^{(n-1)}\) 6p which for the triply charged ions are usually well above the low-lying 4f\(^n\) energy levels. The three electrons 6s\(^2\) and 4f\(^d\) are used in ionic crystals for ionic bonding. The optically active 4f electrons of the rare-earth ions are shielded from the crystal field by the outer, though less energetic, 5s and 5p shells of electrons. As a result the optically active 4f electrons of rare-earth ions in crystals are not strongly affected by their neighboring ligands. If the neighboring ligands are neglected

Figure 2.13: Dieke diagram for Ho\(^{3+}\), Er\(^{3+}\), Tm\(^{3+}\) and Yb\(^{3+}\) [4].
the energy levels of the 4f electrons are just the free ion levels, characterized by L, S, J values, with allowance made for some term mixing. The energy levels of free ions are very sharp. In 1963 Dieke determined the energy levels of trivalent rare-earth ions in lanthanum trichloride [44]. A partial Dieke diagram is shown in Figure 2.13 and it can be found in its complete form in Reference [43]. Note that on the Dieke diagram, the Tm $^3F_4$ and $^3H_4$ levels have been wrongly labeled. The $^3F_4$ is the manifold lying at $\sim 6000\text{ cm}^{-1}$ and the $^3H_4$ manifold is the metastable state lying at $\sim 13000\text{ cm}^{-1}$.

In solids the effect of the neighboring ligands is to split these free ion levels. This effect is known as the Stark splitting. The extent of this crystal field splitting for the rare-earth ions in lanthanum trichloride is indicated by the widths of the levels in the Dieke Diagram. The center of gravity of each crystal field multiplet approximately locates the free ion levels. In general, the Stark splitting of the free ion levels is less than the separation between free ion levels. Hence for rare-earth ions in different host materials the gross features of the energy level diagram are unchanged, and the Dieke diagram can be used as a reference to determine the energy levels of rare-earth ions in different crystals. Nevertheless, the Stark splitting will vary from host to host, reflecting the different symmetries and strengths of the different crystal fields. The interesting features we can outline from this diagram are the following.

_Ytterbium:_ Yb$^{3+}$ has a 4f$^{13}$ configuration so that the electronic energy-level structure simply consists of a $^2F$ manifold which is split by the spin-orbit interaction into a ground $^2F_{7/2}$ term and an excited $^2F_{5/2}$ term at 10000 cm$^{-1}$. In a crystal, these $J = 7/2$ and $J = 5/2$
levels are further split by the crystal field into 4 and 3 Kramer’s doublets, respectively. Despite the spread of the levels (about 500 cm\(^{-1}\) for the ground state and less than 150 cm\(^{-1}\) for the excited state), the absorption and emission spectra overlap. This produces two effects. Photons emitted by Yb\(^{3+}\) ions can be reabsorbed before exiting the crystal. Such self-trapping lengthens the observed lifetime. Also, neighboring ions might undergo energy transfer. Yb\(^{3+}\) ions are small ions easy to imbed in great quantities in most fluorides, allowing for high doping concentrations. This is particularly interesting because the concentration of the active ion should be kept low to avoid cross-relaxation and re-absorption. Thus, high Yb\(^{3+}\) concentration enables increased absorption of excitation in the co-doped crystal as well as the probability that several sensitizing ions surround an active ion. (Still Yb\(^{3+}\) doping mustn’t be so high that back-transfer becomes predominant and quenches the visible emission.) Finally, since the Yb\(^{3+}\) ions absorb light in a fairly broad band between 940 nm and 1 \(\mu\)m, with an absorption maximum near 975 nm in fluoride crystals, they can easily be pumped by very efficient, commercially available, diode lasers. For these reasons Yb\(^{3+}\) is an excellent sensitizer for UC.

_Erbium:_ Er\(^{3+}\) has many levels of luminescence. Because of this rich level structure, Er\(^{3+}\) exhibits a very detailed sharp line luminescence spectrum. Its spectroscopy in several different host crystals has been studied extensively [45-47]. The features of interest here are the following. The \(^4I_{11/2}\) excited state is at \(\sim 10^4\) cm\(^{-1}\) from the ground state \(^4I_{15/2}\) level. A gap of this magnitude is also found between the \(^4F_{7/2}\) and the \(^4I_{11/2}\) manifolds and the \(^4G_{7/2}\) and \(^4S_{3/2}\) manifolds. The visible transitions are the \(^4S_{3/2}\rightarrow^4I_{15/2}\) transition at \(\sim 545\)nm (green) and the \(^4F_{9/2}\rightarrow^4I_{15/2}\) transition at \(\sim 660\)nm (red). The \(^4G_{7/2}\rightarrow^4I_{15/2}\)
transition is at \( \sim 410 \text{ nm (violet)} \) and doesn’t contribute to the photometric efficiency of the emitter but is useful when studying the contribution of the third UC step, as we will see below. We note that the level \( ^4I_{13/2} \) level is metastable.

**Thulium:** As pointed out earlier, \( ^3F_4 \) is the manifold lying at \( \sim 6000 \text{ cm}^{-1} \) and the \( ^3H_4 \) manifold is the metastable state lying at \( \sim 13000 \text{ cm}^{-1} \). Tm\( ^{3+} \) has no level at \( 10^4 \text{ cm}^{-1} \) and no spacing of this magnitude. However, the spacings between the \( ^3H_5 \) level and the \( ^3H_6 \) ground state, the \( ^3F_2 \) and \( ^3F_4 \) states, and the \( ^1G_4 \) and \( ^3H_4 \) states are close enough to this magnitude to allow phonon-assisted energy transfers between the sensitizer and the Tm\( ^{3+} \) ion. Here it is obvious that excitation of Tm\( ^{3+} \) ions is accomplished by energy transfer from Yb\( ^{3+} \). The visible transitions are the \( ^1G_4 \rightarrow ^3H_6 \) transition at \( \sim 480 \text{ nm (blue)} \) and the \( ^1G_4 \rightarrow ^3F_4 \) transition at \( \sim 650 \text{ nm (red)} \). There is also an emission at \( \sim 450 \text{ nm} \) stemming from the \( ^1D_2 \) level which lies at \( 7000 \text{ cm}^{-1} \) above the \( ^1G_4 \) (not represented in Figure 2.13). We note that these two manifolds are not thermally coupled although their emission spectra overlap.

**Other rare earths:** Holmium (Ho\( ^{3+} \)) has also been studied for green and red UC lasers\[23, 48]\. Green emission via UC in holmium can be interesting because unlike erbium, holmium doesn’t have a metastable state at \( \sim 6500 \text{ cm}^{-1} \). We will see in Section 2.2.2.1 that this metastable state contributes greatly to the red UC in erbium, while red UC via non-radiative decay from the green emitting level makes only a small contribution. Therefore in holmium we can expect a visible emission more saturated in the green. However the transfer from Yb\( ^{3+} \) to Ho\( ^{3+} \) is non-resonant, making this system ultimately
less efficient than Er,Yb. Praseodymium (Pr\(^{3+}\)) could be another candidate for sensitized UC however its visible emission spectrum features several peaks outside of the primary colors. Other rare-earths are used in visible light emitting devices: Europium (Eu\(^{3+}\)) is a common dopant for red TV phosphors, and neodymium (Nd\(^{3+}\)) lasers can be frequency doubled to make green lasers. However these ions have no energy levels around 10000 cm\(^{-1}\) and their excitation mechanism involve down-conversion, not up-conversion.

### 2.2.2 Up-conversion mechanisms

#### 2.2.2.1 Up-conversion mechanisms in Er\(^{3+}\)-Yb\(^{3+}\) co-doped systems

Figure 2.14: Up-conversion in Er\(^{3+}\)-Yb\(^{3+}\) co-doped systems.
The mechanism of the infrared-excited green luminescence in Er\(^{3+}\) is the following.

1. A first Yb\(^{3+}\) ion is excited into the \(2F_{5/2}\) level by absorption of a pump photon. Energy transfer from Yb\(^{3+}\) to Er\(^{3+}\) leads to the excitation of the Er\(^{3+}\) \(4I_{11/2}\) level.

2. A second excited Yb\(^{3+}\) ion further excites the Er\(^{3+}\) ion into the \(4F_{7/2}\) state which relaxes through a non-radiative decay to the \(4S_{3/2}\) state. The green emission takes place on the \(4S_{3/2} \rightarrow 4I_{15/2}\) transition at 545 nm.

The red emission takes place on the \(4F_{9/2} \rightarrow 4I_{15/2}\) transition at 660nm. Three different mechanisms can occur to populate the red-emitting \(4F_{9/2}\) state.

(a) The \(4F_{9/2}\) state is populated via non-radiative decay from the \(4S_{3/2}\) state.

(b) The Er\(^{3+}\) ion is excited from the \(4S_{3/2}\) state to the \(2G_{7/2}\) state via the acceptance of a third quantum from the Yb\(^{3+}\). From the \(2G_{7/2}\) state Er\(^{3+}\) relaxes non-radiatively to the \(4G_{11/2}\) state, after which the \(4F_{9/2}\) state is populated via a selective decay coupled with a back transfer of the energy difference to Yb\(^{3+}\). Since three Yb\(^{3+}\) energy transfers are involved in the excitation process, the contribution of this mechanism varies as the third power of the infrared excitation power.

(c) The red-emitting \(4F_{9/2}\) state is reached via excitation of Er\(^{3+}\) in the \(4I_{13/2}\) state, this state first being populated by a non-radiative decay from \(4I_{11/2}\) after the first excitation step.

Sommerdijk showed in Reference [12] that mechanism (c) is the most probable in fluoride crystals with low Yb\(^{3+}\) doping concentration due to the relaxation to the metastable \(4I_{13/2}\) state after the first UC step. Mechanism (a) makes only a small
contribution to the infrared excitation of the red emission as the probability of the $^4S_{3/2}$ to $^4F_{9/2}$ relaxation is very small in co-doped fluoride systems. This is due to the high energy gap (~ 3000 cm$^{-1}$) between the two levels and to the weak ion-lattice interactions in fluorides lattices. Mechanism (b) can also give a strong contribution to the red emission and this contribution becomes stronger at higher rare-earth doping concentrations. Indeed, since the decay from $^4G_{11/2}$ to $^4F_{9/2}$ is mainly facilitated by the transfer of the energy difference back to Yb$^{3+}$, and as the efficiency of the energy transfer increases with increasing concentrations, the probability of this decay increases with Yb$^{3+}$ concentration, resulting in a stronger contribution of mechanism (b). Another important consequence is a lower green-to-red ratio with increasing concentration. We will see how the weight of each contribution is evidenced experimentally in Section 2.3.

We note the following about UC in the Er,Yb system. Sufficient populations on the intermediate levels such as the $^4I_{11/2}$ intermediate state are needed in order to achieve efficient up-conversion visible emission. However, once Er$^{3+}$ ions are excited into these levels they can transfer their excitation energies back to Yb$^{3+}$ ions, therefore depleting the populations. The back transfer of highest concern is the one from the $^4I_{11/2}$ intermediate state. It manifests itself in two ways. First, back transfer causes a decrease in the lifetime of ions in this state. Thereby the output power is not proportional to the fluorescence lifetime of this state. Second, back transfer represents a reduction in the overall transfer efficiency. On the other hand, back transfer in the second step of the excitation process (i.e. from the $^4F_{7/2}$ state) is merely equivalent to a branching transition from the $^4F_{7/2}$ state.
and is negligible compared to the non-radiative decay rate from the $^4F_{7/2}$ state to the green emitting state.

Since Er$^{3+}$ has transitions resonant with 970 nm pump photons, one can wonder about the role of sensitization versus two-step absorption. We saw that Yb$^{3+}$ sensitization can compensate for weak Er$^{3+}$ ground state absorption, but one can wonder if the second step is due to a second transfer from the sensitizer or due to excited state absorption (i.e. via absorption of a pump photon by the acceptor ion). Hewes and Sarver showed in [4] that in co-doped systems the energy is absorbed only by the Yb$^{3+}$ ions and then transferred to the acceptor.

Finally we note that Er$^{3+}$ singly-doped systems pumped around 800 nm have been studied [47]. In this case UC occurs via the two-step absorption $^4I_{15/2} \rightarrow ^4I_{9/2}$ and $^4I_{13/2} \rightarrow ^4S_{3/2}$, the $^4I_{13/2}$ metastable manifold being populated via a non-radiative decay following the ground state absorption. However co-doped systems with Yb$^{3+}$ sensitization are more efficient than single Er$^{3+}$ doping for the reasons already stated: the Er$^{3+}$ dopant level has to be low to prevent cross relaxation between Er$^{3+}$ ions that quenches the upper $^4S_{3/2}$ lifetime and to minimize reabsorption losses caused by the three-level nature of the green transition. Also, once again, the low green output power in Er$^{3+}$ doped crystals is due to the weak ground-state absorption of pump light and excited-state absorption [49].
2.2.2.2 Up-conversion mechanisms in Tm\textsuperscript{3+}-Yb\textsuperscript{3+} codoped systems

![Energy level diagram](image)

Figure 2.15: Up-conversion in Tm\textsuperscript{3+}-Yb\textsuperscript{3+} co-doped systems.

The Tm\textsuperscript{3+} ions are excited into the 1\textsuperscript{G_4} blue emitting level through three successive energy-transfer steps (Figure 2.15)[3]:

1. a Tm\textsuperscript{3+} ion is excited into the 3\textsuperscript{H_5} level by energy transfer from the first excited Yb\textsuperscript{3+} ion, and this Tm\textsuperscript{3+} ion then relaxes into its 3\textsuperscript{F_4} level;
2. the same Tm\textsuperscript{3+} is further excited from 3\textsuperscript{H_4} into the 3\textsuperscript{F_2} level by the second excited Yb\textsuperscript{3+} ion and then relaxes into the lower metastable state, 3\textsuperscript{H_4};
3. the third excited Yb\textsuperscript{3+} ion transfers its excitation energy to this Tm\textsuperscript{3+} ion and excites it from the 3\textsuperscript{H_4} to the 1\textsuperscript{G_4} state which then emits in the blue at 480 nm when it relaxes into the ground state, and the red at 650 nm when it relaxes into the 3\textsuperscript{F_4} state.
Step (1) and (3) are phonon-assisted. A fourth UC step from $^1G_4$ to $^1D_2$ can also occur leading to 450 nm emission when $^1D_2$ relaxes into the $^3F_4$ state (not shown in Figure 2.15). This step is also phonon-assisted.

In the Tm-Yb systems, back transfer manifests itself in the following way. Once Tm$^{3+}$ ions are excited into the intermediate levels such as $^3F_4$, they can transfer their excitation energies back to Yb$^{3+}$ ions, therefore depleting the populations. This energy transfer from the $^3F_4$ state of Tm$^{3+}$ to Yb$^{3+}$ ions decreases as the temperature is lowered indicating that the back-transfer process is accompanied by a net absorption of phonons.

2.2.2.3 Transfer function of UC process

As several pump photons need to be absorbed to produce one visible photon, the UC process is nonlinear. The transfer function of the UC process (i.e. the dependence of visible light emitted on incident infrared light) is obtained by solving the rate equations of the co-doped systems for steady state solutions, which predict the population of all energy levels upon excitation after steady state is reached. Rate equation analysis of Er,Yb and Tm,Yb systems at room temperature are thoroughly available in the literature (e.g. References [3, 50-52]). Here we will present a simplified set of rate equations for the green emission in the Er, Yb system of Figure 2.14, where back-transfers, cross-relaxations and several other Er$^{3+}$ energy levels have been ignored (a complete set of equations can be found in Appendix A):
In the above set of equations \( n_{1y}^b, n_{2y}^b, n_1^{Er}, n_2^{Er} \) and \( n_3^{Er} \) are, respectively, the populations of the \( ^2\!F_{7/2} \) and \( ^2\!F_{5/2} \) levels of \( \text{Yb}^{3+} \) and of the \( ^4\!I_{15/2} \) ground level, \( ^4\!I_{11/2} \) and \( ^4\!S_{3/2} \) (green emitting level) of \( \text{Er}^{3+} \), \( \tau_i \) are the corresponding state lifetimes, \( A_{ji} \) are the decay rates from \( j \) to \( i \), \( \sigma_{yb}^{abs} \) is the absorption cross section for \( \text{Yb}^{3+} \), and \( \gamma_1 \) and \( \gamma_2 \) are the energy transfer rates from \( \text{Yb}^{3+} \) to \( \text{Er}^{3+} \). \( I_{pump} \) is the input irradiance and \( \dot{S}_{green} \) is the photon emission rate of the \( ^4\!S_{3/2} \) to ground state radiative transition (green emission).

Using the mathematical software Mathcad©, we can solve the set of equations (2.4) for \( \dot{S}_{green} \) in the steady-state case, i.e. when all \( \dot{n}_i \) are set to zero. Using the coefficients of Reference [50], the simulation of the transfer function obtained is that shown in Figure 2.16.
Figure 2.16: Calculated transfer function of green UC in Er, Yb systems.

For low input irradiance the transfer function has a slope of $\beta_{\text{green}} = 2$: the green emission is a two step phonon absorption process so its transfer function is quadratic. As input irradiance increases, saturation takes place in the UC process and the slope decreases to less than two. The transfer function can be described by:

$$P_{\text{out}} \propto I_{\text{pump}}^{\beta [\sigma_{\text{Yb}} \cdot I_{\text{pump}}]} \quad , \quad \beta [\sigma_{\text{Yb}} \cdot I_{\text{pump}}] \leq 2$$

(2.5)

where $\beta$ is a decreasing function of $I_{\text{pump}}$.

A similar analysis would show a similar dependence for the red emission with $\beta_{\text{red}} < 3$. At low irradiance and high Yb$^{3+}$ concentration $\beta_{\text{red}}$ is $\approx 2.5$ [3], accounting for the contribution of both two-photon and three-photon processes for the red emission. For the
blue emission in Tm,Yb, \( \beta^{\text{blue}} = 3 \) at low irradiances, as it is a three-photon process. A thorough rate equation analysis of the Tm,Yb system will be developed in Section 3.1. Also, we will see with our experimental results in Section 2.3.3 that at the irradiances of operation for a display, the emitters are usually in regime where \( \beta \) is less than 2 (3 for the blue emitter).

2.2.3 Specifics of the UC emitters

In the course of our study we identified very efficient candidates for UC displays: 1% Er, 18% Yb:YF₃, 1% Er, 18% Yb:NaYF₄ (NYF), and 0.4% Tm, 20% Yb:KY₃F₁₀, red, green and blue up-conversion emitters, respectively. In this work, Tm, Yb:YLF and Er, Yb: KY₃F₁₀ were also used for research purposes. Unless stated otherwise all emitters are in a powder form sieved between No. 400 and 635 stainless steal sieves to obtain a powder of controlled average grain size ranging from 20 \( \mu \text{m} \) to 38 \( \mu \text{m} \). We note that our investigation of efficient emitters (selection of host crystals and doping concentrations) was not exhaustive, as the present work focuses on optimizing UC displays via principles derived from the physical process of UC in powders, rather than fine-tuning the nature of the emitters. However these are the most efficient UC emitters reported to date[53].

2.2.3.1 Selection of doping concentrations

The doping concentration was selected by testing the efficiency of several compositions. The selection process was narrowed down by the following facts. Active ion doping should be kept low to avoid quenching by cross-relaxation and re-absorption. Usually it
is kept under 2%. Sensitizer doping can be higher (> 10%), however not so high that it enables back-transfers to become predominant. It is usually kept under 40%.

2.2.3.2 Selection of host crystals

The choice of a host crystal for efficient up-conversion is lead by several considerations, the most important of which are listed below. First, the host crystal should be such that it can accept trivalent dopant ions without it causing a valence imbalance. When incorporating a triply ionized ion in a divalent site, some form of charge compensation is necessary and that varies from one cell to another. Charge compensation is required when a trivalent dopant ion substitutes for a divalent cation on a regular crystal site. It may take the form of local or remote lattice vacancies, interstitial ions or the incorporation of other impurity cations and anions, in order to maintain overall charge neutrality. As a result all dopant ions no longer experience the same environment. They are located in sites of different symmetry, leading to different crystal fields and different Stark splitting. Furthermore, unintentional lattice defects are always present to some extent even in undoped crystals. If such defects occur in the immediate vicinity of dopant ions they perturb the local site symmetry and introduce new and distinct features in the spectroscopic properties of the dopant ion. In addition, dopant ions may form clusters in the host crystal, which may have their own spectral characteristics. Hence trivalent rare-earths should substitute with trivalent cations rather than divalent cations. The host crystal should accept any desired dopant concentration, and allow as many dopant ions as possible.
The structure of the lattice of the crystal is of great importance too: the nearest-neighbor
distance of rare-earth ions in the crystal should be as small as possible so that energy
transfers can occur efficiently. Indeed, the probability of the main energy transfer of
interest for up-conversion, the electric dipole transition, decreases as \((1/R^6)\) where \(R\) is
the distance between the donor and the acceptor. In addition, short-range exchange
interaction should be allowed (transfer probability decreasing as \(\exp(-2R/R_0)\)).
Considering that only a few sites embed active dopant ions (generally the concentration
of dopant doesn’t exceed 40%), the distance between two sites in the lattice should be as
small as possible.

