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DEPARTMENT OF THE ARMY
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STATEMENT OF THE PROBLEM STUDIED

The research conducted in this program primarily concerned identification of materials that would serve in scalable real time 3D displays. Such materials would have to experience two photon absorption of two different wavelength near infrared beams of light only at the intersection of the two beams. Upon such excitation the material would have to emit visible light. Our focus on scalable materials led us to first study organic dyes dissolved in polymeric hosts which proved to work but were insufficiently efficient for the desired application. We then concentrated on a rare earth doped cubic fluoride crystal that could be dispersed in an index matched binder to form a volumetric 3D display. Significant progress was made towards that goal and a proof-of-principle demonstration medium prepared.

Additional research evolved out of the effort above in which we studied 2D displays based on up-conversion of near infrared light in rare earth doped crystalline particles dispersed in a polymeric host. This involved fluoride crystals doped with Yb^{3+} ions as donor ions and Er^{3+} , Ho^{3+} or Tm^{3+} as acceptor ions. Our work in this area led to ultra high brightness displays ($>10 \text{ kCd/m}^2$) with no noticeable degradation in the emission due to exposure to the pump source. We also demonstrated white light generation efficiency that is comparable to some and better than other existing 2D displays. Means to optimize these displays further were identified.

SUMMARY OF THE MOST IMPORTANT RESULTS

The most important results of this work are presented in the two papers that follow. The first is an invited paper that will be published in the IEEE J. of Displays later this year concerning 2D displays based on up conversion in donor-acceptor rare earth doped particles dispersed in a passive host. In that paper we present critical results on the temperature dependence of the process and on the critical role of scattering inside the medium in determining the irradiance of the pump light. Very efficient operation is observed. The second is a paper to be submitted on the use of stepwise, non degenerate, two photon absorption in singly doped fluoride crystals in a volumetric 3D display. We show this in a bulk crystal and in a medium of particles dispersed in an index matched passive host. This proves the scalability of the concept to practical 3D display sizes.

Review of the properties of Up-Conversion Phosphors for new Emissive Displays

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Abstract

We review the properties of up-conversion materials and assess their potential for a new display technology. Up-conversion materials absorb near infrared light and re-emit in the visible. Some of their 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 operation modes, and the potential for greatly reduced display weight and depth.

I. Background

The concept of frequency up-conversion (UC) of infrared-to-visible light in rare-earth (RE) doped materials was reported more than forty years ago [1], [2]. The efficiency that was observed or expected for this process was low in singly doped media, but it was quickly noticed that the mechanism could be made one or two orders of magnitude more efficient by using ytterbium (Yb^{3+}) as a sensitizer ion in addition to the active ion: erbium (Er^{3+}), holmium (Ho^{3+}), or thulium (Tm^{3+}) [3-8]. Efficient UC materials were extensively investigated, as they could be used for several potentially important photonic applications including UC lasers [9-14] (visible lasers that are pumped by infrared diode lasers), and displays. However, because no powerful and narrow spectrum source existed in the 980-nm region to efficiently excite such up-converters no practical product came out of the research. With the development of powerful 980-nm diode lasers for the telecommunication industry and as part of the Super High Efficiency Diode Sources or SHEDS program [15] led by the Defense Advanced Research Projects Agency or DARPA (a projected diode laser efficiency of 85% optical to electrical is expected at the end of this program), the up-conversion technology which appeared to be too inefficient in the past now has legitimate practical applications.

On the emitter side, fabrication processes leading to materials of higher purity have been successfully explored by Arlete Cassanho. She now uses a process of hydrofluorination 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.

Finally our recent investigation [16-21] of those materials has enabled us to understand the optimal conditions for operation (excitation conditions, screen preparation, choice of materials) as are discussed in this paper.

The combination of the three factors listed above resulted in a maximum visible light power to incident infrared power efficiency measurement for our UC materials listed in Table I. Those numbers show that UC technology is a realistic alternative to the existing display technologies. Up-conversion offers its own set of advantages listed at the end of this paper.

II. Review of results

A. *Materials and general properties*

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:YF₃, 1% Er, 18% Yb:NaYF₄ (NYF), and 0.4% Tm, 20% Yb:KY₃F₁₀ to be desirable red, green and blue up-conversion emitters, respectively. To make this 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 between the crystallites and the polymer caused stresses and separation. A phosphorylated version of PMMA that was developed in collaboration with Prof. Kevin Belfield [22] 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) 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 Fig. 1.

The photo in Fig. 1 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 Fig. 2 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.

The UC materials absorb the infrared excitation light and re-emit the energy through fluorescence in the visible region. Because the viewer is not exposed to visible laser light, there is no speckle as in visible laser displays. 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 Fig. 3 where a wedge technology developed by Adrian Travis [23], [24] at Cambridge Flat Projection Displays Limited is used to project the infrared image onto the screen face, forming the visible image.

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, 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/m^2 without degrading their properties.

B. *Physical mechanism:*

The physical process on which up-conversion is based is as follows: first, photons from the near-infrared pump source are absorbed by the Yb^{3+} sensitizer ions. The absorbed energy is then transferred in two (or three) sequential steps to higher lying energy levels of the active ion (Er^{3+} for green and red, and Tm^{3+} for blue) in a process described schematically in Fig. 4. Visible light is then obtained through fluorescence emission. The precise emission dynamics 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 Figs. 5a and b, along with the corresponding simultaneous Yb^{3+} emission near $1\ \mu\text{m}$. The infrared excitation source was a low-energy, 4-ns pulse near 975 nm. In Fig. 5 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.

C. Excitation wavelengths

The best performing materials to date are all most efficiently excited by a 976 nm pump source as seen from the measured excitation spectra shown in Fig. 6. 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 [21].

D. Emission wavelengths

The emission from the UC emitters was recorded using a Compact Array Spectrophotometer (CAS) (Model CAS140 from Instrument Systems). Each up-converter presents two narrow emission bands. The blue and green emitting materials also emit some red light and the red emitting material emits some green as seen in Fig. 7. However, the unwanted emission bands are well separated and easy to filter out using, for example, common glass filter technology. After filtering, the color of each material is well saturated and the color gamut that results is wider than that for most existing technology (see Fig. 8).

It is interesting to note that, because UC powders can easily be mixed in any proportion without modifying their individual properties, one can conceive of using UC materials to make a white light source of arbitrary x,y coordinate in Fig. 8. In particular, we have succeeded in making a D65 white light source (point E in Fig. 8) that performed

at an efficiency of 7 lm/W by using the appropriate amount of powdered Er,Yb:YF₃ mixed with powdered Tm,Yb:KY₃F₁₀. UC of this sort could be used for an all-solid-state backlight technology for Liquid Crystal Displays (LCD). It may offer an improvement over lamp technology for two reasons: first, current light sources have very broad emission spectra requiring that most of the light be filtered out because it is at the wrong wavelength. The unused emission results in heating of the display which is undesirable for the liquid crystals. Second, use of a UC light source enables tailoring the color temperature of the backlight. This could be done either during system fabrication by mixing the appropriate amount of powders in the source or during operation by physically separating the three color UC powders and allowing the user to control the amount of infrared pump light incident on each primary color.

E. Irradiance dependence of the UC process efficiency

Since the up-conversion process involves sequential energy transfers it is non-linear in nature and since it does not have a threshold, any grey level can be accessed once the response function of the screen is known. However, in order to operate the materials at maximum efficiency the energy density of the pump light on the powder should be maximized. This phenomenon is demonstrated in Fig. 9a showing the ratio of the brightness's measured to the incident infrared power on the screen for the three primary-color emitters deposited on a glass slide. The corresponding brightness's are plotted in Fig. 9b and can be seen to exceed tens of kcd/m² for the three colors without deterioration of the UC emitters.

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. A simplified set of equations is given here for the green emitter, where back-transfers, cross-relaxations and several other Er energy levels have been ignored:

$$\begin{aligned}
\dot{n}_1^{Yb} &= \frac{n_2^{Yb}}{\tau_{Yb}} - \sigma_{Yb}^{abs} \frac{I_{pump}(t)}{h\nu_{pump}} (n_1^{Yb} - n_2^{Yb}) + \gamma_1 n_1^{Er} n_2^{Yb} + \gamma_2 n_2^{Er} n_2^{Yb} \\
\dot{n}_2^{Yb} &= -\dot{n}_1^{Yb} \\
\dot{n}_1^{Er} &= \frac{n_2^{Er}}{\tau_2} + A_{31} n_3^{Er} - \gamma_1 n_1^{Er} n_2^{Yb} \\
\dot{n}_2^{Er} &= -\frac{n_2^{Er}}{\tau_2} + A_{32} n_3^{Er} + \gamma_1 n_1^{Er} n_2^{Yb} - \gamma_2 n_2^{Er} n_2^{Yb} \\
\dot{n}_3^{Er} &= -\frac{n_3^{Er}}{\tau_3} + \gamma_2 n_2^{Er} n_2^{Yb}
\end{aligned} \tag{1}$$

In the above set of equations n_1^{Yb} , n_2^{Yb} , n_1^{Er} , n_2^{Er} and n_3^{Er} are, respectively, the populations of the $^2F_{7/2}$ and $^2F_{5/2}$ levels of Yb^{3+} and of the $^4I_{15/2}$ ground level, $^4I_{11/2}$ and $^4S_{3/2}$ (green emitting level) of Er^{3+} , τ_i are the corresponding state lifetimes, A_{ji} are the decay rates from j to i , σ_{Yb}^{abs} is the absorption cross section for Yb^{3+} , and γ_1 and γ_2 are the energy transfer rates from Yb^{3+} to Er^{3+} .