The structure features are optimal if the Stark splitting is such that resonant transfers can
occur. The host lattice also dictates the optimum excitation wavelength, as well as the
relative importance of competing mechanisms such as branching ratios, back transfer to
\(\text{Yb}^{3+}\) and cross relaxation. Since these rare-earths all have multiple radiative transitions
at different wavelengths of emission, the emission spectrum of the UC material can be
significantly altered depending on the host crystal: selecting the proper host crystal is one
way of quenching one radiative transition in favor of another.

Another important characteristic of the crystals is the existence of phonons in the bulk.
Phonons represent energy propagation in the lattice through atomic vibrations. Their
energy is quantized in vibronic levels and differs from one crystal to another. However,
their number increases with increasing temperature. Phonon energy can interact with the
electronic states of an atom in that it can be absorbed or an atom can release energy as a
phonon during a transition: such non-radiative processes would be a loss for the up-conversion efficiency as the energy is not used to produce light. For rare earth ions, the outer shells also shield the 4f\textsuperscript{th} electrons from crystal vibrations resulting in relatively weak electron-phonon coupling.

Fluorides are reportedly almost ideal hosts for infrared-to-visible up-conversion as they meet most of the required conditions listed above [26, 54, 55]. Indeed, fluorides have a favorable lattice geometry and especially weak ion-lattice interactions: maximum phonon numbers for fluorides are typically around 500 cm\textsuperscript{-1}.

Also for display applications we need stable, pure, reproducible and inexpensive crystals. Fabrication processes leading to materials of higher purity have been successfully explored by Arlete Cassanho of AC Materials [56]. The fluorides are prepared with a Czochralski technique [57]. A proprietary process of hydrofluorination is applied during the growth of the various fluoride crystals which results in materials of better quality, better reproducibility, and higher up-conversion efficiency than have been studied in the past. We note that UC-display applications do not require these materials be grown into a single crystal or laser-grade crystals, as they are used in a powder form. As a result, the materials are inexpensive.

Based on existing literature (e.g. Reference [26]) and our own investigations, we selected the following hosts as best candidates to date for our display applications: sodium yttrium fluoride NaYF\textsubscript{4} (NYF) for the green emitter, yttrium fluoride YF\textsubscript{3} for the red emitter and
potassium triyttrium decafluoride KY₃F₁₀ for the blue emitter. As we will see in Section 2.2.3.3, in addition to meeting the above criteria, UC in these co-doped crystals is most efficient for all three colors when excited around 975 nm. This is a key technology enabling criterion as this is where powerful and efficient diode lasers exist.

We note that blue UC in Tm,Yb system is also efficient with lithium yttrium fluoride (LiYF₄ or YLF) as a host crystal [58]. YLF has been extensively investigated over the years as a laser host crystal. Because of this abundance of spectroscopic data on YLF, we conducted some of our fundamental studies of the Tm,Yb system with this material. However such material is most efficiently pumped at 959 nm. As diode lasers are not as commonly available near 960nm as they are at 976 nm, pumping of the blue UC material in YLF is more difficult than it is in KY₃F₁₀ and not more efficient.

Table 2.3: Structure parameters of host crystals

<table>
<thead>
<tr>
<th></th>
<th>Structure</th>
<th>Space group</th>
<th>Cell parameters (Å)</th>
<th>N₅ᵗ (10²¹.cm⁻³)</th>
<th>Mass density (g.cm⁻³)</th>
<th>ρHOST</th>
<th>ρ100%Yb:host</th>
</tr>
</thead>
<tbody>
<tr>
<td>NYFᵃ</td>
<td>Hexagonal</td>
<td>C₁₃h</td>
<td>aₒ=5.97</td>
<td>13.8</td>
<td>4.30</td>
<td>6.37</td>
<td></td>
</tr>
<tr>
<td>YF₃ᵇ</td>
<td>Orthorhombic</td>
<td>Pnma (D₁₆ 2h)</td>
<td>aₒ=6.35</td>
<td>21</td>
<td>5.06</td>
<td>8.17</td>
<td></td>
</tr>
<tr>
<td>KY₃F₁₀ᶜ</td>
<td>Cubic</td>
<td>Fm3m (O₅h)</td>
<td>aₒ=11.54</td>
<td>15.6</td>
<td>4.28</td>
<td>6.46</td>
<td></td>
</tr>
<tr>
<td>YLFᵇ</td>
<td>Tetragonal</td>
<td>I₄/a (C₄dh 6)</td>
<td>aₒ=5.17</td>
<td>13.9</td>
<td>3.95</td>
<td>6.00</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ From [59]. ᵇ From [45]. ᶜ From [55]. N₅ᵗ: 1 at. % doping represents Nat ions/cm².
Table 2.4: Optical properties of host crystals

<table>
<thead>
<tr>
<th></th>
<th>(\sigma_{\text{abs,Yb}}) ((10^{-21}\text{ cm}^2))</th>
<th>Phonon energy (\hbar\omega_m) ((\text{cm}^{-1}))</th>
<th>Index of refraction (n_D) or ((n_e; n_o)_D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NYF</td>
<td>(~10^a)</td>
<td>&lt;500</td>
<td>1.464; 1.486(^h)</td>
</tr>
<tr>
<td>YF(_3)</td>
<td>0.9(^b)</td>
<td>530(^e)</td>
<td>1.55(^i)</td>
</tr>
<tr>
<td>KY(_3)(<em>F</em>{10})</td>
<td>9.5(^c)</td>
<td>(~400(^f)</td>
<td>1.4876(^j)</td>
</tr>
<tr>
<td>YLF</td>
<td>9(^d)</td>
<td>460(^g)</td>
<td>1.476; 1.453(^i)</td>
</tr>
</tbody>
</table>

\(\sigma_{\text{abs,Yb}}\): Yb absorption cross section at 975 nm assumed from [26],\(^a\) with broad spectrum excitation [51],\(^c\) at 975 nm [55],\(^d\) at 959 nm [50]. \(\hbar\omega_m\): maximum phonon energy,\(^e\) from[51],\(^f\) from[60],\(^g\) from[52].\(^h\) from[61],\(^i\) from[45],\(^j\) this work.

The relevant properties of the fluorides of interest in this work are summarized in Table 2.3 and 2.4.

**NYF:** While there are some reports on the chemistry and structure of NYF, relatively little is known about the optical properties of rare-earth doped NYF. One reason is that it is very difficult to grow as a single crystal and it is mostly available as a powder. The first complete characterisation of the NaF-YF\(_3\) system was conducted by Thoma et al. in 1966 [62], and the first time it was investigated as an up-conversion phosphor is reportedly in 1972 by Menyuk et al. [63]. It gave rise to no further publications until 1989 when Knowles et al investigated it as a laser host [61]. The idea of using this highly efficient crystal for up-conversion was introduced a few years ago to Hans Jenssen of CREOL by François Auzel in a private communication. Here we study the case of the hexagonal phase of NaYF\(_4\). The hexagonal phase has the space group \(C_{3h}^{1}\) with 1.5 formula units per unit cell [59, 61]. The high efficiency of the up-conversion mechanism in co-doped NYF could be ascribed to the multisite character of this matrix. Indeed, the trivalent rare-
earth dopant ions can replace $Y^{3+}$ ions in two sites of $C_{3h}$ symmetry. When they are incorporated in the lattice, Stark splitting occurs and broadens the absorption and emission lines of the trivalent rare-earth ions for both sites, improving the resonances between levels involved in the up-conversion process [64]. Moreover, the back transfer is less important in NYF than in other fluorides, and the multi-photon relaxation is lower as well. We note that this crystal is birefringent which makes it difficult to place in an index matched host as we need to do in display applications. There the emitters are dispersed in a plastic host of an index of refraction tuned to reduce scattering of the powders and we will see in Section 3.2 that this affects the performance of the green UC emitter.

**YF$_3$:** Much of the interest in yttrium fluoride YF$_3$ is for infrared to visible up-conversion applications. The crystal structure of YF$_3$ was known since the early 50’s [65] and YF$_3$ was an early host when many UC systems were studied experimentally in the 70’s [4, 51, 66]. UC in YF$_3$ was already reported as efficient at the time. In their 1998 paper on controlled UC efficiency measurements for green, red and blue emitters, Page et al. mention YF$_3$ as an attractive fluoride host for efficient red UC [26]. Yttrium fluoride YF$_3$ at room temperature exhibits an orthorhombic structure with space group Pnma ($D^{16}_{2h}$) with four molecules per unit cell ($Z=4$) [67]. It is known as the $\beta$-YF$_3$ type and in this form YF$_3$ crystals are non-hygroscopic and colorless under normal conditions. They are very stable and easy to grow.
**KY₃F₁₀:** Potassium triyttrium decafluoride KY₃F₁₀ was grown 30 years ago but its appealing properties as a laser material were not noticed until almost two decades later[68]. Up-conversion in Yb,Er: KY₃F₁₀ has been observed[69], and recently, Braud et al investigated the characteristics of Tm: KY₃F₁₀ as a possible 1.85-µm laser[70]. They also reported on the spectroscopic properties and energy transfer coefficients in Yb,Tm:KY₃F₁₀ [55, 71]. At ambient temperature and pressure, KY₃F₁₀ is an isotropic crystal with a cubic-face-centered structure Fm3m (Ohões) similar to the fluorite structure and the elementary cell contains eight formula unit (Z=8). The trivalent rare-earth dopants substitute for the yttrium ions in sites of C₄ᵥ symmetry [55]. At high pressure the structure becomes Pm3m (Z=1) [72]. This material is very attractive because it can easily be grown in large sizes using the Czochralski crystal growth method and it has good optical and thermo-mechanical properties. Equally important is the fact that it is an isotropic crystal, i.e. it has only one index of refraction (we measured n = 1.4876 at 589 nm) whatever the orientation of the particle. This opens the possibility of index-matching the plastic binder to the particles in our display applications, limiting the back-scattering of the pump light and allowing more pump power to be absorbed by the active material. This would result in higher efficiencies than have been measured so far.

**YLF:** Yttrium lithium fluoride LiYF₄ (YLF) has the scheelite structure with a uniaxial tetragonal lattice (space group C₄ᵥ (I₄₁/a), Z=4). The YLF crystals can be easily doped with trivalent rare-earth ions because the trivalent ions substitute for a trivalent cation Y³⁺ in the single site of symmetry S₄.
2.2.3.3 Excitation spectra

The best performing materials to date are all efficiently excited by a 975 nm pump source as seen from the measured excitation spectra shown in Figure 2.17. In those experiments, a tripled Nd:YAG laser was used to pump a narrow linewidth master oscillator/power oscillator (MOPO) system from Spectra-Physics. The 4-ns idler beam was scanned over the Yb$^{3+}$ absorption region, and the visible emission was recorded using a photomultiplier and a digital oscilloscope. Having all emitters excited by the same wavelength not only reduces production costs, but also simplifies the scanning system design (no achromatism). Furthermore, powerful and efficient diode lasers at this wavelength are readily available.

![Excitation spectra of UC emitters.](image)

Figure 2.17: Excitation spectra of UC emitters.
2.2.3.4 Emission spectra and chromaticity

Figure 2.18: Emission spectra of the green, red and blue emitters operating at maximum efficiency and each has been normalized to its highest peak.

The visible emission of UC emitters is fluorescence and is Lambertian (isotropic). Unlike laser light, it is not speckled. The emission from the UC emitters was recorded using a Compact Array Spectrophotometer (CAS) (Model CAS140 from Instrument Systems). These emitters were operating at maximum efficiency. The excitation was a 975 nm beam modulated at 30 Hz into 2 ms duration pulses and focused to a 950 µm diameter spot. The average power of the pump was 30 mW for the red and green emitters and 90 mW for the blue emitter. As illustrated in Figure 2.18, each up-converter presents two narrow emission bands in the visible. The blue and green emitting materials also emit some red light and the red emitting material emits some green. However, the unwanted emission bands are well separated and easy to filter out using, for example,
common glass filter technology. After such filtering, the color of each material is well saturated.

Figure 2.19: (a) 1931 CIE chromaticity diagram with RGB colors of UC phosphors. The long dashes enclose the region accessed by our UC emitters while the dotted region is that of present day televisions. (b) Unfiltered “red” emitter appears yellow to the eye because of the presence of some green emission.

The colors of the saturated red, green and blue are marked by circles at the tips of the long dashed triangle in the 1931 CIE chromaticity diagram of Figure 2.19 (a) and the color gamut that results is wider than that for most existing technology. The colors of the unfiltered phosphors operating at maximum efficiency are marked in Figure 2.19 (a) by diamonds. The “blue” emitter emits a purple similar to the blue CRT TV phosphor. Despite emitting some red, the unfiltered “green” emitter still appears green to the eye,
due to the higher sensitivity of the human eye to green. Its dominant color is \(~555\ \text{nm}\). The unfiltered “red” emitter appears yellow (dominant \(~570\ \text{nm}\)) as shown in the photo of Figure 2.19 (b). As we mentioned in Section 2.2.2.1, it is possible to shift that color towards the deeper oranges by increasing the concentration of \(\text{Yb}^{3+}\) as it would lower the green to red emission ratio. For instance, the dominant of unfiltered 1\%Er, 22\%Yb:YF\(_3\) is \(~580\ \text{nm}\). However, the overall efficiency of the red emission is also quenched. We note also that we show in Section 2.3.5 that the ratio of green and red emission in Er,Yb systems varies with input irradiance so the unfiltered color of these emitters can slightly shift along the straight line joining the monochromatic green and red.

2.2.3.5 Emission lifetimes

![Figure 2.20: Normalized emission response time of emitters excited at 975 nm with a low energy 4-ns pulse. The samples were tested at 21°C: (a) 1\% Er, 18\% Yb:NYF. \(\text{Yb}^{3+}\) emission at 1 micron (thin line) and \(\text{Er}^{3+}\) green emission at 543 nm (thick line); (b) 0.4\%, Tm 30\%, Yb:YLF. \(\text{Yb}^{3+}\) emission at 1 micron (thin line) and Tm \(^{3+}\) blue emission at 480 nm (thick line).]

The precise dynamics of UC visible fluorescence will depend on the exact pumping conditions. However, typical response times for the normalized visible emission are as
indicated for the green and blue emitter in Figure 2.20 (a) and (b), along with the corresponding simultaneous Yb$^{3+}$ emission near 1 µm. The infrared excitation source was a low-energy, 4-ns pulse near 975 nm. In Figure 2.20 which was obtained at room temperature, we can clearly observe a rise-time in the visible emission signal of about 100 µs for the green and 600 µs for the blue, followed by a decay time that lasts about 2 ms. The rise time observed corresponds to the time required for the donor-acceptor energy transfer to take place and the decay is the luminescence decay of the acceptor ions. These dynamics make UC materials suitable for video rates. The red emitter has a response time similar to that of the green.
2.3 Efficiency of UC materials

2.3.1 Definitions and experimental setup

2.3.1.1 Definition of raw efficiency and maximum efficiency

Raw efficiency is the ratio of total visible emitted power (either in radiometric or photometric units) to the average infrared pump power incident on a sample (Equation 2.6).

\[
\eta_{\text{raw}} \equiv \frac{P_{\text{out}, 4\pi}}{\langle P_{\text{optical}} \rangle_{\text{incident, at sample}}}
\]  \hspace{1cm} (2.6).

According to the transfer function described in Section 2.2.2.3, \( P_{\text{out}} \) varies nonlinearly with input irradiance as in Equation 2.5. So the raw efficiency will also vary with input irradiance, with an order one less than that of the transfer function described by Equation 2.7 where \( \alpha \) is the fraction of incident light absorbed by the sample (0<\( \alpha \)<1). That is:

\[
\eta_{\text{raw}}[I_{\text{inc}}] \propto I_{\text{inc}}^{\beta[\alpha \cdot I_{\text{inc}}]^{-1}}
\]  \hspace{1cm} (2.7).

The calculated variation of raw efficiency with input irradiance derived from the simulation in Figure 2.16 is plotted in Figure 2.21.
Figure 2.21: Calculated transfer function and UC efficiency vs. input irradiance.

As the supra-linearity order of the transfer function decreases with increasing irradiance, the transfer function eventually becomes a linear function of input irradiance, and the raw efficiency reaches a maximum. As input irradiance keeps increasing, the efficiency rolls off. However, the brightness keeps increasing. As illustrated in Figure 2.21, when the efficiency drops by a factor of 4 as the irradiance is increased from that giving maximum efficiency, the brightness increases by 3 orders of magnitudes.

Maximum efficiency $\eta_{\text{raw}}^{\text{max}}$ is obtained when:

$$\frac{d\eta_{\text{raw}}(I_{\text{inc}})}{dI_{\text{inc}}} \propto (\beta[\alpha \cdot I_{\text{inc}}] - 1) \cdot I_{\text{inc}}^{\beta[\alpha I_{\text{inc}}]-2} = 0 \quad (2.8)$$

that is, when $I_{\text{inc}}$ results in
\[ \beta(\alpha \cdot I_{\text{inc}}) = 1 \] (2.9),

and \( \eta^\text{max} \) is the number that we seek and report as the performances of our emitters. The best UC materials are those having the largest maximum efficiencies.

It is important to underline that maximum efficiency is reached for a given peak irradiance \( I_{\text{inc}}^\text{max} \) verifying Equation 2.9 proper to the nature of each emitter (dopants, crystal field parameters, etc.). We must keep in mind that irradiance is radiant power per unit area of illumination. The same maximum efficiency can be attained for various incident peak powers by varying the size of the pump focus according to:

\[ \frac{P_{\text{inc}}}{A_{\text{spot}}} = I_{\text{inc}}^\text{max} \] (2.10).

This allows scaling performances to the size of the display, depending on the application. For example, for a large focus spot, high incident peak power \( P_{\text{inc}} \) is required to reach maximum efficiency. For a pulsed excitation, which is the inherent mode of operation for displays as the pump beam is scanned across the screen, the average incident power is:

\[ \langle P_{\text{inc}} \rangle = P_{\text{inc}} \cdot t_p \cdot f \] (2.11),

where \( t_p \) is the duration of excitation of any given pixel (in seconds) and \( f \) the repetition rate (e.g. 60 Hz). Low average powers are obtained by using short duration excitation.
According to Equation 2.6, the output power produced by an average incident power \(<P_{inc}\) with \(P_{inc}\) satisfying relation 2.10 is then given by:

\[
P_{out} = n_{raw}^{\text{max}} \cdot \langle P_{inc} \rangle
\]  

(2.12),

where \(<P_{inc}\) verifies Equation 2.11.

According to Equation 2.12, if the average incident power required to operate at maximum efficiency is high because of larger focus size or high repetition rates, the output power produced is consequently higher.

UC efficiencies are power efficiencies. We note the following about brightness and brightness efficiencies. UC brightness \(L_{out}\) is determined for an area covered with UC emitters, for instance one pixel, radiating into a hemisphere. One pixel is defined as the area of UC emitters excited by the pump beam. By this we mean that the pixel size is always equal to the spot size of the pump beam focused on the screen (if the pixel is smaller than the pump beam spot then some of the input power is “wasted” as it doesn’t excite UC material). We also assume that the whole \(4\pi\) emission from each individual UC particle is radiated into the hemisphere where the detection takes place (e.g. UC screen made with a reflective substrate). Brightness is a luminous flux per unit area per unit solid angle. For a Lambertian emitter, the brightness is equal to the illuminance divided by \(\pi\) (and not \(2\pi\) as we might reason from the fact that there are \(2\pi\) steradians in a hemisphere [32]). The illuminance is measured as the total luminous flux divided by the area of detection. Two cases arise. If the area of detection is smaller than the pixel, the brightness \(L_{out}\) is equal to:
\[ L_{\text{out}} = \frac{P_{\text{out}}}{\pi \cdot A_{\text{spot}}} \] (2.13),

where \( A_{\text{spot}} \) is the pixel size (equal to the beam spot size) and \( P_{\text{out}} \) is the emitted power obtained in Equation 2.12 measured in lumens. If the area of detection is larger than the pixel, we can define a pixel density \( \rho_{\text{pixel}} \) as:

\[ \rho_{\text{pixel}} = \frac{A_{\text{spot}}}{A_{\text{det}}} \] (2.14),

where \( A_{\text{det}} \) is the area of detection, with \( A_{\text{det}} > A_{\text{spot}} \). The brightness becomes:

\[ L_{\text{out}} = \frac{P_{\text{out}}}{\pi \cdot A_{\text{det}}} = \rho_{\text{pixel}} \cdot \frac{P_{\text{out}}}{\pi \cdot A_{\text{spot}}} \] (2.15).

In particular, it means that the total brightness of a screen depends on the pixel density on the pixel grid. The brightness can be calculated by the more general equation:

\[ L_{\text{out}} = \rho_{\text{pixel}} \cdot \frac{P_{\text{out}}}{\pi \cdot A_{\text{spot}}} \]

\[ \begin{cases} 
\rho_{\text{pixel}} = \frac{A_{\text{spot}}}{A_{\text{det}}}, & A_{\text{det}} > A_{\text{spot}} \\
\rho_{\text{pixel}} = 1, & A_{\text{det}} \leq A_{\text{spot}} 
\end{cases} \] (2.16).

We can define a brightness efficiency \( \eta_{\text{L}} \) as the ratio of the brightness to the average incident power. Considering Equation 2.12, for a screen operating at maximum efficiency the brightness efficiency is:

\[ \eta_{\text{L}}^{\text{max}} = \frac{L_{\text{out}}}{\langle P_{\text{inc}} \rangle} = \rho_{\text{pixel}} \cdot \frac{P_{\text{out}}}{\pi \cdot A_{\text{spot}} \cdot \langle P_{\text{inc}} \rangle} = \rho_{\text{pixel}} \cdot \frac{\eta_{\text{raw}}^{\text{max}}}{\pi \cdot A_{\text{spot}}} \] (2.17),

where \( \rho_{\text{pixel}} \) is defined in Equations 2.16.
For a screen made of a particular UC emitter, $\eta_{\text{raw}}$ is constant, however $\eta_{\text{L}}$ depends on the pixel size and the pixel density. We will illustrate how these scaling laws apply to one of our prototype UC screen in Section 4.1.1.4.

2.3.1.2 Note on intrinsic efficiency and scattering

A larger number for efficiency is sometimes given in other publications where the intrinsic efficiency is used[73, 74]. Intrinsic efficiency is the ratio of total visible power emitted to the power of the infrared pump absorbed by a sample (Equation 2.10).

$$\eta_{\text{int}} \equiv \frac{P_{\text{out}, 4\pi}}{\langle P_{\text{optical}} \rangle_{\text{absorbed}}}$$

(2.18).

The absorbed power is related to the incident power by:

$$\langle P_{\text{optical}} \rangle_{\text{absorbed}} = \alpha \cdot \langle P_{\text{optical}} \rangle_{\text{inc, at sample}}$$

(2.19),

where $\alpha$ is the absorption coefficient of the sample with $0<\alpha<1$.

Thus, the absorbed power is smaller than the incident power and the raw efficiency is less than the intrinsic efficiency. As it will be seen in Section 3.2, if the sample is in a powder form, as it is the case in this research, the probed medium is highly scattering and the quantity $1-\alpha$ accounts for the scattered pump light. In the powders we study most of the light is actually backscattered. Backscattered pump light is unavailable to be absorbed
beyond the first layers of the sample. The result is that powders have an effective absorption coefficient smaller than a clear single crystal of the same material. We estimate backscattering in packed powders with no binder to be $1 - \alpha \sim 60\%$. This also means that in the case of a highly scattering medium, the irradiance $I_{\text{inc}}$ required to verify Equation 2.8 is greater than for a clear single crystal of the same composition, since a large fraction of pump light does not penetrate the sample. It is not available to be absorbed.

2.3.1.3 Raw efficiency experimental measurement setup

We measured raw efficiencies. The detection system was an 80-mm diameter integrating sphere fiber coupled to a Compact Array Spectrometer (CAS) (Model CAS140 from Instrument Systems) shown in Figure 2.22. The spectrometer was calibrated and traceable to the National Research Council (NRC). With the integrating sphere the quantities measured were radiant power densities (in watts per nanometer). The Instrument Systems software IS-SpecWin© offered the built-in capability of integrating the area under the part of the spectrum of interest to obtain the emitted power in the color of consideration, both in radiometric (watts) and photometric (lumens) units. IS-SpecWin© also analyzed the color content of the emission by finding its x,y coordinates on the 1931 CIE chromaticity diagram as indicated in Figure 2.23 which is a screen shot of this software’s output.
Figure 2.22: Experimental setup for efficiency measurements showing the integrating sphere, CAS and cabochon. In the photo the silver mirror is not in place and the green emission of the sample is visible at the upper entrance of the sphere. (Chopper and OD filters not in photo).

Figure 2.23: Screen shot of the IS-SpecWin software output showing an example of the spectro-radiometric measurement of green emission.
For calibrated raw efficiency measurements, the emitters were ground into a powder and then sieved through No 400 and No 635 stainless steel meshes so that the grain size ranged from 20 µm to 38 µm diameter (i.e. one order of magnitude larger than the pump wavelength). The sample holder was specially designed to mimic a point source and to avoid light entrapment to measure as much of the 4\pi visible emission as possible. It was a transparent acrylic hemisphere 10 mm in diameter called a cabochon. 20 mg of powder is packed in a 2-mm diameter-, 3-mm deep cylindrical cavity bored in the center of the hemisphere. The powders, having a mass density of \( \sim 5 \text{ g cm}^{-3} \), resulted in \( \sim 1.5 \text{ mm} \) thick samples. A silver mirror was placed on top of the upper entrance of the sphere to redirect most of the upwards traveling emission back into the sphere. Unless stated otherwise, raw efficiencies were measured with the powder not mixed in any binder (“dry” powder). The cabochon was placed at the entrance of the sphere so that the powder was sitting \( \sim 3 \text{ mm} \) inside the sphere, which is the configuration of calibration for the CAS. Since this setup enabled one to measure most of the light emitted into 4\pi by the emitter, it results in what we call “absolute raw efficiency measurements”. When another type of holder was used according to the requirements of specific experiments, the measurement is no longer absolute, it is relative.
Maximum efficiencies were obtained by measuring raw efficiencies of the color of consideration for various input irradiance until the efficiency curve rolls off. The excitation source was a 975-nm diode laser from Unique-mode (Germany) with the beam profile featured in Figure 2.24 superimposed on the excitation spectra of our emitters. As we can see, its output spectrum is quite broad. It was a multimode diode with collimated beam delivering up to 2 W of cw power. The broad spectrum means that not all of the pump light was near the maximum excitation wavelength as seen in Figure 2.24. We will discuss this issue further later in this thesis.

The beam was focused on the sample inside the holder, and was modulated at 30 Hz by a mechanical chopper. The diameter of the focus spot was estimated by using a pinhole of known diameter placed at the focus of the beam. Slits of various widths on the chopper figure...
allowed selection of several pulse durations (e.g. maximum efficiencies are typically measured for pulse duration of 2 ms). The irradiance of the beam was varied by using selected neutral density filters in the beam path. These were placed after the mechanical chopper to minimal heating of the filters. This way of externally attenuating the pump power rather than driving the diode at a lesser current so that we could avoid having the pump shift in wavelength. The peak wavelength of the infrared emission was fine-tuned via cooling temperature control to match the excitation peak of the emitter studied. The average power of the beam was measured with a Melles-Griot power-meter calibrated at the pump wavelength. This measurement was made once the beam passed through the cabochon to obtain a real measurement of the power incident on the emitters.
2.3.2 Maximum raw efficiencies of powders

Maximum raw efficiencies were measured for our red, green and blue most promising emitters using the setup described and are reported in Table 2.6, with the average input power at which they were measured. The modulation of the 975 nm pump beam was 30 Hz and 2 ms pulse duration. The pump was focused to a 900 µm diameter spot. No binder was present in the samples and no attention to thermal management was paid. Red, green and blue powers were measured by integrating the emission spectral density of 1% Er, 18% Yb:YF₃, 1% Er, 18% Yb:NYF and 0.4% Tm, 20% Yb:KY₃F₁₀ between 600 and 700 nm, 500 and 600 nm, and 425 and 525 nm respectively.

Table 2.5: Maximum raw efficiencies of emitting powders with no binder or thermal management

<table>
<thead>
<tr>
<th>Emitter</th>
<th>Maximum raw efficiency</th>
<th>Average incident irradiance (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>7.8 3.5 6.3</td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>5.8 37 5</td>
<td></td>
</tr>
<tr>
<td>Blue</td>
<td>4.5 3.5 15</td>
<td></td>
</tr>
</tbody>
</table>

Efficiencies relative to incident optical power.

The average input irradiance at which these efficiencies were measured is also given in Table 2.5. However saturation in UC is not a threshold type of process so there is a range of irradiances where the UC transfer function is linear, i.e. for which maximum efficiency is achieved. A practical consequence is that we can access grey levels in UC displays by changing the irradiance within that range. For the Er,Yb based emitters (red and green),
we observed that maximum efficiencies are achievable within about $+\ or\ - 3\text{W/cm}^2$ of the irradiances reported in Table 2.5, i.e. a range of $\sim 6\text{W/cm}^2$. We expect a similar range for the blue emitter however we were not able to access higher irradiances than the one given in Table 2.5 with our experimental setup.

We note that the photometric efficiency of the red is quite low despite a high radiometric efficiency. This is because the red emitted by our UC material is very deep (660 nm) and the human eye sensitivity drops in this region of the visible spectrum. A way of improving this photometric performance is to leak some of the green also emitted by the Er,Yb system (see Figure 2.18). As we add some of the green emission of the “red” emitter by means of a selective filtering, the perceived color of the emitter shifts toward 610 nm. Also, since we’re adding parts of the visible emission that we discarded when restricting ourselves to the power in the red peak, the radiometric efficiency also increases. For instance, the photometric maximum efficiency of a perceived 610 nm red emitter is 5.6 lm/W.

Another observation we can make is that considering the spectral width of the pump beam, many wavelengths emitted by the diode laser do not excite the emitters most efficiently, as can be seen in Figure 2.24. A diode laser with a narrower beam profile would allow a better use of the power emitted by the diode, and consequently improve the efficiencies we obtain.
2.3.3 \textit{Irradiance dependence of UC efficiency}

To convince ourselves of the dependence of UC efficiency on irradiance, and not input power, we conducted the following experiment: we excited a green emitter with the same set of average incident powers, but with the pump beam focused at different spot sizes for each set. Then we plotted the green raw efficiency with respect to input irradiance, i.e. average input power divided by the spot area. As we see in Figure 2.25, all efficiency curves super-impose when plotted with respect to irradiance, except at higher irradiances for the bigger spot size where the efficiency curve rolls off passed maximum efficiency. In this case, the average power required to verify Equation 2.9 is higher than for smaller spot sizes. Sufficiently high average pump power increases the temperature inside the emitter which is detrimental to UC efficiency because of the phonon-assisted transitions involved. We will develop this point in detail later on, but we can already observe that the problem can be resolved with minor thermal management. We also note that, for a bigger spot size more average input power is required to achieve a given efficiency however the resulting output brightness will also increase, according to Equation 2.6. These scaling laws allow some versatility when designing UC displays.
Figure 2.25: Green raw efficiency of 2%Er, 15% Yb:KY3F10 for different pump beam sizes. The excitation was a 975 nm beam modulated at 30 Hz into 2ms duration pulses.

The dependence of UC efficiency on the excitation irradiance can be understood if one considers the rate equations corresponding to the sensitizer (donor)/acceptor system. In Equation 2.4, the energy transfer rate term is a product of the population densities of both dopants in the corresponding initial state. Therefore, the higher the population densities, the higher the transfer rate, and the more efficient will be the up-conversion process. This is achieved by high peak irradiances. As a result, the efficiency increases with incident pump irradiance at low irradiance in the manner predicted by the calculation in Figure 2.21 and demonstrated experimentally in Figure 2.26 for all three colors. Brightness’s (in cd/m²) were measured with the TOP100 accessory of the CAS instead of the integrating sphere. In this case the emitting powder was stacked on a surface to cover an area no smaller than 1 cm². The measurement was done by exciting an area of emitting powder with a focus stop of 1 mm in diameter, which is large enough for the visible emission to flood the 500 µm diameter detection area of the candelameter. As the
thickness of the samples may vary, this is not an absolute measurement but these are typical performances of our emitters.

Figure 2.26: Example of screen performances for the green, red and blue emitters mixed in a p-PMMA binder and deposited on a glass slide: (a) Ratio of brightness to incident infrared input powers versus average incident power at 975 nm and (b) brightness versus average incident power at 975 nm. Note that the spectral width of the diode light source used was quite wide (see Figure 2.24).

Figure 2.26 shows how the UC efficiency reaches a maximum value in both the Er,Yb and the Tm,Yb systems. Two mechanisms contribute to this saturation. First, as pump irradiance increases the energy transfer mechanism becomes more efficient and the population density in the $^4I_{11/2}$ state of Er$^{3+}$ increases. However, back-transfers from Er$^{3+}$ to Yb$^{3+}$ decrease the population in Er$^{3+}$ $^4I_{11/2}$ state at the rate of $\gamma_{Er} n_{Er}^2 n_{Yb}$. This means that as the population in the first Er$^{3+}$ excited state increases the back-transfer rate to Yb$^{3+}$ increases leading to a saturation of the up-conversion process (the same explanation holds for the Tm, Yb system). A second process has been suggested to explain the saturation of the UC efficiency [26]: The Er$^{3+}$ first excited state $^4I_{13/2}$ is metastable and ions that decay
into that state are trapped for a long time (several ms). These ions can not contribute to the green UC process any longer, limiting the number of active ions available.

Regardless of the limiting mechanism, when the first step of the up-conversion process saturates it is the efficiency that reaches a maximum value. The visible output power emitted continues to increase with incident power until the second up-conversion step also saturates for similar reasons. It is therefore advantageous to design a system so that maximum efficiency is reached under mean operating conditions. Higher brightness’s can be attained by increasing the infrared pump power while darker levels are obtained for lower pump powers and with less UC conversion efficiency.

2.3.4 Pump duration dependence of UC efficiency

We mentioned that high peak irradiances increase UC efficiencies. It means the pumping duration should be short (shorter than the Yb$^{3+}$ ion lifetime of a few ms) in order to quickly achieve high transfer rates. By using short pulse duration excitation the pump energy is absorbed and stored in the Yb$^{3+}$ ion excited state before it is lost due to regular radiative decay. This maximizes the population density in the Yb$^{3+}$ $^5F_{3/2}$ state and enhances both steps of the up-conversion process. As a result, by using short pulses a given efficiency (in particular the maximum efficiency) is obtained at lower average input irradiance. This is demonstrated in Figure 2.27 for the green emitter where green efficiency and brightness are shown for different types of excitations.
Figure 2.27: Experimentally measured green (a) raw efficiency and (b) brightness versus incident irradiance in 1% Er, 18% Yb:NYF for different types of excitation: continuous and pulsed at 30 Hz with various pump durations.

Figure 2.28: (a) Blue raw efficiency in 0.4% Tm, 30% Yb:YLF and (b) red raw efficiency in 1% Er, 18% Yb:YF₃ for different types of excitation: continuous and pulsed at 30 Hz with various pump durations.

By reducing the amount of average power required to reach a given efficiency, short excitation pulse duration will further insure that the temperature change of the up-conversion materials is minimized. This increases the efficiency of the process and is
particularly important for the blue emitter: in Figure 2.28 (a) we see how short pulses increase the maximum efficiency of the blue emitter whereas in Figure 2.27, the value of the green maximum efficiency remains unchanged. Indeed the performance of the green emitter is less sensitive to temperature. The green up-conversion mechanism relies on energy transfers from Yb$^{3+}$ to Er$^{3+}$. The energy levels involved are close to being resonant so that the energy transfer processes are not accompanied by the emission of many phonons. On the other hand, the Yb$^{3+}$ and Tm$^{3+}$ energy levels are mismatched and the energy balance of the blue up-conversion process results in an emission of phonons. This increase in the number of phonons translates to an increased temperature of the powder. Such an increase in temperature has been shown to result in a drop in the efficiency of the up-conversion process [4]. By maximizing the population densities through the use of short excitation pulses, the transfer rates are optimized and there is less time for energy to get lost through other de-excitation pathways such as radiative or non-radiative decays, cross-relaxations, and back-transfers. The excitation energy gets to the blue emitting level with a fewer number of steps and transfers when the transfer rates are maximized. This means that the rise in temperature should be less with short excitation pulses. We note also a slight improvement in red UC maximum efficiency with short pulses, as shown in Figure 2.28 (b). Red UC mechanisms also involve phonon-assisted transfers, especially the back-transfer from Er$^{3+}$ to Yb$^{3+}$ as described in Section 2.2.2.1.

This result is particularly interesting for display applications, since in displays the excitation beam is scanned across the emissive screen to form an image hence the pump dwells for a finite time on each emitter in the manner of a short pulse excitation. As the
blue emitter is always the hardest emitter to come by in displays, the improvement of blue maximum efficiency is significant enough (factor of $\sim 4$ from cw to 30 Hz, 2ms pulse duration excitation) to prompt an in depth study of this phenomenon in order to predict how critical temperature effects will be in UC displays. This is developed in Section 3.1.

2.3.5 Irradiance dependence of power spectral density

2.3.5.1 Irradiance dependence of red to green emission power ratio in Er,Yb

We saw how the efficiency of one color varies with input irradiance. However, all materials emit several peaks in the visible as we saw in Section 2.2.3.4. Figure 2.29 shows emission spectra of Er,Yb measured at low and high input irradiance and normalized to the green emission peak. We see that the spectrum at high irradiance contains significantly more red proportionally: the spectral power density of this emitter varies with input irradiance, which is a known characteristic of the Er,Yb system[8, 9].
This is because green and red emission in Er,Yb result from different UC mechanisms as described in Section 2.2.2.1: the green and red emissions come from different excited states, the $^4S_{3/2}$ and $^4F_{9/2}$, respectively, and the green is excited by the two step process and the red by either two- or three step processes labeled (a), (b) and (c) in Section 2.2.2.1. The first evidence of the red to green ratio change with input irradiance is the different slopes of the green and red emission brightness curves, as shown experimentally in Figure 2.30(a) in our green emitter 1% Er, 18% Yb:NYF. These data were obtained by using a short pulse excitation (2 ms and 30 Hz modulation) as to minimize temperature effects. The experimental red to green ratio versus input irradiance in this material is plotted in Figure 2.30(b). We see that it is a significant effect.
Figure 2.30: Experimental emission ratio analysis in 1% Er, 18% Yb:NYF. Green, red and blue are the 545, 660 and 410 nm emission peaks of erbium, respectively. (a) Fluorescence and (b) various ratios of emission powers.

A notable consequence is that by analyzing the ratios of the different peaks of the Er,Yb emission we can estimate the contribution of each UC mechanism to the red emission. If the only process for red UC was process (a), i.e. red light results from a non-radiative decay from the green emitting state to the red emitting state, the proportion of red and green would be dictated by a simple branching ratio of the $^4S_{3/2}$ state. A discrepancy would only be the result of a noticeable temperature increase in the Er, Yb system as non-radiative decay is a phonon-assisted transition, which was not the case in our experiment. As branching ratios depend only on the nature of the emitter, not input irradiance, the red to green ratio wouldn’t vary either. Therefore we can conclude that the contribution of mechanism (a) is small. The contribution of mechanism (b), which involves a third UC step from the green emitting $^4S_{3/2}$ to the $^4G_{11/2}$ level followed by phonon-assisted back transfer to Yb$^{3+}$, can be estimated by monitoring the 410 nm emission from the $^4G_{11/2}$ level to the ground state. In Figure 2.30 we see that the blue and red brightness’s have
similar slopes and that the blue to red ratio varies less significantly than the blue to green or red to green ratios which follow the same trend. The slight variation of the blue to red ratio is the contribution of mechanisms (a) and (c). Note that this ratio would also increase if the temperature in the emitter increases because the back transfer to Yb\(^{3+}\) enabling the red emission is phonon-assisted. In conclusion mechanism (b) predominates over the two-step processes in the particular emitter that we studied here. This is explained by the presence of Yb\(^{3+}\) in high concentration and the relatively high irradiances at which we operate, as predicted in [3, 75]. Also the predominance of the three step phonon-assisted process is evidenced by the pump-induced temperature effects seen for the red emission and not for the green in Figure 2.27 (a) and Figure 2.28 (b). Since the three-step process quenches the green emission the red to green ratio increases with increasing pump power densities.

Using a smaller Yb\(^{3+}\) concentration would quench the red emission however the green emission is also not as efficient. Our green and red emitters were selected by maximizing the efficiency of the color of interest, with no attention paid to quenching the extra color which can be filtered out. For our display application, the consequence is if the materials are not used as monochromatic emitters, the color of the total visible emission will drift with irradiance as the red to green ratio increases. However, since the red to green ratio is dictated only by input irradiance, the change in color is predictable and can be taken into account in the engineering of the screen. To verify this we conducted the following experiment. This ratio was measured with respect to increasing pump power for three different known beam spot sizes and the results are shown in Figure 2.31 (a). As
discussed above, the excitation source used (30 Hz, 2 ms duration pulses at 975 nm) did not induce any temperature increase that could affect the red to green ratio obtained. By plotting the ratio with respect to irradiance rather than power in Figure 2.31 (b) we confirmed that the ratio depends on irradiance only. A practical consequence is that we can use this red to green emission ratio to estimate the effective irradiance of the pump inside an Er,Yb sample.

Figure 2.31: Effect of pump irradiance on red to green emission ratio in 2% Er, 15% Yb:KY$_3$F$_{10}$ for a beam focus of various diameters plotted (a) with respect to input power, and (b) scaled to input irradiance.