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. As a result, the efficiency increases with incident pump irradiance at low irradiance in the manner shown in Fig. 9a for all three colors.

We also find that 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 $\text{Er}^{3+} {}^4\text{I}_{11/2}$ state at the rate of $\gamma_3 n_2^{\text{Er}} n_1^{\text{Yb}}$. 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 [25]: The Er^{3+} first excited state ${}^4\text{I}_{13/2}$ 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 are still attainable by increasing the infrared pump power while darker levels are obtained for lower pump powers and with less UC conversion efficiency.

The best UC materials are those having the largest maximum efficiencies. We use raw efficiency in this paper. Raw efficiency is the ratio of total visible emitted power (either in radiometric or photometric units) to the power of the infrared pump power incident on a sample. A larger number is sometimes given in other publications where the intrinsic efficiency is used [26], [27]. Intrinsic efficiency is the ratio of total visible power emitted to the power of the infrared pump absorbed by a sample. Backscattering of the incident pump light reduces that which gets into the sample and which can be absorbed. Thus, the absorbed power is smaller than the incident power and the raw efficiency is less than the intrinsic efficiency.

A few system design issues need to be considered in order to operate UC screens at maximum efficiency such as properly focusing the infrared pump beam, pixilating the screen, and reducing the pixel size.

F. Pump duration dependence of the UC process efficiency

The pumping duration should also be short (shorter than Yb^{3+} ion lifetime of a few ms) in order to quickly achieve high transfer rates. This is demonstrated in Fig. 10 where the efficiency and brightness of the green emitting material is shown for several excitation pulse durations at 30 Hz and for continuous excitation.

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 $\text{Yb}^{3+} {}^5\text{F}_{3/2}$ state and enhances both steps of the up-conversion process.

A 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. The green and red up-conversion mechanisms rely 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 slightly 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 [28].

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 is less with short excitation pulsed as we demonstrate in the experiment described below.

The visible output emitted by a small volume of dry powdered Yb,Tm:KY₃F₁₀ packed in a hollowed acrylic holder was collected with an 80-mm diameter integrating sphere, fiber-coupled to the calibrated Compact Array Spectrometer. The excitation source, a 975-nm, cw diode laser and a rotating chopper with different slit widths, was used to obtain different pulse duration excitations at 30 Hz (see also [18]). It is possible to evaluate the temperature of the up-converters while in use when the incident intensity is increased and for the different pump durations. The emission spectrum was recorded for each pumping condition. Fig. 11 presents typical spectra in the blue obtained with for two pumping conditions: cw and 30-Hz, 2-ms pulsed excitation. The visible output power was the same (54 μ W) in both pumping conditions.

There are two emission bands near 450 and near 480 nm. The emission band centered at 450 nm originates from the ¹D₂ level of Tm, which lies 7000 cm⁻¹ above ¹G₄. These two levels are not thermally coupled but their emission spectra overlap. Therefore, to correctly estimate the spectral distribution of the 480 nm band as a function of temperature one has to first subtract the tail of the emission band at 450 nm. The resulting spectrum still has several emission peaks. We are particularly interested in the

transitions at 463 nm and at 480 nm in Yb,Tm:KY₃F₁₀. They both originate from the same energy level, the ¹G₄, but from different Stark split sub-levels. Those sub-levels are thermalized and the spectral distribution is therefore a signature of the temperature inside the sample (This is the fluorescence intensity ratio technique or FIR discussed in Refs [29] and [30].). When the ratio of the emission at 463 nm to that at 480 nm is observed to increase, it means that the temperature of the emitting powder has increased. Fig. 11 shows that for the same output luminance, the temperature of the sample is much higher for continuous pumping than it is for pulsed excitation.

G. Temperature dependence of the UC process efficiency

It is actually possible to map the ratio of the emission lines intensity to the temperature of the emitting powder by using the emission spectra measured at temperatures between 21 and 180°C set externally with a hot plate. A thermo-couple was used to record the temperature, and a low-energy, 10-Hz, 4-ns pulse at 975 nm was used to provide UC excitation without affecting the sample temperature. The specific pump wavelength was chosen according to the results in Fig. 6. The total blue up-conversion fluorescence was recorded using the CAS and the normalized efficiency as a function of temperature is shown in Fig. 12. This figure confirms that for all three fluoride crystals, a rise in operating temperature is detrimental to the visible emission. We then measured the ratio of the 463 to the 480 nm line for different temperatures enabling us to determine the temperatures of the emitters for the various excitation conditions in Fig. 11.

Using those ratios, we determined the temperature of the blue emitting powder for various pumping conditions (cw, and 30-Hz, 5 and 2 ms pulses) and we also looked at two types of powder holders (acrylic and copper). The holders were 1-cm long, 2.5-cm

diameter cylinders with a 500- μm deep, 750- μm diameter hole drilled in the center of the face. The temperatures reached are shown in Fig. 13a, and the resulting measured efficiencies are given in Fig. 13b. 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 emission of phonons which raise the temperature of the sample. Second, the results in the acrylic holder show that the emitting powder reaches very high temperatures with cw or long pulse duration excitation.

The lower temperatures attained using short pulse duration excitation explain the higher efficiencies in Fig. 13b. This improvement in efficiency is verified with excitation pulses having duration of the order of the transfer time from Yb^{3+} to Tm^{3+} . For pulses shorter than this transfer time, no improvement can be seen as the energy remains stored in the Yb^{3+} ions. Finally, it is straight forward to reduce the temperature of the emitting powder by using a high thermal diffusivity sample holder. By simply using a copper holder we achieved significant heat extraction resulting in lower emitter temperatures and, as a result, higher efficiencies. 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 to achieve still higher efficiencies.

A numerical model was developed based on the rate equations for the sensitizer/acceptor system. A thorough treatment can be found in [31]. By including

temperature dependences of the transfer rates and cross-relaxation it is possible to accurately reproduce the experimental observations described above.

The experimental results obtained for the red and green up-conversion emitters are very similar. For the green emitter, the up-conversion process requires only two resonant steps. The incident power densities required to attain saturation of the efficiency are smaller and there is less heating of the powder for the same incident power. Analysis of the emission spectra in various excitation conditions reveals that temperatures of only 10 to 20°C above room temperature are generated in the green emitter even when using the acrylic sample holder with a 1-mm diameter hole and even for continuous excitation. This increase in temperature is not sufficient to significantly alter the green emitter up-conversion efficiency. In the red emitter a third up-conversion step contributes to the red emission at higher incident power densities [32]. However, the energy mismatch and non-radiative decays are much less than in the blue up-conversion process, resulting in less heating of the material, and a temperature increase less than 20°C. In a full color screen the temperature would have to be controlled due to heating of the blue emitter.

H. Scattering dependence of the UC process efficiency

Aa UC screen relies on emitters in form of micro-crystallites dispersed in a binder. When there is a large mismatch between the index of refraction of the binder and that of the particles the UC screen appears white due to very strong backscattering of the light incident on it. This strong scattering is present at any wavelength and also exists at the infrared excitation wavelength. The light that is backscattered 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 dry powder efficiency measurements. This

backscattered light represents energy lost for the UC process. Hence, a key step toward optimizing a UC display is addressing scattering issues.

Scattering affects the performance of an UC display three ways. First as just discussed, backscattering of the pump light reduces UC raw efficiencies by preventing some of the pump from penetrating the active material. Second, 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.

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 with index of refraction 1.483 at the optimized pump wavelength in contrast to NYF₄ which is birefringent. The isotropy of KY₃F₁₀ allows complete index matching even though it is not the most efficient host for the green emission from Er. 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. 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 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 pulsed excitation at 12.5 mW average power focused to a

900 μm diameter spot. These pumping conditions were chosen to give maximum UC efficiency with the dry powder.

Fig. 14 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 Fig. 14, 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 Fig. 14 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 ($n_e \sim 1.470$, $n_o \sim 1.449$ at 975 nm). 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.

Fig. 15 shows the corresponding visible emission spectrum for the dry sample and the $n = 1.484$ case of Fig. 14. Even though the infrared light penetrated further in the index-matched sample the green emission did not increase. Furthermore the red emission

is less than for the dry 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.