This experiment also demonstrates once again the important aspect of UC efficiency that it depends on input irradiance and not input power. The spot size of the pump beam on the up converter must be controlled.
2.3.5.2 *Irradiance dependence of power spectral density of the blue emitter*

![Graph showing red to blue emission intensity ratios with respect to input irradiance.](image)

**Figure 2.32:** Red to blue emission intensity ratios with respect to input irradiance

In Tm,Yb both the 480 and 650 nm emissions originate from the $^1G_4$ level. Therefore their relative intensity is a mere branching ratio independent of input irradiance. In Figure 2.32 we plotted the ratio of the 650 nm peak emission intensity to that of the 480 nm peak with respect to average input irradiance for our blue emitter operated as previously. We see that indeed this ratio is about unchanged. The slight decrease at higher irradiances is due to the tail of the 450 nm emission overlapping with the 480 nm peak. The 450 nm radiation comes from the $^1D_2$ level which is not thermally coupled to the $^1G_4$ level: a fourth UC step populates the $^1D_2$ level and the 450 and 480 nm emissions are not related by a simple branching ratio. Plotting the ratio of the red emission intensity to the total blue emission (450 and 480 nm peaks) shows that the proportion of emission from the $^1D_2$ level increases with increasing irradiance over the emission from the $^1G_4$ level. This is because the fourth UC step is more probable at higher population densities.
Still, as the 450 nm emission does not deliver much photometric power, the color of the blue phosphor doesn’t change with irradiance.

2.4 Chapter Two summary

In this Chapter we alluded to two important aspects of the UC processes that need further investigation. One is the UC dependence on temperature, especially for the blue emitter. The other is the role of scattering. We mentioned in Section 2.3.1.2 that scattering reduces the maximum obtainable raw efficiencies. Also, scattering changes the effective irradiance of the pump inside the sample, and we saw how a change in irradiance affects the UC process. The development of these two issues, temperature and scattering, is the object of the next chapter.
CHAPTER THREE: KEY STEPS TOWARDS OPTIMIZATION OF
UC DISPLAYS

3.1 Temperature dependence of UC efficiency

We mentioned on numerous occasions in Chapter 2 that high temperature in UC materials was detrimental to UC efficiency. We saw in Figure 2.28 that it was the case especially for the blue emitter efficiency and to a lesser extent for the red emitter efficiency. Even the green emitter efficiency decreases for sufficiently high average input powers, as observed in Figure 2.25.

Figure 3.1: Effect of temperature on red, green and blue UC efficiency in our most efficient emitters.

In order to evaluate the effect of temperature on the up-conversion process efficiency, we performed an experiment where a hot plate and thermo-couple were used to externally set and monitor the temperature of the emitting medium, and a low-energy, 10 Hz, 4 ns...
duration pulse at 975 nm was used to provide UC excitation without affecting the temperature. The total red, green and blue UC fluorescence was recorded for each of our efficient emitters and the measured, normalized dependence of up-conversion efficiency with increasing temperature is illustrated in Figure 3.1. These data confirm that temperature affects the up-conversion process and increased temperature reduces the UC efficiency of our materials.

In order to ensure that our emitters operate at their best efficiency in a display application, we need to understand and find tools to predict how temperature affects UC efficiency. Our investigation focuses on the blue emitter as its performance is the most affected by temperature and is the most critical to improve on for display applications. The blue emitter reaches maximum efficiency at higher input irradiance than either the green or red emitter and the Tm,Yb system is non-resonant, whereas Er,Yb has mostly resonant transitions and is operated at lower input powers. In Appendix A we give rate equations for Er,Yb.

### 3.1.1 Thermal effects in non-resonant rare earth co-doped systems

In order to understand how high irradiance induces temperature effects in Tm,Yb, we solve the rate equations for this system, taking into account all transfers and transitions: direct transfer, back transfer, cross relaxation and non radiative transitions. With today’s mathematical software (e.g. Mathcad©) it is possible to solve systems of coupled non-linear differential equations numerically. However, using constant energy transfer rate coefficients measured at room temperature doesn’t model properly the results found
experimentally in Figure 2.28. In order to accurately model the UC process in Tm,Yb we must include the temperature dependence of the energy transfer rates in the rate equations model, as well as the temperature changes caused by the various energy transfers. The temperature dependence of the energy transfer rates is given by the theory of phonon-assisted transfers developed for instance by Auzel[40]. However it was never included in the rate equations until this work.

Figure 3.2: UC in Tm,Yb:YLF: energy transfers and transitions.
We consider the Tm,Yb system as described in Figure 3.2. The rate equation analysis is done for Tm,Yb in YLF as the spectroscopic properties of this material are more thoroughly documented than Tm,Yb:KY3F10. In Figure 3.2 the energy levels are drawn to true scale using the spectroscopic data of References [76-78]. In order to avoid unnecessary complication, we do not include the 1D2 level of Tm3+ in our treatment of the system as it does not help to illustrate the problem. The set of rate equations that corresponds to Figure 3.2 ignoring the 1D2 state is, including the appropriate energy transfer, back-transfer, cross-relaxation and spontaneous emission rates:

\[
\begin{align*}
\dot{n}_1 &= \frac{n_2}{\tau_{yb}} - \frac{\sigma_{yb}^{abh} I_{\text{pump}}[t]}{h \nu_{\text{pump}}} (n_1 - n_2) + \gamma_1[T] n_2 n_3 + \gamma_2 n_2 n_4 + \gamma_3[T] n_3 n_6 - \gamma_4[T] n_1 n_6 - \gamma_5[T] n_1 n_6 - \gamma_6[T] n_1 n_7 - \gamma_7[T] n_7 n_1, \\
\dot{n}_2 &= -\dot{n}_1, \\
\dot{n}_3 &= \frac{n_4}{\tau_4} + A_{63} n_6 + A_{73} n_7 - \gamma_1[T] n_2 n_3 + \gamma_3[T] n_1 n_6 - \beta_1[T] n_3 n_6 - \beta_2[T] n_3 n_7, \\
\dot{n}_4 &= -\frac{n_4}{\tau_5} + \frac{n_3}{\tau_5} + A_{64} n_6 + A_{74} n_7 - \gamma_2 n_2 n_4 + \gamma_5[T] n_4 n_6 + 2 \beta_1[T] n_3 n_6 + \beta_2[T] n_5 n_7, \\
\dot{n}_5 &= -\frac{n_5}{\tau_5} + A_{65} n_6 + A_{75} n_7 + \gamma_1[T] n_2 n_3 + \gamma_6[T] n_1 n_7, \\
\dot{n}_6 &= -\frac{n_6}{\tau_6} + A_{76} n_7 + \gamma_2 n_2 n_4 - \gamma_3[T] n_2 n_6 - \gamma_4[T] n_1 n_6 - \gamma_5[T] n_1 n_6 + \gamma_7[T] n_7 n_1 \\
&\quad - \beta_1[T] n_3 n_6 + \beta_2[T] n_3 n_7, \\
\dot{n}_7 &= -\frac{n_7}{\tau_7} + \gamma_3[T] n_2 n_6 - \gamma_6[T] n_1 n_7 - \gamma_7[T] n_7 n_1 - \beta_2[T] n_3 n_7.
\end{align*}
\]

(3.1)

Room temperature values of the various coefficients are given in Table 3.1. The energy levels indicated in Figure 3.2 allow one to calculate the energy mismatch for each energy transfer, back transfer and cross-relaxation. The number of phonons p needed to bridge
that gap determines the temperature dependence of the rate associated with that process.

This number $p$ for each transition was calculated with the effective phonon energy for YLF being taken at $460\text{cm}^{-1}$ (see Table 2.4), and is also given in Table 3.1.

Table 3.1: Room-temperature values of the parameters used in the system of Equation 3.1

| Coefficient | Transition | Value used | Number of phonons $p$ $^e$
|-------------|------------|------------|-----------------
| $\tau_{\text{Yb}}$ | $^{2}\text{F}_{5/2} \rightarrow ^{2}\text{F}_{7/2}$ | $2 \text{ ms}^a$ | 
| $\sigma_{\text{abs}}^{\text{Yb}}$ | $^{3}\text{F}_{4} \rightarrow ^{3}\text{H}_{6}$ | $15 \text{ ms}^a$ | 
| $\tau_{4}$ | $^{3}\text{H}_{5} \rightarrow ^{3}\text{F}_{4}$ | $1 \mu\text{s}^a$ | 
| $A_{63}$ | $^{3}\text{H}_{4} \rightarrow ^{3}\text{H}_{6}$ | $0.9032/\tau_{6}^b$ | 
| $A_{64}$ | $^{3}\text{H}_{4} \rightarrow ^{3}\text{F}_{4}$ | $0.0697/\tau_{6}^b$ | 
| $A_{65}$ | $^{3}\text{H}_{4} \rightarrow ^{3}\text{H}_{5}$ | $0.0271/\tau_{6}^b$ | 
| $\tau_{6}$ | | $2.258 \text{ ms}^b$ | 
| $A_{73}$ | $^{1}\text{G}_{4} \rightarrow ^{3}\text{H}_{6}$ | $0.51/\tau_{7}^b$ | 
| $A_{74}$ | $^{1}\text{G}_{4} \rightarrow ^{3}\text{F}_{4}$ | $0.077/\tau_{7}^b$ | 
| $A_{75}$ | $^{1}\text{G}_{4} \rightarrow ^{3}\text{H}_{5}$ | $0.41/\tau_{7}^b$ | 
| $A_{76}$ | $^{1}\text{G}_{4} \rightarrow ^{3}\text{H}_{4}$ | $0.003/\tau_{7}^b$ | 
| $\tau_{7}$ | | $1.158 \text{ ms}^b$ | 
| $\gamma_{1}$ | $^{2}\text{F}_{5/2} \rightarrow ^{2}\text{F}_{7/2}$ while $^{3}\text{H}_{6} \rightarrow ^{3}\text{H}_{5}$ | $649 \text{ s}^{-1}/N_{\text{at}}^a$ | $+4$
| $\gamma_{2}$ | $^{2}\text{F}_{5/2} \rightarrow ^{2}\text{F}_{7/2}$ while $^{3}\text{F}_{4} \rightarrow ^{3}\text{H}_{4}$ | $3245 \text{ s}^{-1}/N_{\text{at}}^a$ | $+6$
| $\gamma_{3}$ | $^{2}\text{F}_{5/2} \rightarrow ^{2}\text{F}_{7/2}$ while $^{3}\text{H}_{4} \rightarrow ^{1}\text{G}_{4}$ | $4000 \text{ s}^{-1}/N_{\text{at}}^a$ | $+3$
| $\gamma_{4}$ | $^{3}\text{H}_{4} \rightarrow ^{3}\text{H}_{6}$ while $^{2}\text{F}_{7/2} \rightarrow ^{2}\text{F}_{5/2}$ | $9042 \text{ s}^{-1}/N_{\text{at}}^c$ | $+5$
| $\gamma_{5}$ | $^{3}\text{H}_{4} \rightarrow ^{3}\text{F}_{4}$ while $^{2}\text{F}_{7/2} \rightarrow ^{2}\text{F}_{5/2}$ | $210 \text{ s}^{-1}/N_{\text{at}}^a$ | $-7$
| $\gamma_{6}$ | $^{1}\text{G}_{4} \rightarrow ^{3}\text{H}_{5}$ while $^{2}\text{F}_{7/2} \rightarrow ^{2}\text{F}_{5/2}$ | $3014 \text{ s}^{-1}/N_{\text{at}}^c$ | $+5$
| $\gamma_{7}$ | $^{1}\text{G}_{4} \rightarrow ^{3}\text{H}_{4}$ while $^{2}\text{F}_{7/2} \rightarrow ^{2}\text{F}_{5/2}$ | $10000 \text{ s}^{-1}/N_{\text{at}}^d$ | $-4$
| $\beta_{1}$ | $^{3}\text{H}_{6} \rightarrow ^{3}\text{F}_{4}$ while $^{3}\text{H}_{4} \rightarrow ^{3}\text{F}_{4}$ | $500 \text{ s}^{-1}/N_{\text{at}}^a$ | $+3$
| $\beta_{2}$ | $^{3}\text{H}_{6} \rightarrow ^{3}\text{H}_{5}$ while $^{1}\text{G}_{4} \rightarrow ^{3}\text{H}_{4}$ | $3562 \text{ s}^{-1}/N_{\text{at}}^e$ | $0$

$N_{\text{at}} = 1.37 \times 10^{22} \text{cm}^{-3}$. $^a$ From [52]. $^b$ From [79]. $^c$ From [80]. $^d$ Estimated. $^e$ + for emission, - for absorption.
Two cases arise: if there is absorption of phonons during the process, the rate has the functional form [40]:

\[ \gamma[T] = \gamma[T_0] \left( \frac{\bar{n}[T]+1}{\bar{n}[T_0]+1} \right)^\rho \] (3.2),

where \( \bar{n}[T] = \left[ \exp[\Delta E/k(T_0 + \Delta T[t])] - 1 \right]^{-1} \) is the occupation number for the effective phonons of energy \( \Delta E = 460\text{cm}^{-1} \) and \( k \) is Boltzmann’s constant.

If there is absorption of phonons during the process, the functional form of the rate is:

\[ \gamma[T] = \gamma[T_0] \left( \frac{\bar{n}[T]}{\bar{n}[T_0]} \right)^\rho \] (3.3).

The rates affected by temperature change are noted as dependent on the temperature \( T \) in Equation 3.1. Note that the transfer to \( ^3\text{H}_5 \) is resonant, so \( \gamma_2 \) does not vary with temperature. However the transfer is followed by a non-radiative decay that has to be taken into account when calculating the temperature change.

A few other differential equations are needed in order to solve Equations 3.1. First, we need to follow the evolution of the temperature as the material is being pumped. Each phonon being absorbed or emitted changes the energy inside the lattice, and so changes the local temperature. The change of temperature is taken to be proportional to the total
change in phonon density. We also take into account some heat diffusion inside the material, so that the temperature variation obeys:

\[
\begin{align*}
\dot{T} \propto & \ p_{\gamma_1} \gamma_1 \left[ T \right] n_2 n_3 + p_{\gamma_2} \gamma_2 n_2 n_4 + p_{\gamma_3} \gamma_3 \left[ T \right] n_2 n_6 + \\
& p_{\gamma_4} \gamma_4 \left[ T \right] n_1 n_6 + p_{\gamma_5} \gamma_5 \left[ T \right] n_1 n_6 + p_{\gamma_6} \gamma_6 \left[ T \right] n_1 n_7 + p_{\gamma_7} \gamma_7 \left[ T \right] n_1 n_1 - \frac{T}{t_D} 
\end{align*}
\]

(3.4),

where \( t_D \) is a time characteristic of heat diffusivity through the heated region.

In order to obtain the close agreement between numerical results and experimental data, the time characteristic of heat diffusivity in the model was chosen to be \( t_D = 8 \text{ ms} \). We can calculate the thermal diffusivity in YLF from[81]:

\[
\kappa = \frac{k}{\rho \cdot C} = 0.019 \text{ cm}^2 \cdot \text{s}^{-1}
\]

(3.5),

where \( k \) is the thermal conductivity (0.06 W·cm\(^{-1}\)·K\(^{-1}\) in YLF), \( \rho \) is the material density (3.95 g·cm\(^{-3}\)), and \( C \) is the heat capacity (0.79 J·g\(^{-1}\)·K\(^{-1}\)) [82]. Using the relation \( d = (\kappa \cdot \tau_D)^{1/2} \) where \( t_D = 8 \text{ ms} \), we obtain a distance for heat diffusion of 125 \( \mu \text{m} \). This result is consistent with the size of the sample and the absorption depth of the pump beam so this assumption is reasonable.

Finally, the visible fluorescence emission rate is given by the simple equation:

\[
\dot{S}_{\text{blue}} = A_{\gamma_3} n_7 = \beta_{\gamma_3} \frac{n_7}{\tau_7}
\]

(3.6),
and we define the efficiency of the up-conversion process as:

\[
\text{Eff} = \frac{\int_{t_0}^{t_{\text{final}}} \dot{S}_{\text{blue}} \, dt}{\int_{t_0}^{t_{\text{final}}} I_{\text{pump}}(t) \, dt}
\]

(3.7).

Figure 3.3: (a) Calculated and (b) experimental raw efficiencies for 0.4% Tm, 25% Yb:YLF for different types of excitation: continuous, and pulsed at 30 Hz with pump duration of 5 ms (circles), 2.6 ms (up-triangles), 630 μs (down-triangles), and 350 μs (diamonds).

Solving the rate equations numerically and computing the UC efficiency according to Equation 3.6 leads to the calculated efficiencies shown in Figure 3.3 (a) for 0.4% Tm, 25% Yb:YLF for five different types of excitation: continuous, and pulsed with various pump durations. The rate of heat diffusion \( t_D \) was set to 8 ms in these calculations. For comparison, Figure 3.3 (b) shows experimental raw efficiencies of this material obtained for the same excitations. Here the excitation wavelength was 959-nm for optimal excitation[58]. Calculated and experimental data are in close agreement. The
experimental results in Figure 3.3 (b) can not be reproduced by a model that uses only temperature-independent coefficients. Our model is necessary to explain the data and we can conclude that pump duration and temperature play a crucial role in the UC performance.

3.1.2 Temperature probing by FIR in UC emitters

We now evaluate the temperature of our very efficient UC emitters as they are operated and when the incident irradiance is increased. For this we use the Fluorescence Intensity Ratio (FIR) technique [83, 84]. It relies on the temperature dependence of the population of two thermally coupled energy levels. The populations of thermally coupled levels separated by $\Delta E$ follow a Boltzmann distribution so that the ratio of their respective intensities at a given temperature is proportional to $\exp[-\Delta E/kT]$. We can use this ratio to probe for temperature providing a few additional conditions are met. The levels should be at least 200 cm$^{-1}$ apart to avoid substantial overlap of the two fluorescence wavelengths, the fluorescence must be excited by readily available sources and should generate enough signal at wavelengths where detectors exist. FIR is typically used for temperature sensing with rare-earth singly-doped materials, such as Er-doped fibers. In References [83, 84] the levels chosen for FIR in these materials are the green and the red emitting levels. Indeed in this case the red emission stems predominantly from non-radiative decay from the green emitting level. Because of this emission of phonons they are thermally related. Note that in this case the materials are not excited through UC but through direct pumping. In co-doped systems however the emission from these two different Stark levels might be generated by various UC processes other than non-
radiative decay so that their intensity ratio might not be simply correlated to temperature (e.g. irradiance dependence of red and green emission in Er,Yb). Still for Er,Yb based emitters we can use the $^2\text{H}_{11/2}$, and $^4\text{S}_{3/2}$ levels which are thermally coupled (the population of the $^2\text{H}_{11/2}$ level results from thermalization of $^4\text{S}_{3/2}$) and emit strongly in the green at 525 nm and 545 nm, respectively. For instance we can decide to calculate the ratio of the integrated power between 511 and 535 nm and between 535 and 575 nm at various temperatures. An increase in temperature will increase this ratio.

However for the Tm,Yb system we cannot find two thermally coupled levels which meet the requirements for FIR. For instance, $^3\text{F}_2$ and $^3\text{F}_3$ are thermally coupled however there is no strong visible emission from these levels because of the rapid non-radiative decay to $^3\text{H}_4$. Also we cannot use $^1\text{D}_2$ and $^1\text{G}_4$. Indeed, despite the $^1\text{D}_2$ level lying 7000 cm$^{-1}$ above $^1\text{G}_4$, these two levels are populated independently of each other so the intensities of the two emission bands are not thermally related. However, in rare-earth co-doped fluorides the Stark splitting of levels into sub-levels is significant enough that we can use FIR on thermally populated Stark sub-levels providing that they lie sufficiently far apart. In particular the blue emitting level $^1\text{G}_4$ of Tm$^{3+}$ has many sub-levels which are thermalized. We can see the sublevels of the blue emitting $^1\text{G}_4$ level in Tm,Yb:KY$_3$F$_{10}$ in Figure 3.4 which presents typical spectra in the blue obtained with the acrylic holder for two pumping conditions: CW and 2 ms duration pulse excitation at 30Hz. The output power was the same (54 µW) in both pumping conditions. The transitions at 462.7 and 480.3 nm both originate from the $^1\text{G}_4$ level but from different Stark split sub-levels. When the ratio of the emission at 462.7 to that at 480.3 nm is observed to increase, it
means that the temperature of the emitting powder has increased. For instance in Figure 3.4 we see that the intensity of the 462.7 nm peak is proportionally higher than that of the 480.3 nm peak when using CW irradiation. It means that for the same output power, the temperature of the sample is much higher when continuous pumping is used than when pulsed excitation is used.

![Emission spectra of 0.4 % Tm, 20 % Yb:KY3F10 for two conditions of excitation: continuous and modulated at 30 Hz with a 2ms pulse duration. The output power in the blue was the same in both excitation conditions (54 µW). The sample holder was made of acrylic.](image)

Figure 3.4: Emission spectra of 0.4 % Tm, 20 % Yb:KY3F10 for two conditions of excitation: continuous and modulated at 30 Hz with a 2ms pulse duration. The output power in the blue was the same in both excitation conditions (54 µW). The sample holder was made of acrylic.

The 462.7 and 480.3 nm emissions originate from levels sufficiently far apart that we can use these for FIR sensing. However, in order to correctly estimate the spectral distribution of the 480 nm band as a function of temperature, we must remove the overlapping tail of the emission band centered at 450 nm as it originates from the \(^1\)D\(_2\) level and we saw that this level was not coupled with the \(^1\)G\(_4\) level. This can be done by
fitting Lorentzian curves to each peak of the emission spectrum using such software as OriginPro ©[85].