An important characteristic of the Er,Yb system is that the red to green ratio increases with increasing irradiance [8]. The green and red emissions come from different excited states, the $^4S_{3/2}$ and $^4F_{9/2}$, respectively. The green is excited by the two step process described previously and the red by either a two- or three step process [32]. Red light emitted due to a two-step process results from a non-radiative decay from the green emitting state to the red emitting state. Three-step excitation of red emission 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+} . In the presence of Yb^{3+} in the concentrations used and for increasing irradiances the three-step process is enhanced and at high irradiance predominates over the two-step process [8], [33]. 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 [21]. Since the three-step process quenches the green emission the red to green ratio increases with increasing pump power densities.

To illustrate the change in red to green ratio we conducted a separate experiment where this ratio was measured with respect to increasing pump power for three different beam spot sizes (Fig. 16a). As discussed above, the excitation source used (30-Hz, 2-ms pulses at 975 nm) did not induce any temperature increase that could affect the red to green ratio obtained. By plotting the red to green light ratio with respect to irradiance rather than power we confirmed that the ratio depends on irradiance only (see Fig. 16b).

Thus, we can use this red to green emission ratio to estimate the effective irradiance of the pump inside an Er,Yb sample.

We used measurement of the red to green ratio in our scattering experiments to determine that the effective irradiance is a factor of 10 less in the index-matched powder than it was in the dry powder. This change of effective irradiance inside media with different degrees of index matching is explained by the theory of diffuse light-matter interaction inside a scattering-dominated medium compared to an absorption-dominated medium [34]. 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. There are two consequences to this observation: on one hand, 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. On the other hand, the opump 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.

The change in effective irradiance due to scattering has important consequences UC. In Fig. 15 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 (see Fig. 17 a).

Fig. 17 b illustrates the differences in efficiency between low and high scattering samples. In Fig 17 b the improved maximum raw efficiency of the low over the high scattering sample 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 4π . Also, due to the longer pump penetration depth, these emitters can be located deep inside the sample. Because of the geometry and poor surface quality of the aluminum holder used in the experiment, the portion of light radiated towards the bottom and walls is diffused and trapped inside the holder, rather than reflected back into the integrating 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. We expect the increase in absolute raw efficiency when backscattering is reduced to be even larger than shown in Fig 17 b.

I. *Best efficiencies obtained*

Finally, we have measured the absolute efficiencies for our best performing, three primary colors up-conversion emitters, using the calibrated CAS system traceable to the National Research Council. The emitting samples used in the measurements were prepared in the form of packed powder inside a 900- μm diameter, 3-mm deep cylinder at the center of a 2.5-cm diameter acrylic hemisphere. The maximum efficiencies were measured in the absence of a binder and therefore were measured for a high index

contrast, high backscattering sample. We estimated the backscattering of the pump to be 60% for our calibrated measurements.

The powders currently produced by ACMaterials have very high purity and their maximum efficiency has been characterized in our laboratory. The efficiencies given in Table I were measured with respect to incident pump power and can be improved by simply using an index-matched polymeric host. A summary of the results is given in Table I.

III. Conclusion

Up-conversion as a source of red, green and blue emission offers many appealing features for the display industry. A major benefit to using this technology is the ability to operate displays at very high-brightness without deterioration of the emitting materials. Such displays would be very well suited for high-brightness ambient lighting conditions such as encountered outdoors or in airplane cockpits. This high brightness comes along with narrow emission lines and very saturated colors. As a matter of fact, the color gamut obtained through up-conversion is comparable to that of Organic Light Emitting Diodes (OLED) displays. Further, we have demonstrated that by understanding the mechanisms involved in the up-conversion process, it is possible to operate UC materials at efficiencies rivaling those of most current display technologies. As a result, we believe that this new type of emissive display, which is easily visible in the Florida noon time sun-light and offers great design flexibility, has the potential, with proper engineering, to compete with existing technologies. In addition, due to its spectral flexibility and demonstrated efficiencies, UC emission should also be considered as a solution for backlight illumination in LCDs.

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Prior publications:

- A. Rapaport, F. Szipocs, J. Milliez, H. Jenssen, M. Bass, K. Schafer, and K. Belfield, "Optically written displays based on up-conversion of near infrared light," Conference Record of the 20th International Display Research Conference, 111-114 (2000).
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- A. Rapaport, J. Milliez, F. Szipocs, H. Jenssen, A. Cassanho, and M. Bass, "Up-conversion efficiency of potential candidates for photonic displays," presented at the SID, Baltimore, 2003.
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Table I. Maximum raw efficiencies measured to date for the best candidates for green, red and blue up-converters.

Maximum Raw Efficiency		
Emitter	Radiometric Units (%)	Photometric Units (lm/W)
Red	7	3
Green	4	26
Blue	4	3

All efficiencies are relative to optical infrared input power.

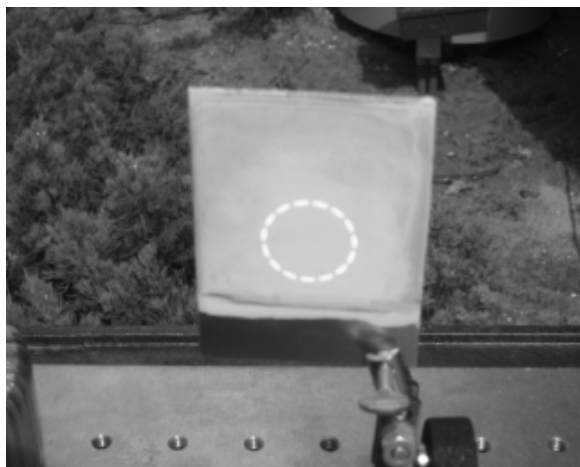
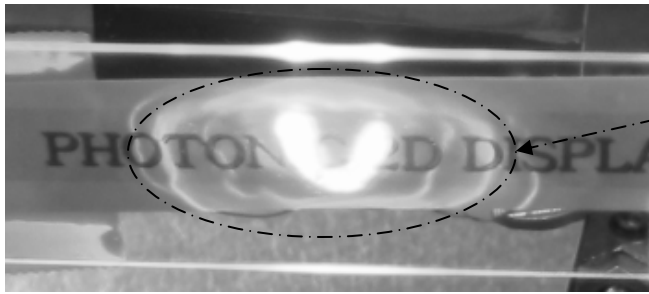


Fig. 1. Photo of a green UC screen taken outdoors during a sunny Florida day at noon. The excitation source was a 500 mW diode laser scanned with two galvanometer mirrors. This screen is about 50 mm on a side.



Layer of UC material plus plastic coated on a microscope slide

Fig. 2. Photo of our first transparent green UC display. Visible light is trapped in the UC powder plus plastic layer and in the glass slide used as a substrate. Green light leaks at every edge making visible the non uniformities in the UC layer. The words “Photonic 2D Display” are printed on a card placed behind the transparent display screen.

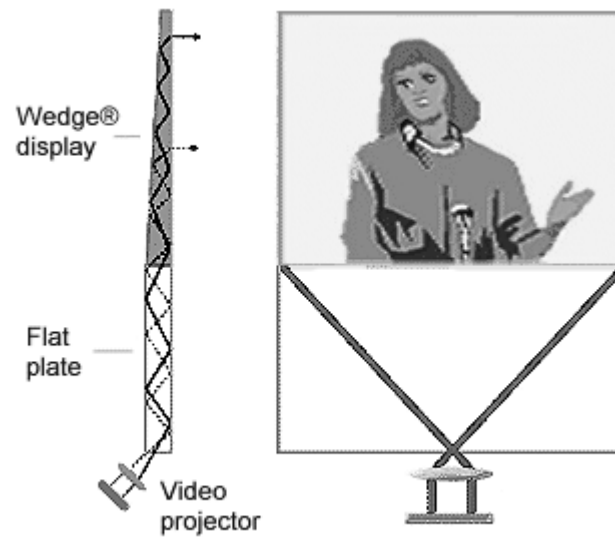


Fig. 3. Wedge technology developed by Adrian Travis at Cambridge Flat Projections Display Ltd.

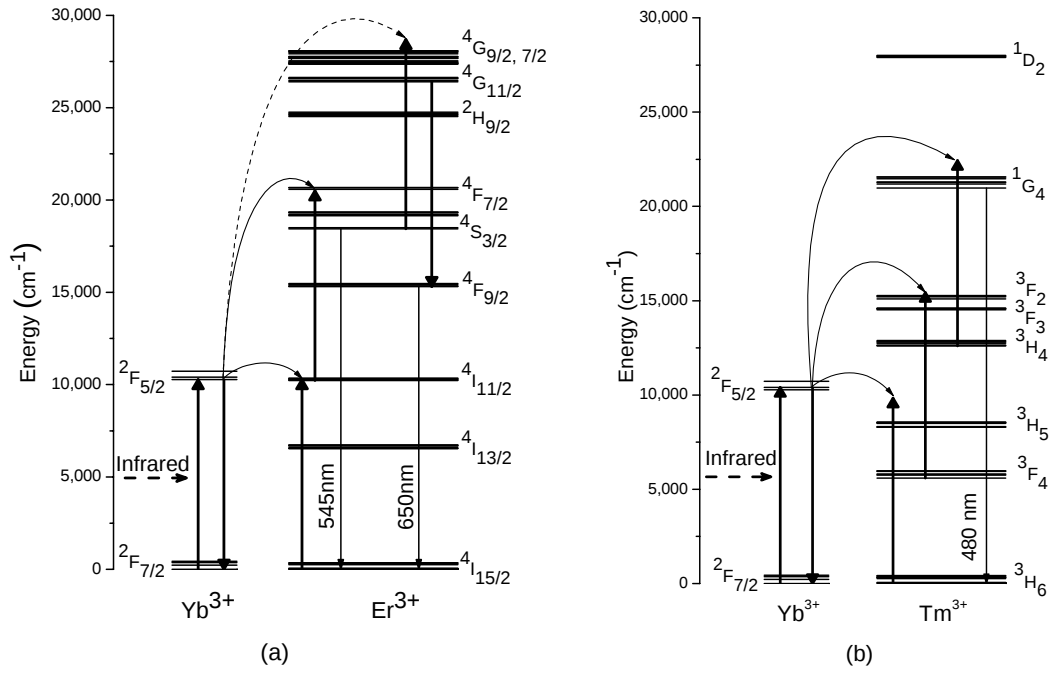


Fig. 4. Energy diagrams and up-conversion process for the green and red emission in Er, Yb system (a) and the blue emission in Tm, Yb system (b).

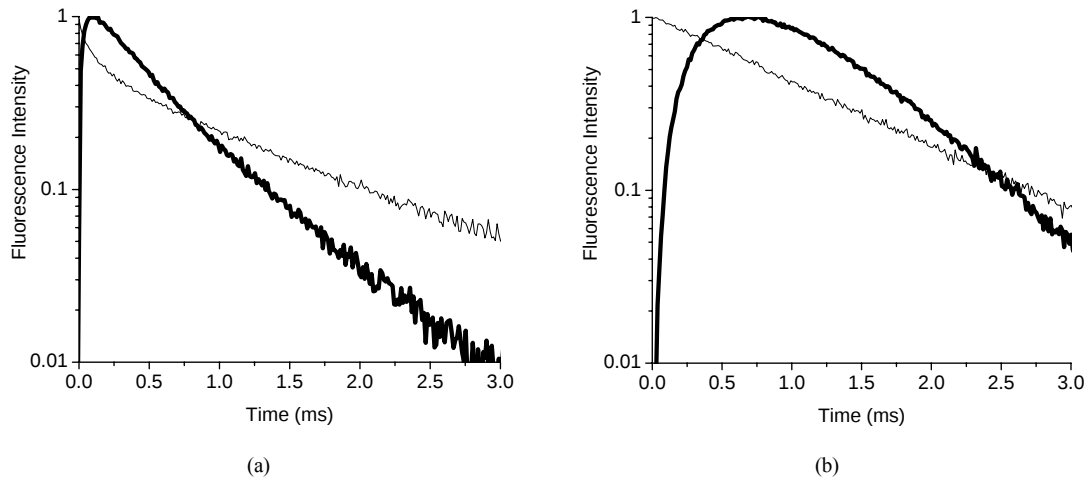


Fig. 5. Normalized emission response time of emitters excited at 975 nm with a low energy 4-ns pulse. The samples were tested at 21 C:

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).

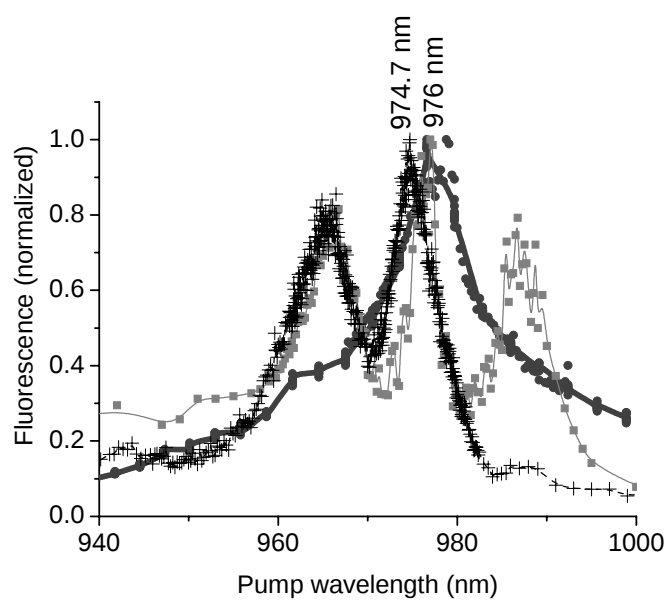


Fig. 6. Normalized excitation spectra of green (circles), red (squares) and blue (crosses) emitters.

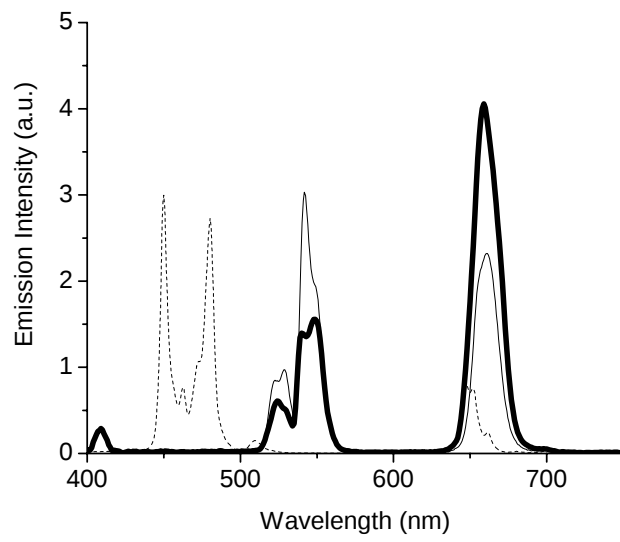


Fig. 7. Emission spectra of green (Er,Yb:NYF, thin solid line), red (Er,Yb:YF₃, thick solid line) and blue (Tm,Yb:KY₃F₁₀, dashed line) emitters.

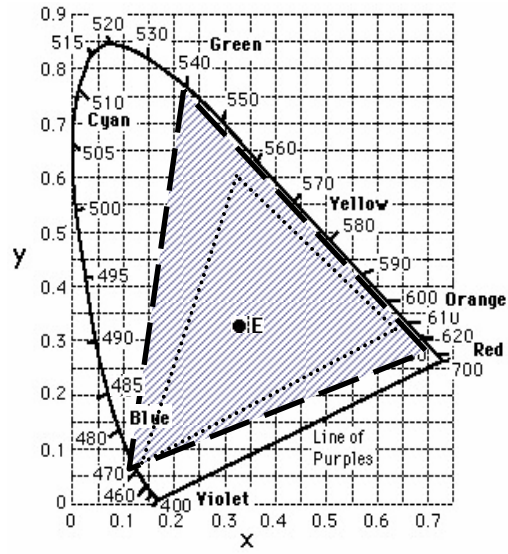
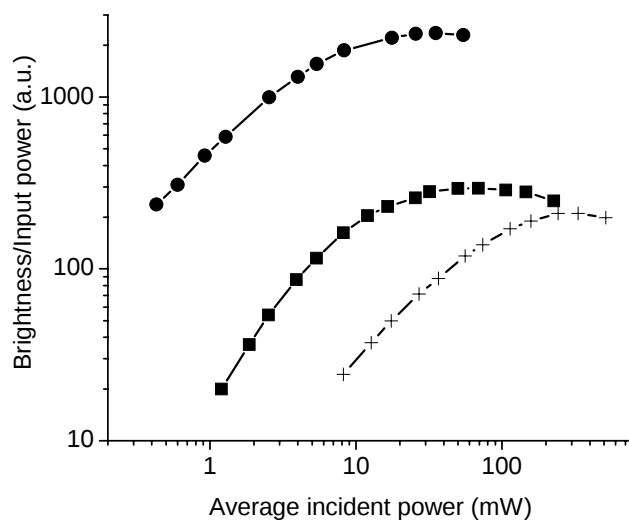
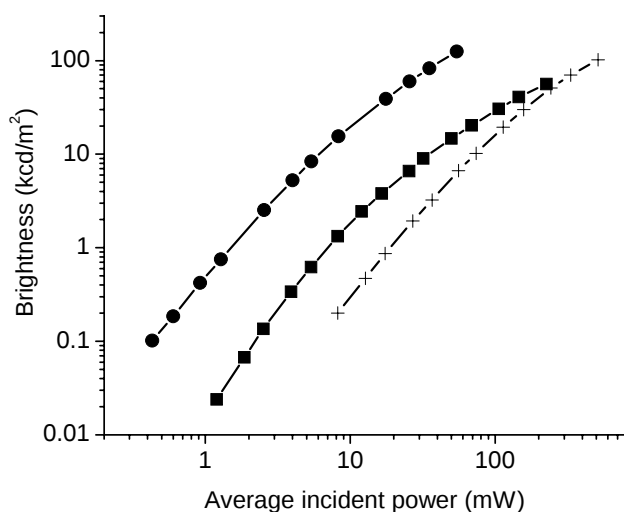


Fig. 8. CIE chromaticity diagram of RGB up-conversion phosphors. The long dashes enclose the region accessed by our UC emitters while the dotted region is that of present day televisions.