Finally, to obtain absolute temperatures, the last step of the method is to map the ratio of the emission lines intensity to the temperature of the emitting powder using the measured emission spectra obtained at temperatures between 21 and 180°C set externally with the hot plate of Figure 3.1. The blue emitter temperature with respect to the 462.7 to 480.3 nm fluorescence intensity ratio corrected for 450 nm emission is given in Figure 3.5 with a polynomial fit (e.g., reciprocal function of a Boltzman distribution.)

![Figure 3.5: FIR of 0.4%Tm, 20%Yb:KY3F10.](image)

The mappings for the green and red emitters are given in Appendix A.
3.1.3 Thermal management for UC emitters

The FIR technique as described above was applied to 0.4 % Tm, 20 % Yb:KY3F10 for various 975 nm pumping conditions (CW, and 30 Hz, 5 and 2 ms duration pulses) and for two types of powder holders (acrylic and copper). The emission spectrum was recorded for each pumping condition by using the integrating sphere and the CAS. Here the holders were 1 cm long, 2.5 cm diameter cylinders with a 500 μm deep, 750 μm diameter hole drilled at the center of a face. They were lodged at the entrance of the sphere (which was set up-side down from the configuration of raw efficiency measurement) and excited from above. Once we removed the tail of the 450 nm emission, we calculated the intensity ratios to determine the temperature of the emitting powder for each case. The temperatures are shown in Figure 3.6 (a), and the resulting measured efficiencies are given in Figure 3.6 (b).

![Figure 3.6](image)

Figure 3.6: (a) UC emitter temperature and (b) relative raw efficiency of a sample of 0.4 % Tm, 20 % Yb:KY3F10 in acrylic and copper sample holders for different excitations: continuous and modulated at 30 Hz and various pulse durations.
Several observations can be made from the temperature plot. First, for a given material and sample holder, the temperature in the powder depends only on the incident infrared power. This can be explained by the fact that the blue up-conversion process is about 4% or 5% efficient. Thus, a large part of the absorbed power is not re-radiated (in the blue, red or infrared) but is diffused non-radiatively inside the material through the emission of phonons which raise the temperature of the sample. Second, the results in the acrylic holder show that the emitting powder can reach very high temperatures with cw or even long pulse duration excitation. This is because when using long pulse duration excitation, the peak population densities are lower than when using short pulse duration excitation for the same average incident power. As a result, the transfer rate probabilities (proportional to the population densities in the initial levels) are lower in the long duration pulse case and the up-conversion efficiency is less (see Figure 3.6 (b)). In order to achieve the same population densities, the average power required is higher using long pulse duration excitation. This results in higher temperature, and consequently, in loss of efficiency for the up-conversion process as shown in Figure 3.1. We call this pump-induced temperature effects. The lower temperatures attained when using short pulse duration excitation explain the higher efficiencies obtained in Figure 3.6 (b). This improvement in efficiency is verified down to excitation pulses of the order of the transfer time from Yb to Tm. For pulses shorter than this transfer time, no improvement can be seen as the energy remains stored in the Yb excited state.

Finally, we see that it is straightforward to reduce the temperature of the emitting powder by simply using a high thermal conductivity sample holder. By simply using a copper
holder, we achieved significant heat extraction resulting in lower emitter temperatures and, as a result, higher efficiencies were detected. Using smaller holes for pixels and designing the holes in order to maximize the thermal contact between powder and substrate should help in operating the powder close to room-temperature, and therefore achieving still higher efficiencies. For instance we used the heat transfer module of the finite element method software for electromagnetism FEMLAB© to simulate how heat would be dissipated in different size pixels. For this we solve the stationary heat flow equation $\nabla(k \nabla T) = Q$ with $k=400 \text{ W/(K}\cdot\text{m})$ in copper and $Q$ is the heat deposited in $\text{W/m}^3$. The results are shown in Figure 3.7. For the same amount of heat deposited temperatures reached in the smaller pixel are lower.

![Figure 3.7: FEMLAB simulation of heat dissipation in (a) 500 μm and (b) 50 μm pixels for the same amount of heat deposited.](image)

The results obtained for the red and green up-conversion emitters are very similar to that of the blue emitter. The rate equations with temperature dependent transfer rate coefficients in Er,Yb are given in Appendix A. However, because the up-conversion process only requires two steps in those emitters instead of three for the blue emitter, the
incident power densities required to attain saturation of the efficiency are smaller and result in less heating of the powder. As a result, after analysis of the emission spectra in various excitation conditions, temperatures of only 10°C to 20°C above room temperature are observed when using the acrylic sample holder with a 1 mm diameter hole, even for continuous excitation. This rise in temperature is not sufficient to significantly alter the up-conversion efficiency for the red and green emitters in our absolute raw efficiency measurements obtained with a pump source modulated at 30 Hz and focused to a 900 μm diameter spot. It could become significant when using a modulation at 60 Hz or a larger spot size, or any scaling process that requires high average powers for a given irradiance. Therefore all three emitters would benefit from moderate thermal management in a display.

Finally, we measured the temperature attained by our most efficient red, green and blue emitter at the maximum raw efficiency of Table 2.5. The temperature of both green and red emitters at maximum efficiency was still 20°C. However that of the blue emitter was 120 °C. In Figure 3.1 we saw that the blue efficiency drops by a factor of ~ 3 from 20°C to 120°C when the blue emitter was operating at low efficiency. In Figure 3.6 we gained a factor 1.2 in maximum efficiency when reducing the temperature from 120°C to 75°C by switching from acrylic to copper holder in the 2 ms pulse duration case. Combining these two experimental results and being conservative, we estimate that we can expect at least 50% increase in efficiency for the blue emitter by using an emitter configured for thermal management such as one with a heat conducting substrate and smaller pixels.
3.2 Scattering effects on UC efficiency

Figure 3.8: Scattering of a 611 nm HeNe laser beam through a collection of UC particles.

When a material is optically excited one issue is that of light penetration into the sample. For instance an uncoated laser grade single crystal excited at normal incidence will have Fresnel losses at its interface. However a UC screen relies on emitters in the form of micro-crystallites dispersed in a binder which raises the issue of scattering. A straightforward evidence of scattering is the white appearance of a UC screen due to very strong scattering of the light incident on it when there is a large mismatch between the index of refraction of the binder and that of the particles. This was the case in the photo of Figure 1.3(a) where the Florida sun light was scattered by the screen which appears white where the infrared beam is not on it (this screen was made with very little binder). We also conducted an experiment where we shined a HeNe laser through a collection of particles dispersed in low density in oils of various refractive indices and the light scattered by the sample was collected by the integrating sphere as illustrated in Figure
3.8. We see that the light is scattered when the index of refraction of the oil differs from that of the material.

This strong scattering is present at any wavelength including at the infrared excitation wavelength. In particular the pump light that is backscattered, i.e. re-radiated towards the origin of the pump source, can not be absorbed by the active medium. We have observed about 60% of the incident infrared light being backscattered from the sample in our raw efficiency measurements in the absence of binder. This backscattered light represents energy lost for the UC process. Hence, a key step toward optimizing a UC display is addressing scattering issues.

3.2.1 Definitions, theory and experimental method

3.2.1.1 Definitions

A theory of elastic scattering in small particles can be found in Reference [86]. Scattering is defined as the re-radiation of light upon excitation of a heterogeneous medium by an electromagnetic wave in any direction. Heterogeneity can be on the molecular scale or in the scale of aggregations of many molecules. Everything except vacuum is heterogeneous in some sense, therefore all media scatter light. However, optically dense media, i.e. where the molecular separation is much less than the wavelength of the incident light (solids, liquids, many gases), are considered homogeneous. In homogeneous media light propagation is not described in terms of scattering but in terms of reflection and transmission. In a formal analogy between
scattering by a particle and propagation through a slab of homogeneous medium \textit{back-scattering} is conceptually analogous to reflection, and forward scattering to transmission.

However, in the case of scattering, light can be re-radiated into many directions. In isotropic scattering, light is re-radiated homogeneously into $4\pi$. In anisotropic media the amount of light re-radiated decreases with increasing scattering angle. This is described by the coefficient $(1-g)$ where $g$ is called the \textit{anisotropy} of the medium and is equal to the mean cosine of the scattering angle: $g = \langle \cos(\theta) \rangle$. For isotropic media $g = 0$. When $g = 1$ all the light is re-radiated in the direction of the incident beam: the medium is equivalent to a homogeneous semi-infinite medium at normal incidence. If the particle scatters more light in the forward direction $g$ is positive, if the light is back-scattered $g$ is negative.

The light that is not re-radiated but transformed into another form (thermal energy for instance) experiences \textit{absorption}. Scattering and absorption account for the total energy loss in the incident beam upon propagating through a scattering medium. We call the decrease in the energy of the incident beam in the presence of the scattering medium the extinction of the light. Let us consider one single arbitrary particle in a non-absorbing medium. The extinction cross-section $C_{\text{ext}}$ is defined as the sum of the absorption cross section $C_{\text{abs}}$ and the scattering cross section $C_{\text{sca}}$:

$$C_{\text{ext}} = C_{\text{abs}} + C_{\text{sca}}$$ (3.8).
3.2.1.2 Light propagation in a scattering medium

We consider a beam of incident irradiance $I_0$ propagating along the depth $z$ of a semi-infinite particulate medium of particle density $\rho$ cm$^{-3}$. Let us first ignore multiple scattering, i.e. the contribution of light scattered by other positions in the medium. Then the irradiance of the incident beam at depth $z$ is attenuated according to:

$$I(z) = I_0 \exp(-\alpha_{\text{ext}} \cdot z)$$ (3.9),

where $\alpha_{\text{ext}}$ is the attenuation coefficient in cm$^{-1}$ defined in Equation 3.3.

$$\alpha_{\text{ext}} = \rho \cdot C_{\text{ext}} = \rho \cdot C_{\text{abs}} + \rho \cdot C_{\text{sca}} = \mu_a + \mu_s'$$

$$\mu_a = \rho \cdot C_{\text{abs}}$$

$$\mu_s' = \mu_s \cdot (1 - g) = \rho \cdot C_{\text{sca}}$$ (3.10),

where $\mu_a$ and $\mu_s$ are respectively the absorption coefficient and the scattering coefficient in cm$^{-1}$ and $g$ is the anisotropy. $\mu_s'$ is called the reduced scattering coefficient.

Two kinds of media can be differentiated: absorption dominated media and scattering dominated media. An absorption dominated medium is defined as a medium where $\mu_a > \mu_s'$: absorption events occur more rapidly than effective scattering events (e.g. doped single crystals). In scattering dominated media $\mu_a < \mu_s'$: multiple scattering events occur before an absorption event occurs (e.g. particles in a non-absorbing binder of highly mismatched index of refraction). In an absorption dominated medium light propagates along $z$ until it is completely absorbed. It is described by Beer’s law:
\[ I(z) = I_0 \exp(-\mu_a z) \] (3.11).

The penetration depth is defined as the depth at which the irradiance has dropped to 1/e or 37% of the incident irradiance. In absorption dominated media the penetration depth \( d \) is:

\[ d = \frac{1}{\mu_a} \] (3.12).

For the case of a scattering medium, let us now consider multiple scattering as it likely occurs in most scattering media. The propagation law is more complex. It was evaluated in Reference [87] for propagation of intense laser radiation in pigmented tissues which contains absorbing structures 10 to 200 \( \mu \text{m} \) in size.

\[ I(z) = I_0 \cdot k \exp(-z/\delta) \text{ for } z > \delta \]

\[ \delta = \frac{1}{\{3\mu_a[\mu_a + \mu_s \cdot (1 - g)]\}^{1/2}} \] (3.13),

where \( \delta \) is the penetration depth of diffusion theory and \( k \) is a scalar factor greater than unity that accounts for the accumulation of light at the surface because of backscattered reflectance. The Monte Carlo simulation for \( k \) done in [87] shows that \( k \) is a function of the diffuse reflectance of the scattering medium.

In this case, the penetration depth \( d \) for a scattering medium is:

\[ d = \delta[1 + \ln(k)] \] (3.14).
There are two important differences between propagation in a clear medium and a scattering medium. First, comparing Equations 3.12 and 3.14, the penetration depth in a scattering dominated medium is shorter than in absorption dominated medium. Then, in a scattering medium the factor \( k \) augments the irradiance at the surface: due to backscattering the surface irradiance is greater than the incident irradiance or the irradiance in a clear medium. We can understand this as the light being confined in a smaller area than the original beam size due to multiple scattering in the medium. These results are summarized by Figure 3.9.

![Figure 3.9: Light propagation in scattering and clear media](image)

If we now apply the above to our UC emitters, scattering affects the performance of an UC display three ways. First, backscattering of the pump light reduces UC raw efficiencies by preventing some of the pump from penetrating the active material. Second, scattering inside the medium alters the penetration depth of the pump light and a change in penetration depth corresponds to a change in the number of ions that can participate in the UC process. Since UC is a nonlinear process determined by the pump
light irradiance, the third and most critical way in which scattering affects performance is through altering the irradiance and hence, the efficiency of UC within the display screen.

3.2.1.3 Experimental methods

To demonstrate the effect of scattering on UC efficiencies, we studied the simple case Er,Yb:KY₃F₁₀. We chose this host because it is a cubic material of index of refraction ~1.484 at 975 nm, in contrast to birefringent NYF (see Table 2.4). The isotropy of KY₃F₁₀ allows complete index matching even though it is not the most efficient host for the green emission of erbium. We also chose the Er,Yb system because, as described above, its temperature is not significantly affected by absorption of 975-nm pump light and up-conversion at the irradiances of operation. The crystallites were sieved to 20 ± 10 µm (i.e. one order of magnitude larger than the pump wavelength) and packed into a holder of 2 mm diameter and 1 mm depth made of aluminum to minimize any temperature effects. Cargille™ oils of different indices of refraction were placed in the powder to vary the index match and thus the degree of scattering. The nominal index of refraction of the oils is nD measured at 22°C. The powder density was maintained at 50% by volume. We placed the sample in its holder at the entrance of the same integrating sphere used for efficiency measurements. The samples were excited at 975 nm with a 30 Hz, 2 ms duration pulsed source at 12.5 mW average power focused to a 900 µm diameter spot. These pumping conditions were chosen to give maximum UC efficiency for the packed powder in the absence of binder.
Figure 3.10: Backscattering of the pump light for different matching fluid indices of refraction for 2% Er, 15% Yb:KY$_3$F$_{10}$ excited at 975 nm. The thin solid line spectrum corresponds to 100% backscattering from dry alumina powder.

Figure 3.10 shows the near infrared portion of the emission spectrum measured with the CAS for samples of different matching fluid indices of refraction (dry to perfect match). In Figure 3.10, the reference spectrum corresponding to 100% backscattering was obtained using a sample of packed alumina powder: alumina doesn’t absorb at the pump wavelength and we checked that in this configuration the integrating sphere collected all of the 12.5 mW of infrared pump power. The UC materials show a peak at 975 nm corresponding to the pump light backscattered by the powder and a broad feature at 1 µm due to Yb$^{3+}$ emission. We see that decreasing the index mismatch by using a binder of near perfect index match reduces backscattering from 70% (dry) to 15% for n = 1.484. Oils of indices 1.468 and 1.500 (not represented on Figure 3.10 for clarity) also yield 15% backscattering. Clearly, perfect index match at the pump wavelength is not required
to significantly reduce backscattering. This observation relaxes the constraints on the index of the binder which is noteworthy as the host for the green emitter NYF is birefringent. Furthermore, it lifts any concerns regarding dispersion, intrinsic or due to thermal effects or aging of the polymer. For instance, in the case of a transparent display, the index match would have to be in the visible. The dispersion between 975 nm and the visible being in the third decimal place for all three emitters, the screen would still be optimized for reduced backscattering.

3.2.3 Internal scattering effect on efficiency

Figure 3.11 shows the corresponding visible emission spectrum for the dry sample and the n = 1.484 case of Figure 3.10. The change in effective incident irradiance with the severity of scattering is evidenced by the proportionally greater red intensity in the high scattering sample. This change in the red to green emission ratio was not due to pump-induced temperature effects: the temperature increase was measured to be less than 20°C. We saw in Section 2.3.5.1 that the red to green emission ratio was greater at higher pump irradiances and this is what is observed here. We can use the red to green emission ratio to estimate the effective irradiance of the pump inside an Er,Yb sample with the method described in Section 2.3.5.1: we measure this ratio at various incident powers in the high and low scattering samples. The scaling factor of the x axis necessary to superimpose the ratio curves is the change in irradiance. We determined that the effective irradiance is a factor of 10 less in the index-matched powder than it was in the dry powder.
Figure 3.11: Visible emission spectra for 2% Er, 15% Yb:KY$_3$F$_{10}$ excited at 975 nm under 12.5 mW average input power for a scattering sample and an index-matched sample.

The change in effective irradiance due to scattering has important consequences for UC. In Figure 3.11 we see that the green emission does not increase in the index-matched case despite the improved pump penetration. At equal pump power, an index-matched sample absorbs more pump light but the UC process is less efficient at that power since the irradiance is less because of reduced scattering. The decreased irradiance demands more input power to saturate the efficiency in the index-matched sample. In a low scattering sample, however, the penetration depth is longer than for a high scattering sample and less pump-light is backscattered. More active ions can be excited leading to higher maximum raw UC efficiency compared to the high scattering case. Further, since maximum efficiency in the low scattering sample is reached at higher input powers the brightness will be greater. In order to demonstrate this we measured the absolute raw efficiency of this 2% Er, 15% Yb:KY$_3$F$_{10}$ emitter, i.e. with the setup described in Section 2.3.1.3. Figure 3.12 illustrates the differences in efficiency and resulting...
brightness’s between low and high scattering samples. We see how in the index-matched sample the maximum efficiency is improved, how it is reached at a higher input power (a) and consequently how the output power is also significantly higher (b).

Figure 3.12: (a) Raw efficiency and (b) brightness of 2% Er, 15% Yb:KY$_3$F$_{10}$ for a high scattering sample and an index-matched sample.

3.2.4 Maximal raw efficiencies of red, green and blue UC emitters

We measured the maximum raw efficiencies for our best red, green and blue emitters immersed in 3 μL of index-matched oils. Once again the pump modulation produced 2 ms duration pulses at 30Hz which were focused to an 850 μm diameter spot. For all three colors maximum efficiency was obtained with a pump irradiance of 20 W/cm$^2$. The results are given in Table 3.2
Table 3.2: Maximum raw efficiencies of UC emitters in index-matched oil

<table>
<thead>
<tr>
<th>Emitter</th>
<th>n_D of oil</th>
<th>Radiometric (%)</th>
<th>Photometric (lm/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>1.550</td>
<td>10.5</td>
<td>5</td>
</tr>
<tr>
<td>Green</td>
<td>1.460</td>
<td>8</td>
<td>52</td>
</tr>
<tr>
<td>Blue</td>
<td>1.488</td>
<td>5.5</td>
<td>4.2</td>
</tr>
</tbody>
</table>

We see that the maximum raw efficiencies of all three emitters were significantly improved compared to the results of Table 2.5. This is not an upper limit but only a minimum of what we can expect. Indeed the experimental configuration didn’t allow us to collect all of the visible light emitted by the index-matched sample. For a non-scattering sample, the emitters radiate visible light into $4\pi$. Despite the use of a silver mirror to “seal” the integrating sphere, some of the light is not captured by the sphere. This collection issue doesn’t apply for the highly scattering sample for which most of the light emission takes place at the surface of the sample and is scattered into the sphere. Also, more importantly, as more average input power is required to reach maximum efficiency in the index-matched sample, the temperature inside the sample increases and is poorly dissipated by the acrylic of the cabochon. We saw in Section 3.1 how this was significant especially for the blue efficiency. Using a heat diffusive substrate as described in Section 3.1.3 would solve this problem and we estimate that up to 50% improvement on the numbers obtained in Table 3.2 can be expected. Another way would be to use a structured emitter: the first few layers of the emitter would be non-scattering to prevent backscattering of the pump light, and the core of the emitter would be more scattering in order to keep the irradiance of the incident beam high. In this manner, high raw efficiencies could be reached at lower input powers. Finally, here we discussed only
one grain size distribution of particles of random shapes. Attention to particle shaping and size could further improve our results.

### 3.3 Chapter three summary

We investigated two processes which are detrimental to UC efficiencies. One is pump-induced temperature rise in UC emitters, particularly the blue emitter due to the non-resonant of the UC process in this material. The other is scattering in the emitting powders which decreases the amount of pump available to be absorbed by the emitter through back-scattering. Scattering also increases the incident irradiance at the surface of the emitters while shortening the penetration depth. We showed how a combination of simple thermal management, e.g. using a heat diffusive substrate and short pulse excitation, and dispersing the emitters in index-matched binders significantly increases raw UC efficiencies for all three emitters. We can apply these results to engineer bright and efficient UC displays.
4.1 Three color displays

4.1.1 Monochromatic emissive screens optically written in reflection

Figure 4.1: Green, red and blue emissive UC screens optically written in reflection via vector-scan (top) in the shade and (bottom) in the sun. For the red screen rhodamine B was incorporated in the binder to absorb the green emission of erbium. The substrate is aluminum. The screens are 5 cm on a side.