(a)

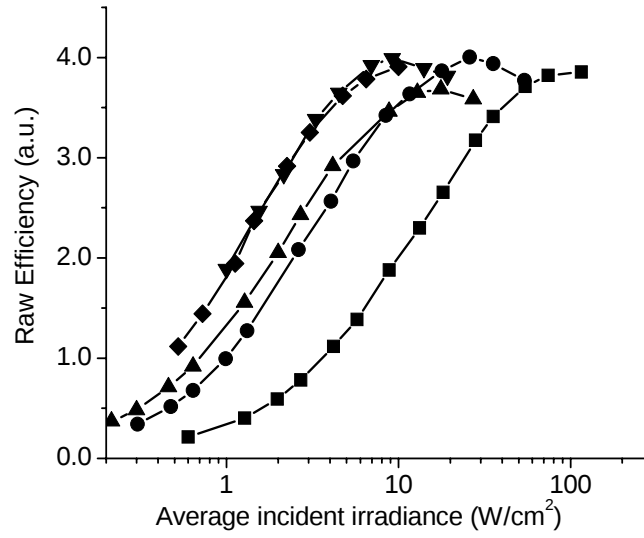


(b)

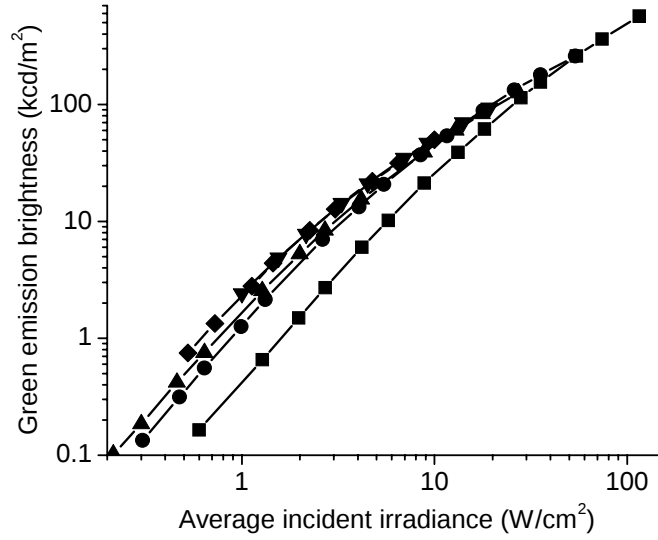
Fig. 9. Example of screen performances for the green (circles), red (squares) and blue (crosses) emitters mixed in a p-PMMA binder and deposited on a glass slide.

a- Ratio of brightness to incident infrared input powers.

b- Brightness.



(a)



(b)

Fig. 10. Experimentally measured green up-conversion power efficiency (a) and brightness (b) versus incident irradiance in 1% Er, 18% Yb:NYF for five different types of excitation: continuous (squares), and pulsed at 30 Hz with pump duration of 5 ms (circles), 2.6 ms (up triangles), 700 μ s (down triangles) and 150 μ s (diamonds).

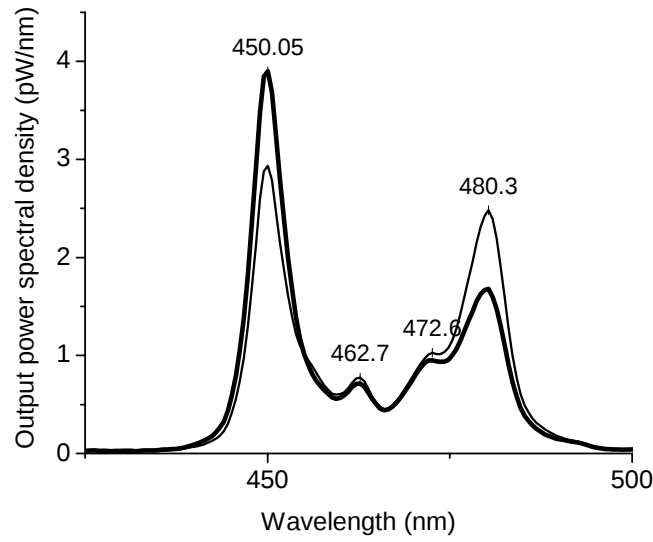


Fig. 11. Emission spectra of 0.4% Tm, 30% Yb:KY₃F₁₀. Two conditions of excitation were used: the bold line corresponds to continuous pumping; the thin line represents 2 ms duration pulse pumping at a repetition rate of 30 Hz. The output luminance in the blue was the same in both excitation conditions (54 μ W). The sample holder was made of acrylic.

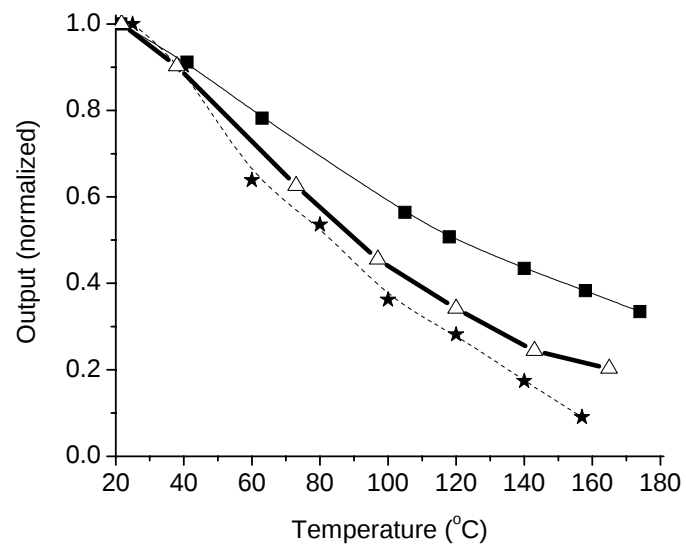
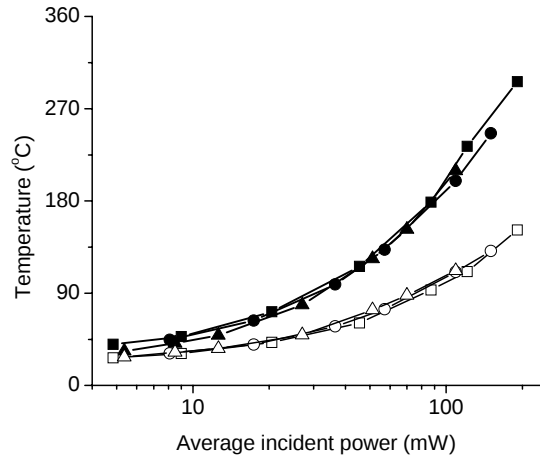
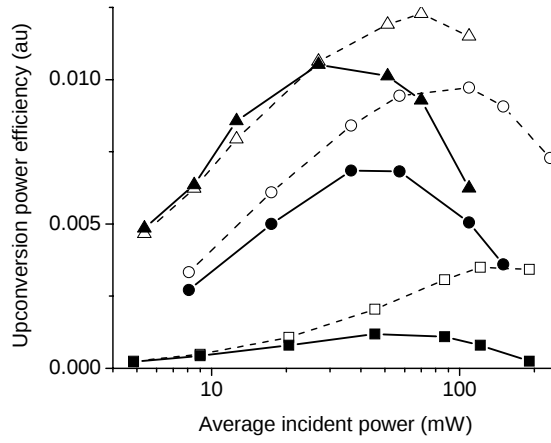


Fig. 12. Normalized output power at low incident pump intensity from the red (thin line and solid stars), green (thin line and solid squares), and blue (thick line and hollow triangles) up-conversion materials as a function of temperature.