Monochromatic UC screens were made by casting UC powders mixed in a binder on an aluminum substrate. These screens were not pixilated. On such a screen an image is formed by exciting the screen in reflection, i.e. the viewer is on the same side as the source of the pump beam. An image is formed by either raster-scanning or vector scanning the infrared beam across the screen. The pixel size is defined by the pump
beam spot and the scattering. For these screens, we were targeting the highest powder
density we could deposit and seal with a binder on the substrate: it was not meant to
optimize the screen for scattering issues. We did use an aluminum substrate as means to
minimize pump-induced temperature effects in the UC materials.

The casting technique employed was layering powder mixed in dissolved binder and
evaporation of the solvent. The particle size and the proportion of powder and binder
were determined so the solution could be easily cast, give homogenous layers, and so the
screen wouldn’t damage too easily. Accordingly, the particle size is about 5 to 10
microns and the (dry) density was 2/3 powder, 1/3 polymer by volume. We note that the
UC materials are safe under MSDS, but since they are fluoride compounds in the form of
powders, basic safety rules apply when handling it: gloves and mask, and grinding in a
glove box.

4.1.1.1 Preparation of powders

AC materials provided UC material coarsely powdered. To be able to cast the powder on
the substrate, the particles had to be reduced to fine size. The size selection was dictated
by practical issues rather than scattering issues. These include preventing the clogging of
the micro-pipette tip and the particles settling too quickly when being cast (see below).
Scattering issues were not taken into consideration for that particular kind of screen. The
particles were reduced to ~10 microns by wet-milling with a Micronizing Mill by
McCrone, Inc. It’s a planetary grinder type of mill with corundum cylindrical elements
in an inert polypropylene jar. The mill accepts as starting material particles under 400
microns in diameter. The coarse particles were lightly ground with an agate mortar and
pestle. The powder was then sieved between a 400 micron mesh stainless steel sieve and a 106 micron sieve in order to start with a certain size distribution. The particles were mostly ~ 200 microns in size.

Figure 4.2: Particles of Er,Yb:NYF. 1 graduation on the scale is 2.5µm.

5 g of powder (~ 1 µL) was milled with 7 mL of high purity methanol for 2 minutes. The slurry was poured into a glass bottle. The bottle was put in an ultrasound bath for a few minutes to separate finer particles from the particles of interest. Once removed from the sonicator, it was left to settle for 30 seconds after which the heavier particles settled in the bottom and we decanted the suspension to eliminate the sub-micron particles. This allows a tighter size distribution. The solvent was evaporated under vacuum using a Rotary Evaporator by Yamoto, Inc. The resulting size distribution was ~ 5 to 20 microns with the peak near 10 microns (see Figure 4.2). We note that because Er,Yb: NYF is not a single crystal at its growth, each particle of this material might still be an agglomeration of several finer particles, because the milling didn’t break these bounds.
4.1.1.2 Polymeric binder

The binder we use is p-PMMA. The phosphorylation of the PMMA is necessary for the binder to withstand the particles otherwise surface tension and thermal expansion at room temperature makes the polymer crack as illustrated in Figure 4.3 (a). The binder was prepared by Dr Belfield’s team at the Chemistry Department of UCF. However it was observed that while the polymer didn’t crack, the dispersion of powder was not homogeneous either. This is because the powder re-agglomerates. To remedy to that we used a surfactant PMMA-co-methacrylic acid (PMMA co-PMA) which was added at 10 % by weight (10 wt%) to the p-PMMA. The surfactant was a commercial grade compound. To evidence the effect of the surfactant we made low density samples of particles in the binder with or without surfactant. The powder density in the binder was 30%. In Figure 4.3 (b), no surfactant was used and the islands are particles which were not properly wetted by the polymer. In Figure 4.3 (c), surfactant was used and the sample becomes clear as all particles are wetted.

Figure 4.3: Particles in binder for (a) regular PMMA, (b)p-PMMA with no surfactant and (c) p-PMMA with surfactant. Powder density in polymer was 30% for these samples. 1 graduation is 0.5 mm.
Dissolving the polymer takes two factors into consideration: the evaporation time of the solvent, and the viscosity of the solution. Many solvents dissolve the polymer. The solvent used here was dioxane. It was chosen for its high boiling point as the evaporation needs to be slow for stability. Anisole also worked. Solvents with lower boiling point (THF, methanol, acetone, etc.) created bubbles, and evaporated too quickly to allow homogeneous settling of the powder. The viscosity of the binder was set to 10 vol%. If it’s too viscous it becomes difficult to cast, and the viscosity should be kept under 20 vol%. If it’s too fluid it takes longer to dry, and the particles might settle too quickly and not homogeneously. A good viscosity ranges from 10 to 20 vol%. Polymer and surfactant are dissolved separately, both in dioxane, using magnetic stirring for several hours. Then the surfactant is slowly incorporated into the polymer warmed to ~ 45ºC. The typical quantities for one layer are 45 mg of p-PMMA in 300 µL dioxane, 5 mg of surfactant in 200 µL dioxane for a total of 50 mg polymer in 500 µL dioxane (10% viscous). In the case of the red emitter we added rhodamine B dye directly in the polymer. This dye absorbs at 550 nm and re-emits at 610 nm.

4.1.1.3 Casting of screens

The area cast was 5 x 5cm. A first layer of clear (undoped) binder was cast to create better adherence of the mix to the aluminum substrate. Once this first layer dried the powder and binder mix was cast layer by layer. A “doped” layer is: 100 µL of powder in 500 µL of dissolved polymer (10% viscous) pipetted with a 500 µL micro-pipette. The amount of powder was measured by weight. By referring to Table 4.1 we determine the corresponding weight needed to obtain 100 µL of powder.
Table 4.1: Mass density of UC emitters and of polymer

<table>
<thead>
<tr>
<th>Material</th>
<th>Red emitter</th>
<th>Green emitter</th>
<th>Blue emitter</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass density (g cm⁻³):</td>
<td>5.62</td>
<td>4.67</td>
<td>4.70</td>
<td>~1</td>
</tr>
</tbody>
</table>

Mass densities of UC emitters calculated from data in Table 2.3 for the Yb⁺⁺⁺ doping concentrations used.

The cast was done by pipetting (in one time) the set volume of solution, depositing it on the substrate and spreading it evenly across the surface using a cylindrical rod with spacers illustrated in Figure 4.4. The spacing was simply done by wrapping tape at two ends of the rod so that the thickness under the rod would match the volume to spread. Considering the area, the viscosity of the solution, and the tolerance on our improvised scraper, the volume of solution for one layer was 500 µL. Thus the spacing on the spreader rod was set to 200 µm.

Figure 4.4: “Scraper”.

The first layer of clear polymer solution is left to evaporate for 4 hours. Then 4 layers of powder in binder were cast one hour apart. The resulting dry screen is ~200 µm thick. The thickness is the result of cosmetic concerns: when casting the screen, the first layer of powder in binder didn’t seem homogenous in appearance because the surface of the aluminum substrate was not perfectly flat or a few air bubbles might have been present, so layers were added until the screen was visibly homogeneous. Mock screens with...
fewer layers that didn’t look homogeneous in aspect were tested too and the image optically written on the screen was homogenous and most of the infrared was either absorbed or backscattered even in thinner screens. The inhomogeneity that we see is actually on the macroscopic scale, but locally the pump sees a homogeneous volume. This is because the screen is highly scattering due to the low proportion of polymer, and most of the pump absorption occurs within less ~50 µm. For this particular type of screen, adding layers does not change the screen performance.

As we will see the resulting screens are very bright and adequately served our demonstration purpose. The screens we describe here were made in May 2004 and two years later their performances remain unchanged. Other screens have been used for an even longer time and have also not suffered any degradation. However the casting technique is not very practical. Casting by evaporation is clearly not the best way of making a screen. Using a solvent-less, moldable polymer might be easier as long as the powder can be homogeneously incorporated into it.

4.1.1.4 Performances of UC reflective screens

We characterized the performances of the particular screens we made. Since these screens were hand-made the results obtained must be considered examples of performances and not optimized values. For each screen we characterized one “pixel” of the screen with a 975 nm diode laser beam focused to a 1 mm spot and modulated at 60 Hz for various pulse durations. One “pixel” is defined as the spot made by the pump beam, i.e. the size of one pixel is the same as the beam spot size. In the following we detail the results for the green UC screen. The brightness of the green emission (which is
the same quantity as luminance) was measured with the TOP100 spectrometer accessory of the CAS by Instrument Systems. The area of the detector (0.5 mm in diameter) was flooded with green light. We measure the brightness of the total green emission, i.e. by integrating the luminance spectral density curve between 500 and 600 nm. In Figure 4.5 we plotted the ratio of brightness to average incident power with respect to average incident power.

For that particular screen, the maximum raw brightness efficiency for the green emission was measured to be \(~2.1 \text{ (kcd/m}^2\)/mW\) for a 1 mm diameter spot size. The data shown in Figure 4.5 demonstrates the results of Section 2.3, that is, the efficiency depends on pump peak irradiance. For one “pixel”, and for a pulse length \(t_p \geq 1\text{ms}\), maximum efficiency is obtained for a peak irradiance of \(~70 \text{ W/cm}^2\). For instance, for a 1 ms pulse duration source modulated at 60 Hz and focused to a 1 mm diameter spot, this irradiance
corresponds to an average incident power of ~33 mW (see Equations 2.10 and 2.11) which produces a maximum brightness efficiency as demonstrated in Figure 4.5 (a). In Figure 4.5 (a) we also see that it is not the only incident power producing maximum efficiency for this excitation. Indeed the corresponding brightness efficiency curve levels off to a maximum value for a range of input powers. We arbitrarily define the grey level range as the range of peak irradiances where the brightness efficiency drops by a factor of 2% from its maximum value. The grey level range was estimated to be ~ 50 to 120 W/cm². For a 1 ms pulse duration it corresponds to a range of powers between 25 and 60 mW. In Figure 4.5 (a) we verify that for powers within this range the brightness efficiency is ~ constant and maximum, and in Figure 4.5 (b) we see that the produced brightness’s range from ~50 to 125 kcd/m² for this particular excitation. For a pulse length $t_p \leq 1$ ms, the peak irradiance needed for maximum efficiency becomes

$\sim 60 \cdot \frac{1 \text{ ms}}{t_p (\text{in ms})}$ W/cm² and the grey level range is rewritten accordingly. As mentioned in Section 2.3.4, 1 ms is related to the excitation lifetimes of the dopants.

The performances of the red and blue UC screens that we made are given in Table 4.2. Since the human eye is less sensitive in the blue and the red, the brightness efficiency for these screens is less than for the green UC screen. We still measure tens of kcd/m² of brightness’s at maximum efficiency for a 1ms pulse duration, 60Hz excitation and a 1 mm beam spot.
Table 4.2: UC screens specifics for operation at maximum brightness efficiency for a 1 mm diameter pixel and focus spot

<table>
<thead>
<tr>
<th>UC screen</th>
<th>Maximum brightness efficiency ((kcd/m²)/mW)</th>
<th>Required peak irradiance (W/cm²) for ( t_p \geq 1 \text{ms} )</th>
<th>Estimated grey level range (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green</td>
<td>2.1</td>
<td>70</td>
<td>[50 to 120]</td>
</tr>
<tr>
<td>Red</td>
<td>0.35</td>
<td>70</td>
<td>[50 to 120]</td>
</tr>
<tr>
<td>Blue</td>
<td>0.5</td>
<td>100</td>
<td>[100 to 170]</td>
</tr>
</tbody>
</table>

Peak irradiances for \( t_p \leq 1 \text{ms} \) should be scaled by \( \frac{1}{t_p \text{ (in ms)}} \).

These values are specific to these particular screens and for brightness’s measured for a 1 mm spot size by flooding the area of detection. It is important to understand how all quantities scale with pixel size (which is equal to the beam spot size) and area of detection. By operating at maximum efficiency, we mean operating at maximum power efficiency as defined in Equations 2.6-9. We saw in Section 2.3.1.1 that this maximum power efficiency is invariant with beam spot size, but the maximum brightness efficiency depends on pixel size and pixel density on the screen area of consideration (see Equation 2.17). The output brightness of the screen is the maximum brightness efficiency corrected for pixel size and density times the average power of the pump needed to reach the required peak irradiance. This average power needed from the source depends on pump focus (the tighter the focus, the less power needed) and duration of illumination of the pixel (Equation 2.10 and 2.11). The following are guidelines on how these factors scale and what performances they produce for the green UC screen operating at maximum efficiency, i.e. with a peak irradiance requirement of 70 W/cm² (or 70·(1 ms/\( t_p \text{ ms} \)) W/cm² for \( t_p \leq 1 \text{ms} \)). In what follows we still assume that the physical size of the pixel is always the same as the focus spot size of the 975 nm pump beam.
Table 4.3 illustrates the pulse duration dependence of the average power required to achieve maximum efficiency at 60 Hz for a 1mm diameter spot size. In this case we used the maximum brightness efficiency given in Table 4.2. In Table 4.3 we also calculated for each pulse length the resulting brightness and luminous intensity for one green pixel. The luminous intensity is the brightness times the pixel area. We note that the total luminous flux (i.e. output power in lumens) is then obtained by multiplying the luminous intensity by the solid angle which is a constant ideally equal to $\pi$ for Lambertian emitters. However for this screen, considering its high scattering and the low surface quality of our aluminum substrate, we estimate that not all the light emitted is collected. This can be improved by proper light extraction through index matching, pixel shaping and using a better reflective substrate. Since it doesn’t add to our demonstration here to precisely calculate the luminous flux we only report the luminous intensity (in candelas). We see that for pulse durations shorter than 1 ms, the average power, brightness and luminous intensity are the same as for a pulse duration of 1 ms.

In Table 4.4 we set the pulse duration to 1 ms and we vary the focus spot size. Again we calculate the performances from one green pixel, assuming that the area of detection is smaller than the pixel. Here we must use Equation 2.17 to properly scale the brightness efficiency from the value in Table 4.2. We see that for the screen operating at maximum efficiency, the brightness doesn’t depend on spot size, however the luminous intensity (and output power) do.
In Table 4.5 we project the pixel density and power requirements for a 1 x 1m UC screen operating at a target brightness of 1 kcd/m². If the screen is made like our prototype and for all pixels operating at maximum efficiency, the number of pixels needed is the ratio of the targeted total luminous intensity (1000 cd for a 1 m² area screen) to the luminous intensity of one individual pixel as reported in Table 4.4 for each pixel size. Table 4.4 also gives the average power required for one pixel. Multiplied by the number of pixels which are on, it yields to the total average input power requirement. Most images only require about 15% of the pixels to be at full brightness at any one time but we can study the extreme case of a full green display of maximum brightness. We see that ~ 610 W of total optical power would be required. Excitation tiling will be needed in order to achieve this. This means several diodes would be used, each to address different parts of the screen. Contrary to tiled LCD where the electrodes physically separate each tile, in a UC display the tiling would be seamless. Assuming one uses 5 W diode lasers (122 of them), we can break such a display down as shown in Table 4.6. We underline that these data are given for operation at maximum efficiency. In this case, when using tiling, making a high definition screen only depends on how tightly the pump can be focused, with no deterioration of the performances.
Table 4.3: Output of the green screen for different pulse durations at 60 Hz for one pixel, 1 mm diameter, obtained by focusing the pump light on the screen surface to a spot of the same diameter as the pixel

<table>
<thead>
<tr>
<th>Pulse length (ms)</th>
<th>Peak irradiance needed (W/cm²)</th>
<th>Average pump power (mW)</th>
<th>Brightness from one pixel (kcd/m²)</th>
<th>Luminous intensity from one pixel (mcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>70</td>
<td>66</td>
<td>138</td>
<td>108</td>
</tr>
<tr>
<td>1</td>
<td>70</td>
<td>33</td>
<td>69</td>
<td>54</td>
</tr>
<tr>
<td>0.5</td>
<td>140</td>
<td>33</td>
<td>69</td>
<td>54</td>
</tr>
</tbody>
</table>

Table 4.4: Output of the green screen for different pixel diameters for a 1 ms, 60 Hz excitation obtained by focusing the pump light on the screen surface to a spot of the same diameter as the pixel. The target peak irradiance is 70 W/cm² to operate at maximum efficiency

<table>
<thead>
<tr>
<th>Spot diameter (mm)</th>
<th>Average pump power (mW)</th>
<th>Brightness efficiency (kcd/m²/mW)</th>
<th>Brightness from one pixel (kcd/m²)</th>
<th>Luminous intensity from one pixel (mcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33</td>
<td>2.1</td>
<td>69</td>
<td>54</td>
</tr>
<tr>
<td>0.5</td>
<td>8.25</td>
<td>8.4</td>
<td>69</td>
<td>13.5</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0825</td>
<td>840</td>
<td>69</td>
<td>0.135</td>
</tr>
</tbody>
</table>

Table 4.5: Application to a large 1 x 1 m monochrome green screen (if made the same way as this screen), for a target brightness of 1 kcd/m², refreshed at 60 Hz.

<table>
<thead>
<tr>
<th>Spot diameter (mm)</th>
<th>Number of pixels needed</th>
<th>Total average pump power necessary to light up 100% of the pixels (W)</th>
<th>Total average pump power necessary to light up 15% of the pixels (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18,520</td>
<td>610</td>
<td>92</td>
</tr>
<tr>
<td>0.5</td>
<td>74,075</td>
<td>610</td>
<td>92</td>
</tr>
<tr>
<td>0.05</td>
<td>7,407,500</td>
<td>610</td>
<td>92</td>
</tr>
</tbody>
</table>
Table 4.6: Application to large display obtained by tiling 1225 W diode lasers to excite 100% of the pixels

<table>
<thead>
<tr>
<th>Spot diameter (mm)</th>
<th>Number of pixels written by a single diode</th>
<th>Pulse duration required on each pixel (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>152</td>
<td>105</td>
</tr>
<tr>
<td>0.5</td>
<td>607</td>
<td>26</td>
</tr>
<tr>
<td>0.05</td>
<td>60,717</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Finally we note that the reflective screens we described above are simple prototypes to demonstrate the brightness capabilities of conformable types of UC displays. They are straightforward to address since they are not physically pixilated. However they suffer from low contrast and high scattering. As a result they might not appear as bright as they really are, and an image displayed on such screens can seem fuzzy. Transparent screen and/or pixilated screens would be attractive choices for manufacturing a UC display.

4.1.2 Transparent screens and pixilated screens

4.1.2.1 Transparent screens

There are two incentives to render the emitter doped-binder transparent. One is to reduce scattering to improve raw efficiencies as we saw in Section 3.2 regardless of the mode of operation (in reflection or in transmission). The binder p-PMMA-co-surfactant has an index of refraction close to that of the UC emitters (~1.51). It is adequate to use to obtain near-index match for all three emitters when the powder density in the polymer is not too high (i.e. so that all particles can be properly encapsulated). This is why the sample in
Figure 4.2 (b) which had a low particle density in p-PMMA, 30 wt %, appears fairly transparent and we don’t see the particles. The other incentive is to make fully transparent displays. In this case the mix is cast on a transparent substrate such as glass (see Figure 1.3(b)), or CVD diamond for a transparent substrate with outstanding heat dissipation properties. We can even use as a substrate the color filter needed to eliminate the extra visible emission of the UC materials. This illustrated in Figure 4.6 where we cast a blue UC screen on a BG14 glass filter and addressed the screen in transmission by vector scanning.

Figure 4.6: Example of blue UC screen written in transmission. The substrate is 5 cm on a side. A 975 nm, 500 mW diode laser beam was scanned by galvanometer mirrors on the screen (average power on one pixel was less than 10 mW).

The green emitting transparent screen of Figure 1.3 (b) was made with the same casting technique as used for the reflective screens, but with a low density of particles, 30wt%, in the binder and glass as a substrate. The same excitation was used as for the photos of the reflective UC screens. Clearly this is a very bright emissive transparent screen,
however the green light is still scattered in the emitter-doped-binder (the displayed imaged looks fuzzy) and by the glass. This is because the index-match is not perfect and there is no pixel to confine the lambertian emission of one spot, some of which rattles around in the thickness of the glass. Still it shows the possibility of a transparent display.

![Graph](image)

Figure 4.7: Tunable index of refraction in sol-gels. The proportions are in dry wt%.

It is possible to obtain better to nearly perfect index match by tailoring the refractive index of the binder. In polymers, this is done by polymerizing two monomers of high and low indices of refraction in various proportions. For instance, 6F and PB or 6F and TVE polymerize into PFCB of tunable index[88, 89]. Sol-gels also allow index tuning and we experimented with this binder[90-92]. Samples were made at Ecole Polytechnique (France) under the direction of F. Chaput by varying proportions of M-TEOS (CH$_3$-Si-(O-C$_2$H$_5$)$_3$, index 1.43) and φ-TEOS (φ-Si-(O-C$_2$H$_5$)$_3$, index 1.56). A catalyst in aqueous solution proprietary to F. Chaput acts as a surfactant and allows better
optical quality of the resulting gel. The individual sols were dissolved in aqueous solutions, M-TEOS by 42 wt% and φ-TEOS by 58 wt%. We mixed them in different proportions to make samples of 1 mL in solution and added 10 µL of catalyst. We spin-coated squares of silicon wafer 2 cm on a side which we then dried in an oven. The index of refraction of the samples was measured by ellipsometry. In Figure 4.7 we plot the index of refraction obtained with respect to the proportion of each sol. We note that we were not able to make satisfyingly stable sol-gels for concentrations of φ-TEOS larger than 50%. It seems that the two sols don’t mix well in this case.

We attempted to incorporate our UC emitters in these sol-gels. First we made samples in a cylindrical 3 mm-diameter, 2 mm-deep cavity bored in acrylic cabochons. In order to allow better adherence and reduce surface tensions the walls of the sample holder were pre-coated with 6 µL of the sol-gel solution which we put for 5 minutes in an oven at 70°C so the pre-treatment layer would still be soft. In a separate container we mixed 10 mg of 20 µm diameter particles of Er,Yb:NYF in 15 µL of sol-gel of various indices dissolved in water by 50 wt%. We degassed the resulting solution for two minutes in an ultrasonic bath before depositing the mix inside the cabochon. The sample was dried for 30 minutes in the oven at 70 °C. This temperature was set to minimize thermal expansion issues. Even with these precautions many of our samples presented cracks or bubbles at the surface or near the acrylic walls due to the too high a temperature expansion mismatch of our emitters in sol-gels and the acrylic cabochons. Still these were high powder density samples with the additional complication of being encapsulated in the acrylic holder. Figure 4.8 shows a set of successful samples for various indices of
refraction. The samples were placed on a high-reflectance flat surface under a white diffused neon light and photographed with a Camedia Olympus© digital camera. The color of these images was not processed. Er,Yb:NYF is a birefringent crystal and in no or index-mismatched binder as in (a) it has a pink color meaning some of the visible spectrum is scattered. We can see the progression of index-matching as the pink hue disappears in (b) and (c) and reappears in (d). A good match for this birefringent crystal is $n \approx 1.46$ which is confirmed by comparing the green raw efficiencies of the samples (Figure 4.9).

Figure 4.8: Er,Yb:NYF in sol-gels of index of refraction (a)1.42, (b)1.46, (c)1.48 and (d)1.57.
Figure 4.9: Green raw efficiency of Er,Yb:NYF in sol-gels of various refractive indices. The 975 nm excitation beam was modulated at 30Hz with a 2ms pulse duration and focused to 900μm.

Sol-gels were also used to create a first instance of a thin structured emitter. On a glass substrate 2 cm on the side, we deposited a layer of polymeric adhesive of the same size. Such adhesive is adherent on both sides. We “dipped” the substrate, adhesive side faced down, on a stack of finely ground Er,Yb:NYF particles for them to adhere to the substrate. Then we spin-coated (at 2000 rpm for 15 seconds) n=1.46 sol-gel solution on top of it in order to both seal and act as a scattering reducing layer. The screen was gently dried at 70°C for 20 minutes. The result was a near-transparent, slightly diffusive screen which demonstrated the feasibility of this technique. However it only allows thin layers of emitters, since only one layer of powder can stick on the adhesive. Stacking up layers could be a solution, as long as the adhesive sticks to the sol-gel and no solvent is used that would dissolve the polymeric adhesive.
In the course of our study, only p-PMMA withstood high concentrations of particles in the binder without cracking. The other binders would need to be phosphorylated (or equivalently treated). An alternative is to use polymer jellies, such as LS-3249 polymer gel by Lightspan (NuSil)©[93]. These do not harden. Of course such a mixture is not rigid so they would need to be encapsulated in a hard shell. In a pixilated screen in particular jellies would minimize the problems of heat expansion while remaining practical since the pixel grid constitute hard walls and we can seal the pixel top and bottom with a protective layer which can also constitute the filtering system. Which ever binder we use, most of them don’t absorb at our 975 nm excitation wavelength and they are not damaged by IR light as they are by UV light.

4.1.2.2 Pixilated screens

Figure 4.10: Three color pixels of a CRT screen[94].

In an actual three color UC display the screen would most likely be pixilated to improve contrast (see Section 4.1.3.1), light extraction and cooling of the UC phosphors. The manufacturing of such pixilated screens can been done via the same well developed techniques already used in production lines for existing mature technologies. One straightforward option is to use the same process as the one used to make CRT screens.
This process has been well optimized over the past 80 or so years in which CRT technology was developed. An illustration of a CRT pixilated screen is shown in Figure 4.10. The color phosphors are prepared in separate transfer films which are composed of several stacks of layers, including the color filter, the phosphor and various additional protective layers proprietary to fabrication methods (see Figure 4.11)[94, 95]. All layers contain water soluble photopolymers to allow exposure and development. The transfer film is pressed onto the pixel grid stacked on the substrate (a glass panel for CRT screens). Then the pixels are selectively exposed through a mask with UV light so as to cure the photosensitive polymer where the pixels are formed. What wasn’t exposed is washed away with water (development). This process is repeated for the red, green and blue pixels.

![Figure 4.11: Example of structure of CRT transfer film][95].

An alternative method to make pixilated screens would be to ink jet print the UC emitters-binder mix onto a substrate. Ink jet printing of our phosphors and binders has
already been demonstrated by Vadim Laser of VLEngineering [96]. It could be done on a plain substrate (i.e. one with no physical pixels). This is a simple method to improve contrast compared to our casting method described above. In case of a pixel grid, the ink jet printer would be aligned with the pixels. Current ink jet printers can handle quite a dense resolution, so the main constraint would be the alignment process.

The pixel grid should preferably be black to maximize screen contrast and of high heat dissipation coefficient. Using micro-lithography, the pixels on the grid can be shaped to allow maximum light extraction and cooling of our emitters. In Figure 4.12 we show pixels of different shapes and sizes made by Prof. Huikai Xie at University of Florida (Gainsville, FL). It was done on a silicon wafer, and this wafer can be coated with silver inside each pixel for instance to improve light extraction, and coated with black paint in between pixels to ensure good contrast.

![Image of pixel patterns](image)

**Figure 4.12:** Pixel patterns by micro-lithography in silicon wafers. In all cases the total area of the pattern was 1 mm on the side. The depths of the pixels are, from left to right, 50 μm, 50 μm and 100 μm.
4.1.3 Display considerations

In this work we have assessed the performances of three color UC screens in terms of the scientific results we have obtained on the UC processes. The next step is the engineering of such UC displays. The ultimate rating of the performances of the fully integrated display involves additional criteria other than just emitter performances. These criteria include screen contrast and efficiency of the scanning system. Most engineering solutions are application-related but we can present an overview of such display considerations.

4.1.3.1 Importance of contrast

![Figure 4.13: High and low contrast red, green and blue screens (top) indoors and (bottom) outdoors.](image)

The performance of a display screen are often rated in terms of contrast. Contrast is related to the ratio of the brightness’s of two neighboring areas. The higher this ratio, the brighter the brights will appear to the human eye, and the darker the darks, regardless of
their respective absolute brightness’s. This is because the human eye is more sensitive to relative brightness’s than absolute ones. It means that the perceived brightness is not always equal to the one that is measured. For instance in Figure 4.13 we painted a dark color ink on a portion of our green and blue UC screens. If we disregard the 4 corners of the lissajou pattern on the top row photos which are brighter due to an artifact of the vector scan (see next Section), the pattern displayed on these screens is generated with an infrared beam of invariant irradiance, so it should appear homogeneously bright. Yet on the inked background we see the green greener and the blue bluer than on the white looking background. As for the red screen, we photographed with poor ambient lighting so the background appears darker and again the red appears redder in the high contrast case. We also see the edges of the pattern sharper on the higher contrast portion. This is because the eye is also more sensitive to very high (and very low) spatial frequencies when the contrast is high. We could improve the contrast by casting an index-matched (transparent, low scattering) particle – binder combination on a dark color substrate. High contrast would be easily obtained in pixilated screens by using a black matrix for instance and designing the pixels so as to minimize light leakage in the screen surface.

4.1.3.2 Examples of scanning methods

Until now we have mainly shown examples of displays addressed by an infrared beam deflected by galvanometer mirrors which moves the beam to any point on the screen. This is vector scanning. Images are formed by the combination of moving the beam directly to the next “on” pixel at any desired speed and modulating the diode laser’s intensity for grey level effects. The galvanometers operate discretely, i.e. the beam is
moved to a finite number of points and the dwell time on each spot is usually longer than
the transit time between two points. This means the average incident irradiance on the
screen is less in-between points and so is the brightness of the UC process. The average
incident irradiance is also higher if the beam is set to stay on the same point or if the local
curvature of the pattern is high (e.g. sharp corners). This is why the Lissajous patterns of
Figure 4.10 are brighter in their corners. This could be corrected by a proper modulation
of the diode laser intensity. Such vector scanning is simple to implement, however it is
adequate only for simple patterns, not images with a large amount of information to be
displayed. Indeed the frequencies needed to drive the mirrors in order to display full
screen images would be too high for the galvanometers to withstand.

![Figure 4.14: Raster scan of excitation beam.](image)

When a large amount of information must be displayed on the screen, a raster scan
method is preferred. This is the scanning system used in CRTs. The beam is
continuously swept along a row of pixels by a high frequency mirror then is brought to
the next row by a low frequency mirror (see Figure 4.14). As it dwells on each pixel the
intensity of the excitation beam is modulated according to the color and the brightness of
the information to be displayed, from off (dark pixel) to fully on (full brightness pixel).
We demonstrated the feasibility of raster scanning our UC screens with a dual axis
acousto-optic deflector from NEOS. It is composed of two acousto-optic modulators (AOMs), one for each of the X and Y directions. An AOM is a medium with index of refraction that can be changed by passing an acoustic signal through it. When the acoustic signal forms a grating in the sample the light beam will be deflected by some angle. The angle of deflection depends on the wavelength and angle of incidence and the frequency of the acoustic wave. The incident beam must be collimated and of the correct wavelength for the AOM to be efficient. The NEOS AOMs were optimized for 632 nm. Therefore they were quite lossy for our infrared excitation beam. However they served our purpose of demonstration.

The setup was the following. The diode laser beam was collimated and passed through the AOMs. They were driven by Labview to sweep 40x40 points at 60 Hz. Labview was also used to modulate the diode laser intensity to form an image in grey levels. A straightforward way to form an image on the screen is to place the screen at the focal plane of a converging lens to focus the scanned beam into tight pixels. However due to the small angular spread of the AOMs (5 degrees), we then need to compromise between size and resolution of the display (a resolved display being one where neighboring “pixels” don’t overlap), as both size and spot size are proportional to the focal length of the lens. Indeed the size of the display is equal to the angular spread time the focal length of the lens (see Figure 4.15) and the size of each spot is given by the Raleigh criterion $1.22 \cdot \lambda \cdot f/\text{number}$, where $\lambda$ is the wavelength of the beam and $f/\text{number}$ is the ratio of the focal length to the diameter of the lens (note that the actual spot is bigger than the Raleigh criterion due to first order aberrations from the lens). Therefore, if the focal
length is short in order to achieve tight focus on each pixel, the size of the display will also be small. If we choose a longer focal length we can increase the size of the image, however the resolution is low. Also, our beam was not perfectly collimated so to increase the sharpness we would need to place a long focal length lens far from the AOMs which would increase the third order aberrations. Finally, with a single lens, the rays at the largest angle of deflection have a steep angle of incidence on the screen which could create some distortion and would be undesirable if the pixels are confined into a physical grid. With the help of Prof. J. Rolland we implemented an imaging system which increased the image size while keeping a reasonable resolution and angle of incidence of the beam on the display and is not too cumbersome. It consisted in first using a short focal length lens L1 to obtain an image with a high resolution, then using an afocal telescope to increase the magnification of our imaging system. An afocal telescope is formed by two lenses L2 and L3 where the second lens L3 is placed so as its object focal plane is at the image focal plane of the first lens L2. For high transverse magnification L2 and L3 are of short and long focal lengths respectively. The telescope was positioned so that the image through the first single lens L1 was formed at the object focal plane of L2 (see Figure 4.16).
Figure 4.15: Single lens imaging system: variation of image size with two different focal lengths. The solid ray is the image of the marginal ray through a lens of short focal length $f_1$, and the thick dashed ray, its image if this lens had a longer focal length $f_2$. The focal planes in each case are marked $f_1$ and $f_2$ respectively.

Figure 4.16: Image size magnification with telescope. Planes $f_i$ and $f'_i$ are respectively object and image focal planes of lens $L_i$. 
We used 50 mm, 10 mm and 50 mm focal length lenses for L1, L2 and L3, respectively. The f/ number of L1 was 1. We achieved ~ 2 x 2 cm images but the pixels were still barely resolved. An example of raster scanned images is shown in Figure 4.17 for our three color reflective UC screens. We also were able to display complex moving images. The images formed by raster scan in Figure 4.17 appear blurrier than with vector scan images because of the lower resolution of the raster scan. The resolution could be improved by using a micro-lens array after the telescope to further focus each individual spots. Also, in addition to a larger beam spot size, the scanning rate is much higher than with raster scan (for a refresh rate of 60Hz, the beam dwells ~ 10 μs on each of the 40 x 40 points). Therefore the average irradiance of the beam is low and we didn’t obtain images as bright as with vector scan. Improvement in the optics and using a less lossy deflecting system than the AOMs would easily improve the raster scan method. For example, namely using a MEMs scanner would provide throughput improvement [97, 98]. Still, our work demonstrated the feasibility of such a raster scanned UC display.

Figure 4.17: 40x40 point images formed by raster scan at 60 Hz on emissive red, green and blue UC screens. The total power of the scanned beam was 500mW at the screen. It was focused to ~0.5 mm diameter on the screens. The image displayed was ~20mm on a side.
4.2 White backlight

Because UC powders can easily be mixed in any proportion without modifying their individual properties, one can conceive of using these efficient UC materials to make a white light source. Such a white light source will have all the advantages of UC-based displays such as high brightness, high efficiency, and long lifetime. Indeed it is important to underline that because the up-conversion excitation source is in the infrared the low energy pump photons do not produce damage in the UC materials. This applies to all three color emitters. As a result, we have been able to operate UC white-light sources at tens of kcd/m² without degrading their properties. UC of this sort could be used for an all-solid-state backlight technology for LCD. It may offer advantages over mercury based lamp technology for several reasons. Current white light sources have very broad emission spectra requiring that most of the light generated be filtered out because it is at the wrong wavelength. The unused emission results in undesirable heating of the display. With UC phosphors it is possible to create a white emitter without requiring filtering technology and to tailor the color temperature. However, we saw that the supra-linearity of the UC process and the dependence of its efficiency on incident irradiance depend on the properties of the emitter. As a result, it is not straightforward to tailor a white emitter with optimum performances.
4.2.1 Engineering of a white emitter: methods

The base UC materials used in the white light technology reported here are those we already identified as most efficient: 1 % Er, 18 % Yb:YF₃, 1 % Er, 18 % Yb:NYF, and 0.4 % Tm, 20 % Yb:KY₃F₁₀. These very efficient red, green and blue UC emitters can be combined in appropriate proportions to produce white light efficiently with any desired color, x,y, coordinates.

4.2.1.1 White light by partitive mixing

One way to do this is by partitive mixing, i.e. by physically separating the red, green and blue UC powders and allowing the user to control the amount of infrared pump light incident on each primary color to obtain the desired white. As we saw in Section 2.2.3.4, both Er,Yb and Tm,Yb systems emit two narrow, well separated bands in the visible, green and red, and blue and red (see Figure 2.18), and unfiltered, the colors of the designated red, green and blue phosphors are the yellow, orange and purple indicated by diamonds in the 1931 chromaticity diagram of Figure 2.19. The UC RGB colors are obtained by filtering out the secondary visible band. The resulting triad of primaries defines the wide color gamut on the 1931 CIE chromaticity diagram of Figure 2.19 which, of course, encloses the region of white light.

At sufficiently high brightness’s it is even possible to forego the use of filters to remove the second color from each emitter. This is because the triad of colors provided by the unfiltered phosphors (yellow, orange and purple) at these irradiances produces the desired white point allowing the UC phosphors to make white light without the subtraction of color. Still if white is achieved by varying the input irradiance, simple engineering is
required to make partitive mixing feasible. Indeed, in Section 2.3.5 we explained that the proportion of the two visible colors emitted by one unfiltered phosphor varies with input irradiance. The color of the blue emitter doesn’t vary much, however that of the Er,Yb based emitters shifts towards the reds at high incident irradiances. Still, this shift is predictable and can be tabulated with respect to input irradiance.

At lower brightness’s (lower input irradiances), the unfiltered color of our current best red emitter lies above the white point in the green-yellow region. Filtering can still be foregone if we select a red emitter with a slightly higher concentration of Yb$^{3+}$. As discussed in Section 2.2.3.1 this would increases the red to green ratio, although it may reduce the efficiency of the phosphor. Still it is possible to reach an attractive compromise between very high efficiency and simplicity of engineering. For instance, 1 % Er, 22 % Yb:YF$_3$ lies at (0.49,0.48) and has a maximum raw efficiency of 4.5% or 2.1 lm/W with no binder.

4.2.1.2 Tailoring of a white light emitter operating at predetermined efficiency

Another way to make a white light source is to tailor the emitter by mixing different powders operating at predetermined efficiencies. In the mixed powder the generation of red, green and blue light is selected so that at a certain irradiance the desired white light is emitted. This is the method we investigated to create a D65 white emitter having theoretical x,y color coordinates = (0.3127, 0.3297).

The UC materials were ground into powder and sieved between No. 400 and 635 stainless steel sieves to obtain a powder of controlled average grain size ranging from 20
µm to 38 µm. The emission spectra and efficiencies of the emitters were measured by using the setup for raw efficiency measurements described in Section 2.3.1.3. The powder was packed in a cabochon with no binder. We know from Section 3.2 that using a binder greatly improves the performances of our emitters however for our proof of principle, at this point we won’t pay too much attention to performances which will be addressed in Section 4.2.3. The pump was modulated at 30 Hz and produced 2 ms duration pulses. The beam was focused to 900 µm diameter.

Figure 4.18: Measured colors of 0.4 % Tm, 20 % Yb:KY3F10 (“Blue emitter”) and 1 % Er, 18 % Yb:YF3 (“Red emitter”) excited with a 110 mW average power, 976 nm diode laser beam focused to a spot 900 µm in diameter. The diode was modulated at 30 Hz and produced light in 2 ms duration pulses. Standard D65 white is also indicated on this 1931 CIE chromaticity diagram.

As in most displays the blue emitter performance is most critical. Therefore, the average output power of the diode, 110 mW, was selected to operate the blue emitter at maximum efficiency (see Table 2.5). At the resulting irradiance the efficiencies of both green and
red emitters roll off however their brightness’s continue to increase. We measured the emission spectra of each emitter for this excitation in order to determine the proportion of powders to be mixed. It happened that the color of the designated red emitter 1 % Er, 18 % Yb:YF₃ for that particular excitation (0.437, 0.532) is complementary to the color of the designated blue emitter 0.4 % Tm, 20 % Yb:KY₃F₁₀ (0.160, 0.079) as we show in Figure 4.18. This meant that we did not need to add any of the designated green emitter to obtain that particular white. The proportion of powders was calculated by scaling and adding the two emission spectra with the mathematical software OriginPro© [85] until the resulting spectrum was that of the desired white. We determined that the “blue” and “red” powders should be mixed in a 1:2 proportion by weight. Doing so we obtained white light at (0.3120, 0.325) on the 1931 CIE chromaticity diagram with a measured raw efficiency of 7 lm/W and the emission spectrum shown in Figure 4.19. This is not an optimized performance as this emitter was tailored with no binder.

Figure 4.19: Measured emission spectrum of the tailored UC D65 white-light emitter operating at 7lm/W efficiency.
The result above applies to the particular efficiencies at which each powder was operating, i.e. for the excitation wavelength and irradiance that we used. Once again, we note that a different excitation for that mix of powder will result in an alteration of the white color because UC efficiencies depend on pump irradiance and wavelength in a way that is specific to the nature of each emitter. With no filtering the perceived color of the Er,Yb-based phosphors vary with input irradiance. Also, the green and red efficiencies in the Er,Yb system increase at a higher rate with increasing irradiance than does that of the blue emission in the Tm,Yb system (see Figure 2.26 for instance). As a result, their respective brightness’s might vary, altering the proportions needed to make the correct white. In Figure 4.20, we show how the color of our white emitter changed when we modified the incident irradiance by significantly decreasing the average power of our diode in the previous experiment. 50 mW average power produces light at Point B and 20 mW at Point C. Enlarging the focus spot of the beam will have a similar effect as it also decreases the irradiance of the pump. Thus, the mix of colors and the resulting white color that is produced can change with the specifics of the excitation.
Figure 4.20: Color of the “white emitter” as the efficiency of individual powders was modified. Points A, B and C were obtained by varying the average input power in the setup used to tailor the white emitter: 110 mW (Point A), 50 mW (Point B) and 20 mW (Point C). Point D is the white obtained in a white light diffuser demonstration: the pump was modulated at 60 Hz instead of 30 Hz as for point A and the scattering properties of the powder in a p-PMMA binder were different from the dry powder used in case A. For this emitter, the proportions of blue and red powders were ~ 3:2.