(a)



(b)

Fig. 13. Up conversion temperature and efficiency of a sample of 0.4% Tm, 30% Yb:KY₃F₁₀. The solid symbols correspond to an acrylic sample holder and the open symbols are for a copper sample holder with the hole containing the powder a cylinder 750- μ m in diameter and 500- μ m deep. The squares are for cw excitation, the circles are for 30 Hz, 5 ms duration pulses and the triangles are for 30-Hz, 2 ms duration pulses. The excitation wavelength was 975 nm.

a- Temperature of the emitting powder

b- Relative efficiency measured

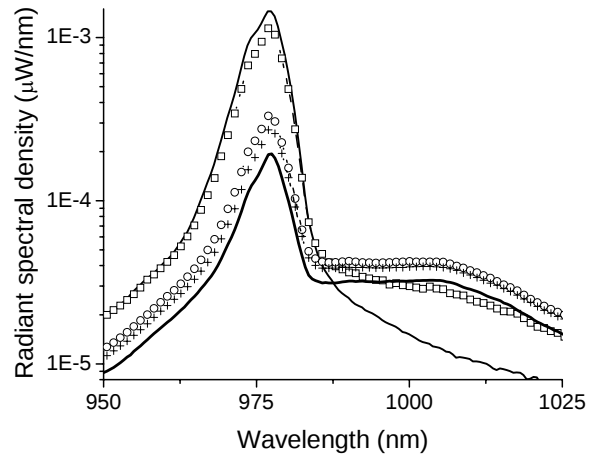


Fig. 14. Backscattering of the pump light for different matching fluid indices of refraction for 2% Er, 15% Yb:KY₃F₁₀ excited at 975 nm: Dry (squares), index of matching fluid, $n = 1.412$ (circles), $n = 1.432$ (crosses), $n = 1.484$ (thick solid line). The thin solid line spectrum corresponds to 100% backscattering from dry alumina powder.

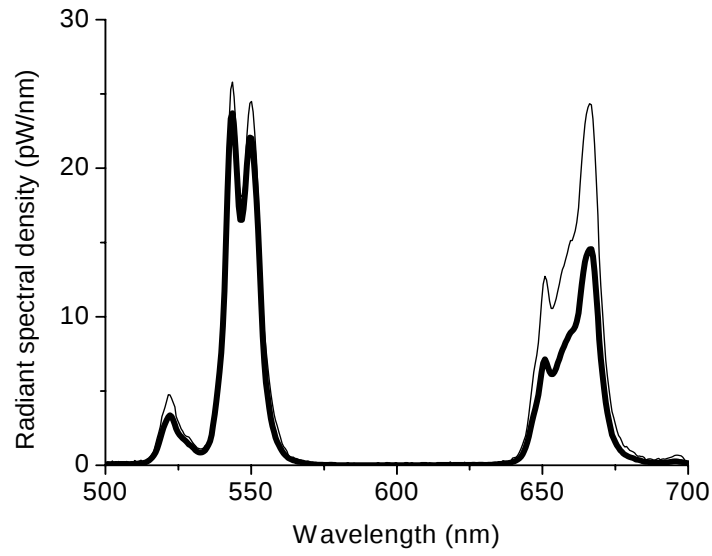


Fig. 15. Visible emission spectra for 2% Er, 15% Yb:KY₃F₁₀ excited at 975 nm under 12.5 mW average input power for a dry sample (thin line) and an index-matched (thick line) sample, $n = 1.484$.

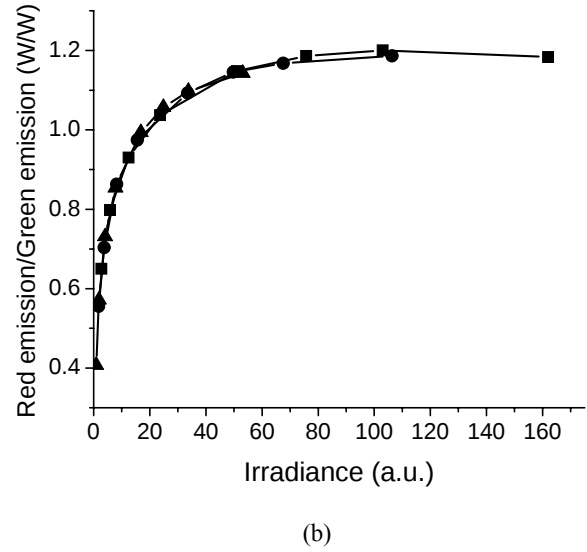
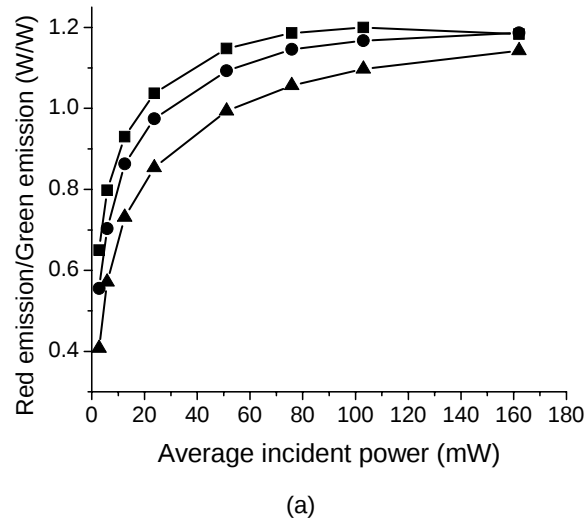
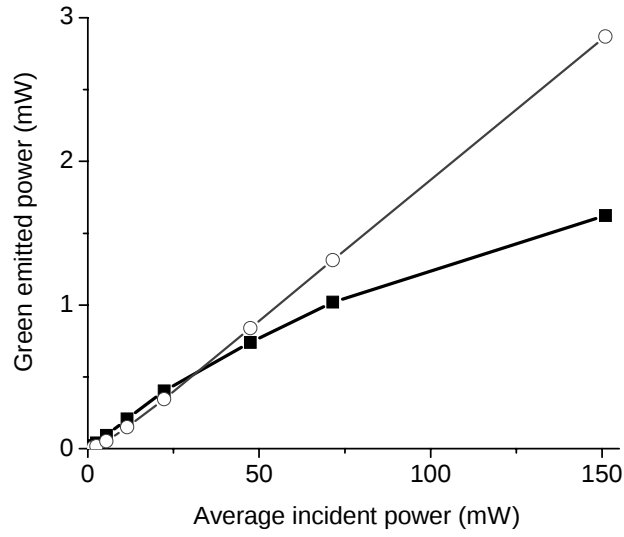
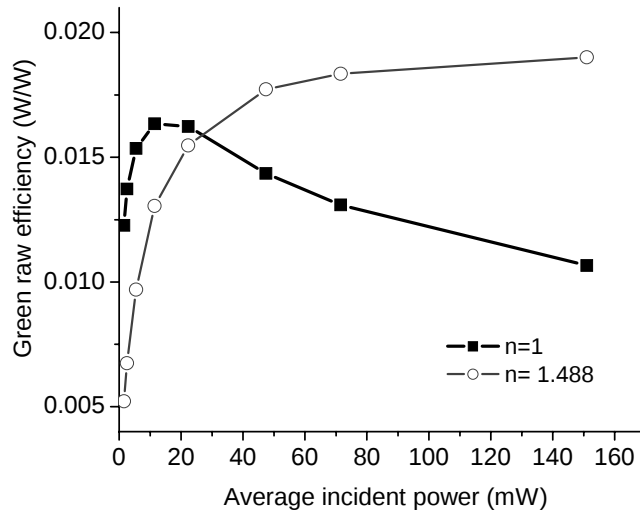


Fig. 16. Effect of pump irradiance on red to green emission ratio in 2% Er, 15% Yb:KY₃F₁₀ for a beam focus diameter of 850 μm (squares), 1 mm (circles) and 1.4 mm (triangles) plotted in (a) with respect to input power, and in (b) scaled to input irradiance.



(a)



(b)

Fig. 17. Green emission (a) and UC raw efficiency measurement (b) of 2% Er, 15% Yb:KY₃F₁₀ for both a dry, high-scattering powder (squares) and an index-matched sample by immersion in $n_D=1.484$ index oil (circles).

Paper 2:

Development of a scalable volumetric three-dimensional up-conversion display

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ABSTRACT

Several rare-earth doped fluoride crystals that are excited to emit visible light by sequential two photon absorption have been investigated as display medium candidates for static volumetric three dimensional displays. Dispersion of powders of these materials in a refractive index matched polymer is reported since such a medium may result in a scalable display. The scattering problem in such a medium is greatly reduced by index matching the polymer to the crystalline particles while the uniformity and efficiency of emission from each volume element is maintained by using only as much polymer as is necessary to fill the voids between particles and cover the boundaries of the sample.

Keywords: Up-conversion, 3D, volumetric display, scalable display medium.