On the other hand, if the irradiance available is limited it is possible to chose UC emitters that work at that irradiance to produce white light. Here again we can choose a yellow emitter with higher Yb$^{3+}$ concentration to increases the proportion of red light emitted keeping in mind that it may cause the overall efficiency to go down. Mixing a deeper orange emitting powder with our efficient blue emitting powder will produce a color below the white temperature color line on the CIE chromaticity diagram, even at lower irradiances. Any desired white is then obtained by adding in the right proportion the third powder, our efficient green emitting 1 % Er, 18 % Yb:NYF. This is similar to partitive mixing described above, but here the emitters are not physically separated.
Finally, the all important results of Chapter three also apply here: when created to make white light by mixing powders, the resulting emitter must be used in similar scattering and temperature conditions as when it was designed. The following application illustrates this point.

4.2.2 Simple demonstration of a white light back-panel

We demonstrated a simple backlight-type panel of white light using a UC-based white emitter. We placed white paint on one side of a standard glass microscope slide to act as a light diffuser. This is clearly not an optimized diffuser but enables our demonstration. As in the design of a D65 white emitter described above, we mixed two powders, our efficient blue, 0.4 % Tm, 20 % Yb:KY\textsubscript{3}F\textsubscript{10}, and red, 1 % Er, 18 % Yb:YF\textsubscript{3}, emitters. The resulting powder was dispersed in p-PMMA serving as a passive polymeric binder, and deposited on the edge of the microscope slide. This edge had been polished beforehand for better light penetration to the inside of the diffuser. The white emitting powder was then excited with light from a diode laser operating at 976 nm. To cover the a length of the microscope slide edge we scanned the infrared beam with an acousto-optic modulator to form a ~1 mm long line of 8 spots of 950 µm diameter. Each spot was illuminated by diode laser light for 2 ms at 60 Hz with an average power of 220 mW. In this manner we recreated the excitation used to tailor the white emitter at point A: the refresh rate was doubled but the incident peak irradiance at focus of the infrared beam was the same.

Bright white light was observed flooding the diffuser. We measured the brightness of the diffused white light with a Top 100 candelameter from Instrument Systems coupled to
the CAS. At ~1 cm from the edge within the diffuser where the light was fairly homogeneous, we measured 2 kcd/m². This result was obtained despite the simplicity of the diffuser and while half of the lambertian emission of our white emitter was not guided in the diffuser. Clearly, the emission from our white light source can be greatly improved by using a better diffuser and light guiding.

The x,y coordinates of this experimental white were (0.275, 0.330). It is Point D in Figure 4.20. It is not at Point A which was the white color specifically tailored for the same incident peak irradiance. Given that the perceived color of the blue emitter is invariant, the complementary yellow color that produced Point D was in fact greener than for point A. This results from the combined effects of scattering and temperature.

As the powder was placed in a binder of similar index of refraction, it created a clearer medium than the highly scattering one used to tailor the white emitter at point A. By changing the scattering properties of the sample, the pump irradiance experienced by each emitter was modified despite using effectively the same excitation as used to design the white light emitter. As discussed in Section 3.2.1.2, the multiple scattering of the pump light inside a scattering-dominated medium causes the light distribution to be confined near the surface through which light enters such a medium. The pump light concentrates near the surface, resulting in higher pump power densities in the first layers of the sample. Therefore, in the case of a large index mismatch (e.g. dry powder) the effective irradiance of the pump is higher than for an index-matched sample (e.g. dispersed in a binder of comparable index of refraction). Also, in a scattering medium
the penetration depth of the pump light is less than in a clear medium, meaning that a smaller volume of the active medium can absorb the pump light, reducing the efficiency of the UC process.

In addition to scattering, we also modified the local temperature of the emitter. In our demonstration, in addition to not having the powder in an acrylic holder as above, we used twice the refresh rate as when we tailored point A: for the same peak irradiance, the average incident power was double, resulting in an increase of local pump-induced temperature in the powder. We saw in Section 3.1 that the UC process in the blue emitting Tm,Yb system involves non-resonant energy transfers from the Yb$^{3+}$ to the Tm$^{3+}$ ions. As a result its UC efficiency depends on temperature much more significantly than the green emission in Er,Yb system which involves more nearly resonant energy transfers. In the Er,Yb system, the UC efficiency of the red emission is more dependent on temperature than that of the green emission as more non-radiative decays and non-resonant energy back transfers to Yb$^{3+}$ are involved. Therefore a change in temperature within the white light emitter will also affect the two up converters differently, resulting in a color shift.

In our backlight application, the increased local pump-induced temperature and the reduced irradiance in the tailored powder in the p-PMMA binder made the Er,Yb:YF$_3$ powder emit more green, and the total emission insufficiently blue. As a result, we prepared a powder with more blue emitter than the 1:2 ratio called for above. The new weight ratio of blue to red powders was 3:2 and achieved the very satisfying white light
source at the color point D in Figure 4.20. The color can be easily fine tuned by tailoring the mix of emitter particles in the binder. By tailoring we mean selection of the UC emitters, choice of the ratio of the different color emitters in the white light source and the particle sizes. The color shift due to temperature change can be avoided by properly selecting the operating conditions as discussed in Section 3.1. That is by use of a proper heat-diffusive substrate and pulsed excitation.

![Image of a simple white backlight using a painted standard glass microscope slide as a diffuser. The white-light emitter mixed in a polymeric binder was cast on the left edge of the slide and excited over 1 cm with a 1.2 W average power, 970 nm diode bar modulated at 60 Hz, 12 % duty cycle. Photo in true color.]

However, we observed that the changes were not visually significant (e.g., the white light source always looked white) indicating that only simple engineering will be required for this white light source. To demonstrate the simplicity of this concept and to show a path to practical implementation of a white light source we obtained a 975 nm emitting, 1 cm long bar of diode lasers from n-Light Inc, that was mounted for us by Northrop Grumman CEO. The diode was modulated at 60 Hz with a 12 % duty cycle for a total average
power of 1.2 W. By placing a simple cylindrical lens in front of the diode bar to focus the laser light onto the edge of the microscope slide coated with our phosphors we demonstrated the white light emission shown in Figure 4.21. Clearly, placing several such lens-bar combinations along the coated sides of a proper diffuser will make possible a very bright, very simple, long lived white light source. The bars can be operated in a modulated manner at say 60 Hz to provide the desired short excitation to minimize emitter heating.

4.2.3 High brightness, high efficiency white light source

Until now we discussed methods of implementing a white light emitter with no particular attention to performances. As in three color displays these performances can be greatly improved by using thermal management as discussed in Section 3.1. Also, we can achieve high brightness, high efficiency white light emitter by incorporating it in an index-matched binder. In order to evaluate the performances capabilities of such an optimized white emitter, we tailored a white emitter in the manner described in Section 4.2.1.2, i.e. by mixing powders of blue and yellow emitters. Since these powders have different indices of refraction, only one powder will be perfectly index-matched. However we saw that precise index matching was not required to significantly improve raw efficiencies so we still expect improvement for both powders. As when no binder was used, we choose to optimize the performance of our most critical emitter: the blue emitter.
Following the tailoring process described in 4.2.1.2, we record separately the emission spectra of the blue and red emitters with the raw efficiency measurement setup, this time with powders immersed in index matching oil at 1.488. Again the irradiance was selected to operate the blue emitter at maximum efficiency. Immersed in 1.488 index oil, the red emitter also operates close to maximum efficiency with this irradiance. We then process the spectra to determine the proportion necessary to make white. We note that the color of the red emitter has drifted slightly towards the green as the effective irradiance decreases in the low scattering sample, but not significantly enough that we can’t make white light, as we can see in Figure 4.22. On the 1931 chromaticity diagram the intersection of the straight line joining blue and yellow points and the black body locus is now at higher blackbody temperature than D65 (i.e. “bluer” white). Still, a white which doesn’t sit exactly on the black body locus but close can have the same color temperature as the nearest Planckian radiator on the locus (see chapter on isotemperature.
in Reference [36]). Here we choose to tailor a white close to D65. This time the proportion of blue to red powders was 3:2.

In a cabochon, we mixed 7 mg of blue and 14 mg of red emitting powder in 3 μL of 1.488 index-matching oil and measured absolute raw efficiencies with a 975 nm beam focused to 900 μm diameter and modulated at 30 Hz producing 2ms duration pulses. At an irradiance of 110/spot size W/cm², we obtained a D65 iso-temperature white at (0.29,0.32) with a measured maximum efficiency of 13.5 lm/W. The emission spectrum at maximum efficiency is plotted in Figure 4.23 where it is compared to the one with no binder. Clearly we can make a competitive white light source which has all the advantages of UC technology.

Figure 4.23: White light emitter in high and low scattering conditions.
4.3 Chapter summary

The final design of a UC display will depend on the application however it mostly relies on already existing engineering techniques. We described examples of how to make and operate simple prototypes of three color UC displays. We demonstrated that these crude prototypes could be operated at very high brightness’s without degradation. We also discussed how to make a UC white light emitter. We describe a method of producing white light by mixing powders in proportions determined by their individual emission spectra at a given pump irradiance that allows one to precisely and systematically design a white emitting powder with UC materials. We demonstrated the high efficiency, high brightness of a UC white light emitter.
CHAPTER FIVE: CONCLUSIONS AND FUTURE WORK

5.1 UC display

UC materials were demonstrated to be efficient emitters for a novel technology of optically written emissive displays. The UC efficiencies were found to strongly depend on choosing proper operating conditions. It is essential for high efficiency UC to employ high pump irradiance, maintain the emitter at near room temperature and prepare the emitter in an emitter-binder combination resulting in minimal scattering. With this understanding it was possible to predict how to optimally use UC emitters in a wide range of applications. In particular, very efficient UC emitters were shown to be applicable to make full color 2D displays and very efficient white light sources. Advantages of this technology are: efficient emitters, very high brightness, long environmental stability, no degradation upon operation, safe and inexpensive materials and operating conditions, significantly reduced display bulk, capable of conforming to any desired shape, and great versatility. Initial applications include very high brightness displays for use in high ambient lighting conditions such as in automobiles and aircraft, and very bright, long lived white light sources.

A summary of demonstrated performances is given in Table 5.1.
### Table 5.1: Measured maximum raw efficiencies of UC emitters

<table>
<thead>
<tr>
<th>Emitter</th>
<th>Maximum raw efficiency</th>
<th>Index matched binder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No binder</td>
<td>lm/W</td>
</tr>
<tr>
<td>Red</td>
<td>7.8</td>
<td>3.6</td>
</tr>
<tr>
<td>Green</td>
<td>5.8</td>
<td>37.5</td>
</tr>
<tr>
<td>Blue</td>
<td>4.5</td>
<td>3.4</td>
</tr>
<tr>
<td>White</td>
<td>4.5</td>
<td>7</td>
</tr>
</tbody>
</table>

Efficiencies relative to optical power of 975 nm pump and with no thermal management.
5.2 Future work

High efficiencies were reported for UC emitters. However these are not the upper limits possible. The efficiencies of the materials studied can be further improved over the results in Table 5.1 by the following steps: finding the absolute UC efficiency of the blue emitter when maintained at room temperature; measuring absolute efficiency of all three emitters excited by a diode laser with a narrower spectrum of emission centered at 975 nm; pursuing index matching improvement by using proper binder, shaping the particles and studying the effect of size distribution on scattering. Other materials (crystal hosts and doping concentrations) can also be investigated with the methods demonstrated in this thesis.

Most of the physics necessary to apply UC to displays or light sources has been explored. Once a particular applications have been defined, prototypes can be engineered. This includes making pixilated screens with high contrast ratio and developing or adapting a scanning technique to the planned application.
APPENDIX A: RATE EQUATION WITH TEMPERATURE DEPENDENT COEFFICIENTS IN ER,YB SYSTEMS.
Figure A.1: Er, Yb energy transfers and transitions (in YLF). For clarity, not all radiative decays are represented.
Considering the transfers and transitions illustrated in Figure A.1, the rate equations with
temperature dependent coefficients for the Er,Yb system are given in Equation A.1. For
phonon-assisted transitions, $\gamma[T]$ is given by Equations 3.2 or 3.3. Transfer rate
coefficients independent of temperature mean that the transfer was resonant.

$$\begin{align*}
\dot{n}_1 &= \frac{n_2}{\tau_{\text{Yb}}} - \frac{\sigma_{\text{abs}}^{\text{pump}}}{h\nu_{\text{pump}}} \left[ \right] (n_1 - n_2) + \gamma_1 n_2 n_3 + \gamma_2 n_2 n_5 + \gamma_3[T] n_2 n_4 + \gamma_4 n_2 n_7 \\
&\quad - \gamma_5[T] n_1 n_6 - \gamma_6[T] n_1 n_7 - \gamma_7 n_1 n_5, \\
\dot{n}_2 &= -\dot{n}_1, \\
\dot{n}_3 &= \frac{n_4}{\tau_{\text{Yb}}} + A_{53} n_5 + A_{63} n_6 + A_{73} n_7 + A_{83} n_8 - \gamma_1 n_2 n_3 + \gamma_7 n_1 n_5 + \beta n_4 n_5 \\
&\quad + \beta_2 n_4 n_7, \\
\dot{n}_4 &= -\frac{n_4}{\tau_{\text{Yb}}} + A_{54} n_5 + A_{64} n_6 + A_{74} n_7 + A_{84} n_8 - \gamma_3[T] n_2 n_4 + \gamma_6[T] n_1 n_7 - \beta_1 n_4 n_5 \\
&\quad - 2 \beta_2 n_4 n_7 + \beta_3 n_3 n_7, \\
\dot{n}_5 &= -\frac{n_5}{\tau_{\text{Yb}}} + A_{65} n_6 + A_{75} n_7 + A_{85} n_8 - \gamma_2 n_2 n_5 - \gamma_7 n_1 n_5 - \beta_1 n_4 n_5 + \beta_2 n_4 n_7 + \beta_3 n_3 n_7, \\
\dot{n}_6 &= -\frac{n_6}{\tau_{\text{Yb}}} + A_{76} n_7 + A_{86} n_8 + \gamma_3[T] n_2 n_4 + \gamma_5[T] n_1 n_8 + \beta n_4 n_5, \\
\dot{n}_7 &= -\frac{n_7}{\tau_{\text{Yb}}} + A_{87} n_8 + \gamma_2 n_2 n_5 - \gamma_6[T] n_1 n_7 - \beta_3[T] n_3 n_7, \\
\dot{n}_8 &= -\frac{n_8}{\tau_{\text{Yb}}} + \gamma_4 n_2 n_7 - \gamma_5[T] n_1 n_8.
\end{align*}$$

(A.1)

The definitions of the coefficients are given in Table A.1.
Table A. 1: Coefficients in Er, Yb rate equations. The number of phonons is given for YLF as the host crystal

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Transition</th>
<th>Number of phonons $p^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{Yb}$</td>
<td>$^2F_{5/2} \rightarrow ^2F_{7/2}$</td>
<td></td>
</tr>
<tr>
<td>$\tau_4$</td>
<td>$^4I_{13/2} \rightarrow ^4I_{15/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{53}$</td>
<td>$^4F_{9/2} \rightarrow ^4I_{15/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{54}$</td>
<td>$^4F_{9/2} \rightarrow ^4I_{13/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{63}$</td>
<td>$^4F_{9/2} \rightarrow ^4I_{15/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{64}$</td>
<td>$^4F_{9/2} \rightarrow ^4I_{13/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{65}$</td>
<td>$^4F_{9/2} \rightarrow ^4I_{11/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{73}$</td>
<td>$^4S_{3/2} \rightarrow ^4I_{15/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{74}$</td>
<td>$^4S_{3/2} \rightarrow ^4I_{13/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{75}$</td>
<td>$^4S_{3/2} \rightarrow ^4I_{11/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{76}$</td>
<td>$^4S_{3/2} \rightarrow ^4F_{9/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{83}$</td>
<td>$^4G_{11/2} \rightarrow ^4I_{15/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{84}$</td>
<td>$^4G_{11/2} \rightarrow ^4I_{13/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{85}$</td>
<td>$^4G_{11/2} \rightarrow ^4I_{11/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{86}$</td>
<td>$^4G_{11/2} \rightarrow ^4F_{9/2}$</td>
<td></td>
</tr>
<tr>
<td>$A_{87}$</td>
<td>$^4G_{11/2} \rightarrow ^4S_{3/2}$</td>
<td></td>
</tr>
<tr>
<td>$\gamma_1$</td>
<td>$^2F_{5/2} \rightarrow ^2F_{7/2}$ while $^4I_{15/2} \rightarrow ^4I_{11/2}$</td>
<td>0</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>$^2F_{5/2} \rightarrow ^2F_{7/2}$ while $^4I_{11/2} \rightarrow ^4S_{3/2}$</td>
<td>+12</td>
</tr>
<tr>
<td>$\gamma_3$</td>
<td>$^2F_{5/2} \rightarrow ^2F_{7/2}$ while $^4I_{13/2} \rightarrow ^4F_{9/2}$</td>
<td>+3</td>
</tr>
<tr>
<td>$\gamma_4$</td>
<td>$^2F_{5/2} \rightarrow ^2F_{7/2}$ while $^4S_{3/2} \rightarrow ^4G_{11/2}$</td>
<td>+9</td>
</tr>
<tr>
<td>$\gamma_5$</td>
<td>$^4G_{11/2} \rightarrow ^4F_{9/2}$ while $^2F_{7/2} \rightarrow ^2F_{5/2}$</td>
<td>+1</td>
</tr>
<tr>
<td>$\gamma_6$</td>
<td>$^4S_{3/2} \rightarrow ^4I_{13/2}$ while $^2F_{7/2} \rightarrow ^2F_{5/2}$</td>
<td>+3</td>
</tr>
<tr>
<td>$\gamma_7$</td>
<td>$^4I_{11/2} \rightarrow ^4I_{15/2}$ while $^2F_{7/2} \rightarrow ^2F_{5/2}$</td>
<td>0</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>$^4I_{13/2} \rightarrow ^4I_{15/2}$ while $^4I_{11/2} \rightarrow ^4F_{9/2}$</td>
<td>0</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>$^4I_{13/2} \rightarrow ^4I_{15/2}$ while $^4I_{13/2} \rightarrow ^4F_{9/2}$</td>
<td>+5</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>$^4I_{15/2} \rightarrow ^4F_{9/2}$ while $^4S_{3/2} \rightarrow ^4I_{13/2}$</td>
<td>+5</td>
</tr>
</tbody>
</table>
The temperature variation obeys:

\[
\dot{T} \propto p_{\gamma_1 \gamma_2} n_2 n_5 + p_{\gamma_4 \gamma_4} n_2 n_4 + p_{\gamma_5 \gamma_5} n_1 n_8
\]

\[+ p_{\gamma_6 \gamma_6} [T] n_1 n_7 + p_{\gamma_7 \gamma_7} [T] n_1 n_4 + p_{\beta_1} \beta_3 n_3 n_7 - \frac{T}{t_D}\]  

(A.2),

where the phonon numbers \(p_\gamma\) are given in Table 5.2 for YLF as a host crystal.

The green and red fluorescence emission rates are:

\[
\dot{S}_{\text{green}} = A_{\gamma_1} n_7, \\
\dot{S}_{\text{red}} = A_{\beta_3} n_6.
\]  

(A.3).

Considering Equations A.1-3 and comparing them to the equations obtained for the Tm, Yb system in Section 3.1.1, we see that fewer rate coefficients in Er, Yb system are temperature dependent. In particular the forward UC steps from \(\text{Yb}^{3+}\) to \(\text{Er}^{3+}\) are resonant whereas the UC steps in the Tm, Yb system are phonon-assisted. This is why UC efficiency in Er, Yb systems is less affected by temperature. We verified that indeed our green and red emitters didn’t suffer pump-induced temperature effects when we measured their absolute raw efficiencies. To that end we used the FIR technique described in Section 3.1.2 to probe their temperatures. As reported in Section 3.1.3, the temperature of the green and red emitters was unchanged in the conditions of excitation we used. However, different pumping conditions might induce temperature effects. For instance, changing the repetition rate of the pulsed excitation from 30 Hz to 60 Hz could
make for sufficiently high average input powers that it would create temperature induced effects in the green and red emitters. Sufficiently high temperatures are detrimental to both red and green UC efficiencies. Therefore it is useful to monitor the temperature of both these emitters as well as the blue emitter. This is why we also document the FIR to temperature mapping for the Er, Yb based emitters. The FIR to temperature mapping for Er,Yb NYF is in Figure A.2 and that of Er,Yb YF$_3$ is in Figure A.3.

*Figure A.2: FIR in 1% Er, 18% Yb:NYF. 525 and 545 nm peaks are respectively the integrated powers between 511 and 535 nm and between 535 and 575 nm.*
Figure A.3: FIR in 1% Er, 18% Yb:YF₃. 525 and 545 nm peaks are respectively the integrated powers between 511 and 535 nm and between 535 and 575 nm.
LIST OF REFERENCES


[33] C. R. Nave, "Quantum Physics", [http://hyperphysics.phy-astr.gsu.edu/hbase/quacon.html#quacon](http://hyperphysics.phy-astr.gsu.edu/hbase/quacon.html#quacon), 1997.

[34] C. R. Nave, "Light and Vision", [http://hyperphysics.phy-astr.gsu.edu/hbase/ligcon.html#c1](http://hyperphysics.phy-astr.gsu.edu/hbase/ligcon.html#c1), 1997.


Personal communication, A. Cassanho.


[96] Personal communication, V. Laser.