1. INTRODUCTION

It has been more than hundred years since the German scientist Karl Ferdinand Braun invented the cathode ray tube (CRT) and since then thousands of researchers have been developing this and other two dimensional (2D) display systems. Thanks to all these efforts, there are today, plasma, projection liquid

crystal and flat-panel liquid displays in addition to CRT based TVs and computer screens in the home. Three dimensional (3D) displays on the other hand have received much less attention and are much less developed. There are several commercialized 3D displays in the market but most of them are not ‘true’ 3D display. They are stereoscopic displays that take advantage of human binocular vision and present slightly different images to each eye. The brain then interprets these slightly different images into a 3D pattern. Such stereoscopic 3D display is the most commonly used 3D technology at the moment since it can be realized by using current 2D display technology. However, a stereoscopic display system still has several disadvantages such as convergence and accommodation mismatch which often makes the viewer feel uncomfortable. A volumetric 3D display would not have this kind of problem since in it there would be a real 3D image. There are two kinds of volumetric 3D displays: the swept volume display is sketched in Fig. 1 and the static volume display is shown in Fig. 2. In a swept volume 3D display a flat or spiral-shape screen is rotated to generate a volume filling screen on which light can be projected. If the light is projected with proper timing a 3D image would appear in the volume swept by the rotating screen.¹ A rotating flat screen containing light emitting diodes at each pixel which are turned one and off at the proper times could also be used.^{2,3} However, generating a volume filling screen by mechanical rotation has consequent problems. For example, to generate images at a high enough refresh rate to prevent visual jitter, the screen must rotate at a high speed. Such moving parts in a system are problematic because of short life, noise and instability. Also the image will be dim because the rapid refresh rate allows only short illumination of any point on the rotating screen negating taking advantage of the integration of light in the retina.⁴ In a static volume display there are no moving parts.⁵⁻⁶

Static volumetric 3D displays can be classified by how their volume pixels (voxels) are activated and what kind of display medium is used.⁷ In our work we consider a 3D display with a passive display medium based on a rare earth doped material. Its voxels can be activated by sequential absorption of light from two invisible near infrared laser beams as shown in Fig. 2. At the intersection of the two laser beams in this display medium electrons are excited from the ground state (E_0) to some intermediate energy level (E_1) and then to an upper energy level (E_2) by sequential two-photon absorption. That is, a first absorption of near infrared light populates the intermediate level. This is followed by a second absorption which excites the

medium in the intermediate state into the upper level from and it is from transitions of the medium in this state that visible light is emitted. We reported previously on the possibility that organic dye doped media might serve in such a passive medium 3D display.⁸ The excitation process in the organic dye doped medium was simultaneous two-photon absorption instead of sequential two-photon absorption. That is both excitation beams had to be present simultaneously to achieve two photon excitation in the dye doped medium. This process may be less efficient than sequential two photon absorption reported in the present paper.

A useful volumetric 3D display medium such as we demonstrate must have good optical properties (that is scatter and stress free), it must be transparent in the visible and at the wavelengths used to excite visible emission from a voxel. It must have good mechanical properties and it must be possible to produce it in large enough samples to be useful in a volumetric display. More specifically, it must be possible to produce the display medium in volumes about 30 cm on a side at reasonable cost while retaining the desired optical properties. We report candidates for 3D volumetric display media that are excited to emit visible light by sequential two photon absorption (TPA) of near infrared laser light and that may meet both the optical and manufacturability criteria.

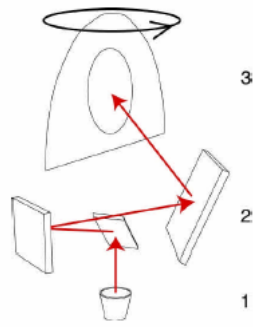


Figure 1: Schematic illustration of swept volume 3D display principle. A fast projector (1) illuminates a rotating projection surface (3) via several relay mirrors (2) which rotate with the screen¹.

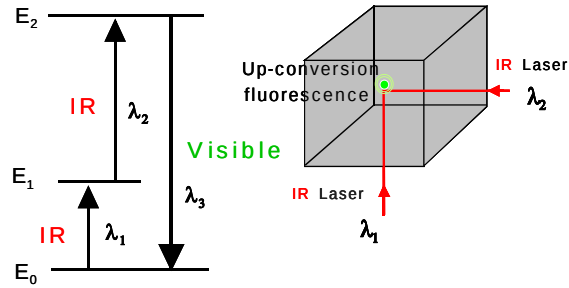


Figure 2: Schematic diagram of static volume 3D display. Two frequency two step process is shown on the left hand. Voxel is generated in the display medium by two different frequency IR laser beam at the cross point.

2. DISPLAY MEDIUM

There are several different types of static volume 3D display systems employing different passive display media. Some employ a gaseous display medium.⁹⁻¹¹ Gases are easy to produce and can be viewed through windows in their containers. However, most gases that are of use in 3D displays are toxic, must be kept at high pressure and require specially designed containers that assure that the gas stays confined and does not erode the container or its windows. Organic dye doped liquids could serve as a 3D display medium but it is not always easy to confine the liquid and the dyes and solvents may have hazardous properties. On the other hand, dye doped polymers or rare-earth doped fluoride crystals may serve as 3D display media.

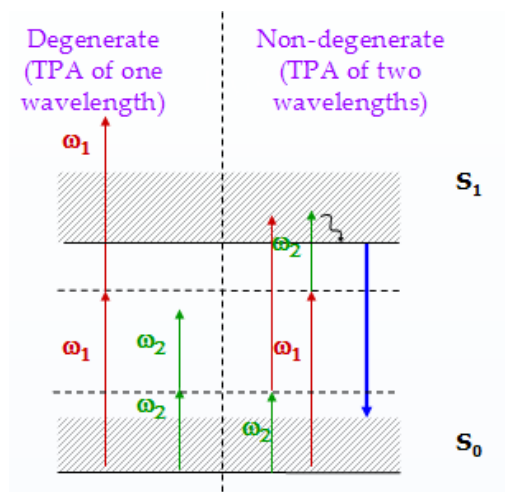


Figure 3: Energy diagram of organic dye

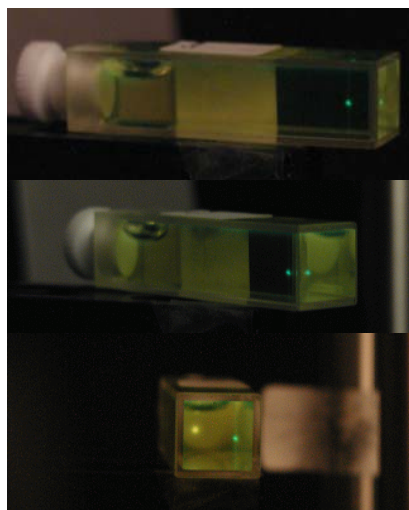


Figure 4: Voxel in Organic dye. Degenerate TPA by single wavelength can be observed easily in the bottom picture.

As discussed in Ref. 8 some dyes in liquid and polymeric solutions that can be excited to emit visible light by simultaneous absorption of two infrared light sources of different wavelengths (non-degenerate TPA as indicated in Fig. 3) can be attractive candidates for 3D display media. Since organic dyes can be tailored for desired properties there is a continuous and wide range of wavelengths accessible for both two-photon absorption

(TPA) and visible emission. Additionally, dyes can be doped in polymeric hosts to produce clear, non-scattering solid volumes that can easily be scaled up. However, dyes have several disadvantages. They almost always present some residual degenerate TPA which causes an undesirable line of visible emission along one or both of the laser beam paths (See Fig. 4). There can be significant self-absorption of the emitted visible signal in dye solutions due to too small a Stokes shift. Since TPA in dyes is not a stepwise absorption but involves simultaneous absorption of two photons through a virtual intermediate state it is not likely to be efficient enough for practical use. The exciting beams for such a process must simultaneously in time overlap in space and this requires long pulses ($>$ several nsec) with high peak powers.

There are several advantages to using RE doped materials as the 3D display medium. Since stepwise excitation implies the succession of two linear processes, it is efficient at lower peak power than non-degenerate simultaneous two-photon absorption in organic dyes. This relaxes the requirements on the pump sources to achieve bright voxels. Furthermore, the real intermediate energy level can be used to store energy and the temporal overlap of the addressing beams is not a necessity.

We have conducted several experiments with rare-earth doped fluoride crystals provided by AC Materials: 1% Ho:YLF, 1% Er:YLF and 2%Er:KY₃F₁₀. We used two optical parametric oscillators in a Master Oscillator-Power Oscillator configuration (MOPO) pumped by the same flashlamp pumped, Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser as the sources for the two different pump wavelengths.

The experimental set-up is shown in Fig. 5. A delay was introduced in one of the laser paths in order to make sure that the first excited state was populated before hitting the material with the second-step pump wavelength.

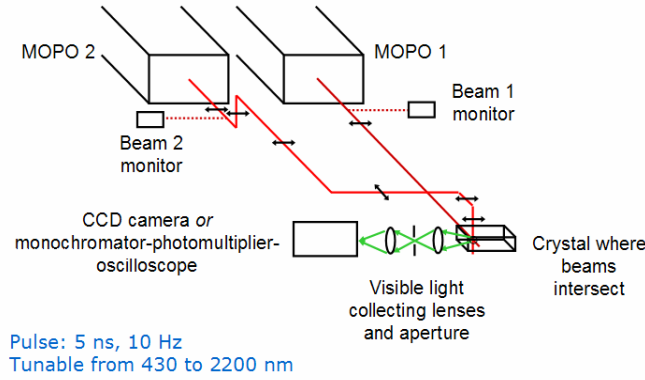


Figure 5: Setup for fluorescence measurement

The brightest two-frequency two-step (TFTS) up-conversion emission was obtained with Er:KY₃F₁₀ when it was pumped with 1491.1 nm first and then with 848.4 nm (see Figs. 6 and 7). Efficient up-conversion alone makes Er:KY₃F₁₀ a strong 3D display candidate. However, Er:KY₃F₁₀ has several more advantages over other materials. Using Er-doped fluoride single crystals directly as the 3D display medium presents some difficulties. First, growing large single crystals is not easy. Second, even if it were possible to make single crystals big enough for a display medium it would be very expensive to do so. As a solution to the 3D display medium scalability issues, M. Bass and H. Jenssen proposed a 3D display based on a dispersion of emitting particles in a transparent host.¹²

In making possible the concept in Ref. 12 is one of the most important properties of KY₃F₁₀. Its crystal structure is cubic which means that it is isotropic and is characterized

by a single index of refraction. This is important when we want to grind the crystal into powder and disperse the powder into an index matched passive host. Since KY_3F_{10} is a cubic material, it is possible to index-match the host for any orientation and polarization without the problems of dealing with a birefringent material. $\text{Er:KY}_3\text{F}_{10}$ has refractive index of 1.4876 (n_d) and there are commercially available polymers of the same index on the market. Also there are commercially available diode lasers for its two peak excitation wavelengths.

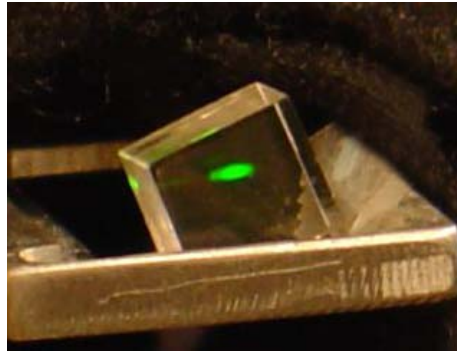


Figure 6: Voxel in $\text{Er: KY}_3\text{F}_{10}$.

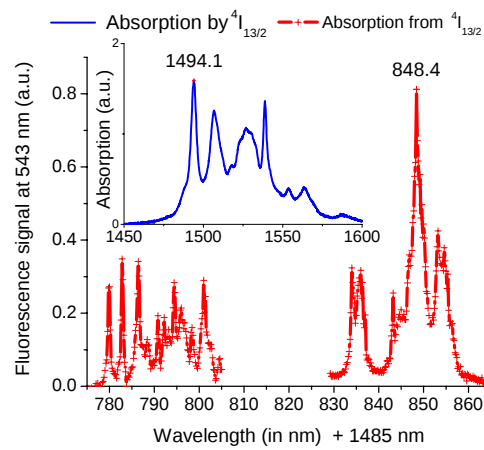


Figure 7: Absorption and excited state absorption in $\text{Er: KY}_3\text{F}_{10}$.

We performed extensive experiments on dispersion of Er:KY₃F₁₀ crystal powders ranging in size from 20 to 400 μm in different polymer hosts. A major objective of these experiments was to make 3D display media with as high a density of homogeneously distributed emitting material as possible to assure both efficient and uniform voxels. A solution to this problem was to pack the crystalline powder in a certain volume and encapsulate it with the polymer. Here encapsulate means that we added only as much polymer as was necessary to fill the voids between particles and cover the boundaries of the sample. This technique resulted in display media with improved uniformity and emission strength when compared to simply dispersing powder inside the polymer since the density of emitters in any volume element was higher and constant throughout.

When making a static volumetric 3D display, the active medium used has to be transparent to let the pump light in and the emitted light out. Index matching is therefore a very important factor to consider as it reduces light scattering at the interfaces between the crystallites and the polymer host. An extensive search to find the proper polymer has been performed. Perfluorocyclobutyl (PFCB) polymer has good optical properties and can be produced to have the index of refraction that we need¹³⁻¹⁴. We have observed that proper adjustment on refractive index of perfluorocyclobutyl (PFCB) polymer drastically reduced scattering from the crystal powder in the polymer as shown in Fig. 8.

Making samples with no defects such as cracks or bubbles has proven to be a difficult process. A properly chosen polymer and polymerization process can reduce this problem. We were able to get eliminate bubbles by thermal polymerization in a vacuum

oven and obtained samples with very low scattering. However, after a few days we observed formation of cracks and voids between the crystallites and the host polymer. This is most likely due to the difference between their thermal expansion coefficients. To reduce this problem, we have tried partial polymerization of mixture of crystal powder and PFCB to make a softer sample to prevent such break up. However, un-polymerized remnants of polymer precipitated and made the sample become opaque in time.



Figure 8: Er:KY₃F₁₀ powder in the index matched PFCB polymer (left) and when index is not well matched (right)

Phosphorylation a polymer host helped the polymer hold crystalline powder much better better in our optically-written 2D display studies.¹⁵ We expect phosphorylation will help similarly with the PFCB polymers as index matched passive hosts for 3D displays.

CONCLUSION

Several candidates for use as a static volume 3D display medium were studied. Rare-earth doped fluoride crystals have been investigated and appear to be promising candidates. We observed Er:KY₃F₁₀ to be a most efficient visible light emitter upon TFTS upconversion. Dispersion of rare-earth doped crystal powder in a refractive index matched polymer has been proposed to make scalable display medium. We tested Er:KY₃F₁₀ crystal powder of dispersed in different polymers and demonstrated that encapsulation of

the crystal powder enabled the homogeneous dispersion of particles. A properly index matched polymer will significantly reduce the scattering problem leading to a good scalable display medium. Proper modification of the polymer to accept the inorganic particles will reduce deterioration of the sample with time.

ACKNOWLEDGEMENTS

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LISTING OF PUBLICATIONS AND REPORTS

(a) Papers published in peer reviewed journals

“Dependence of Two Photon Absorption Excited Fluorescence on the Angle between the Linear Polarizations of Two Intersecting Beams” (Alexandra Rapaport, Ferenc Szipocs and Michael Bass) Applied Physics Letters, **82**, No. 25, 23 June 2003

“Dependence of Two Photon Absorption Excited Fluorescence in Dye Solutions on the Angle between the Linear Polarizations of Two Intersecting Beams” (Alexandra Rapaport, Ferenc Szipocs and Michael Bass) Applied Physics B – Lasers and Optics, Vol. 78, No. 1, pp. 65-72 (January 2004)

Properties of a new, efficient, blue emitting material for applications in up-conversion displays: Yb,Tm:KY₃F₁₀”, Alexandra Rapaport, Janet Milliez, Ferenc Szipocs, Michael Bass, Arlete Cassanho and Hans Jenssen, Applied Optics, Fall 2004

“The role of pump duration on temperature and efficiency of up conversion in fluoride crystals co-doped with ytterbium and thulium”, Alexandra Rapaport, Janet Milliez, Michael Bass, Arlete Cassanho and Hans Jenssen, Optics Express 12, No. 21, pp. 5215-5220, Oct. 18, 2004

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(b) Papers published in non-peer reviewed journals or in peer reviewed conference proceedings

“Up-conversion efficiencies of potential candidates for photonic displays” (Janet Milliez, Alexandra Rapaport, Ferenc Szipocs, Hans P. Jenssen, Michael Bass, and Arlette Cassanho) SID Annual Conference, May 2003, Paper 41.4

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(c) Papers presented at meetings, but not published in conference proceedings

“Fabrication of photoluminescent screens for optically written displays based on up-conversion of near infrared light” (Qhiong-hua Wang, Michael Bass, Alexandra Rapaport, Jason Eichenholz and Shin-Tson Wu) Society for Information Display - International Display Manufacture Conference 2003

(d) Manuscripts submitted, but not published

(e) Technical reports submitted to ARO under grant number: DAAD19-02-1-0248

1. Interim Report No. 1, Dec. 2003

2. Interim Report No. 2, Dec. 2004

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Arlette Casanho, Owner, AC Materials

REPORT OF INVENTIONS

“Display media using emitting particles dispersed in a transparent host”

US Patent No. 6,327,074 B1
(M. Bass and H. Jenssen)

Division of US Patent No. 6,327,074 B1

“Display medium using emitting particles dispersed in a transparent host”

US Patent No. 6,501,590 B2
(M. Bass and H. Jenssen)

Division of US Patent No. 6,327,074 B1

“Dispersed crystallite up-conversion displays”

US Patent No. 6,654,161 B2
(M. Bass, H. Jenssen and
Alexandra Rapaport)

“Composites of inorganic luminophores stabilized in polymer hosts”

US. Patent No. 6,844,387
(M. Bass and K. Belfield)

Optically Written Display

US Patent No. 6,897,999 B1
(Jason Eichenholz, M. Bass and
Alexandra Rapaport)

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With each paper.