Research Article

Abdalla M. Darwish*, Sergey S. Sarkisov*, Simeon Wilson, Jamaya Wilson, Eboni Collins, Darayas N. Patel, Kyu Cho, Anit Giri, Lynn Koplitz, Brent Koplitz, and David Hui

Polymer nanocomposite sunlight spectrum down-converters made by open-air PLD

<https://doi.org/10.1515/ntrev-2020-0079>

received August 11, 2020; accepted September 16, 2020

Abstract: We report, for the first time to our knowledge, on the polymer nanocomposite sunlight spectrum down-converters made by the concurrent multi-beam multi-target pulsed laser deposition (CMBMT-PLD) of phosphor and polymer in ambient air. Phosphor PLD targets were made of down-converting rare-earth (RE)-doped fluorides $\text{NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$, and $\text{NaYF}_4\text{:Yb}^{3+}, \text{Tm}^{3+}$ with a Stokes shift of 620 nm (from 360 to 980 nm), minimizing the effect of re-absorption. The phosphors were synthesized by the wet method. Polymer target was made of poly (methyl methacrylate) known as PMMA. Target ablation was conducted with 1,064 nm beams from an Nd:YAG Q-switched laser. Beam intensity was $2.8 \times 10^{16} \text{ W/cm}^2$ for both targets. The substrate was a microscope glass slide. Phosphor nanoparticles with a size ranging from 10 to 50 nm were evenly distributed in the polymer matrix during deposition. The nanoparticles retained the crystalline structure and the fluorescent properties of the phosphor target. There was no noticeable chemical decomposition of the deposited polymer. The products of laser-induced reaction of the

polymer target with atmospheric gases did not reach the substrate during PLD. Post-heating of the substrate at $\sim 90^\circ\text{C}$ led to fusion of separate polymer droplets into uniform coating. Quantum yield of the down-conversion polymer nanocomposite film was estimated to be not less than $\sim 5\%$. The proposed deposition method can find its application in making commercial-size down-converter coatings for photo-voltaic solar power applications.

Keywords: solar power, photo-voltaic cells, luminescent solar concentrators, pulsed laser deposition, quantum cutting, rare-earth compounds

1 Introduction

There is growing interest in adoption of green-energy technologies that rely heavily on solar power. Alongside the importance of electrical performance come features such as aesthetics, convenience, and safety. These concerns have motivated those working on luminescent solar concentrators (LSCs) for use in buildings [1]. LSCs are large windows filled/coated with luminescent materials that absorb UV/blue spectral components of sunlight and re-emit at near-infrared (NIR) wavelengths. The window acts as a lightguide that redirects the re-emitted radiation to small edge-attached photo-voltaic (PV) cells to generate electricity (Figure 1a). Because LSC area exposed to sunlight is much larger than the edges, LSCs can greatly increase the flux of radiation incident onto the perimeter PV devices and increase the photocurrent, acting as a solar concentrator. In building-integrated applications, LSCs can be introduced without compromising a building's aesthetic value. Down-converting films can also be deposited directly over PV cells to convert UV/blue sunlight into NIR radiation and thus improve the efficiency [2] (Figure 1b).

Existing solar spectrum down-converters have numerous problems, such as limited spectral coverage, re-absorption, and toxicity [3–5]. The search for better down-converting materials thus continues. One possible

* **Corresponding author: Abdalla M. Darwish**, Physics and Pre-Engineering Department, Dillard University, New Orleans, LA 70122, United States of America, e-mail: adarwish@dillard.edu

* **Corresponding author: Sergey S. Sarkisov**, SSS Optical Technologies, Huntsville, AL 35816, United States of America, e-mail: mazillo123@yahoo.com

Simeon Wilson, Jamaya Wilson, Eboni Collins: Physics and Pre-Engineering Department, Dillard University, New Orleans, LA 70122, United States of America

Darayas N. Patel: Department of Mathematics and Computer Science, Oakwood University, Huntsville, AL 35896, United States of America

Kyu Cho, Anit Giri: Army Research Laboratory, Weapons & Materials Research Directorate, Aberdeen Proving Ground, MD 21005, United States of America

Lynn Koplitz, Brent Koplitz: Chemistry Department, Tulane University, New Orleans, LA 70118, United States of America

David Hui: Department of Mechanical Engineering, University of New Orleans, New Orleans, LA 70148, United States of America

Figure 1: (a) The concept of LSC. The nanoparticles of a luminescent material in the nanocomposite coating absorb incident UV/blue sunlight (blue arrows; photons with energy $h\nu_1$, where h is Planck's constant and ν_1 is the frequency of UV/blue radiation) and re-emit at an NIR wavelength (red arrows; photons with energy $h\nu_2$, where ν_2 is the frequency of NIR radiation) in glass window guiding it to a PV cell attached to the edge. (b) The concept of sunlight spectrum down-converter over a PV cell. A down-converting film over a conventional PV cell absorbs incident UV/blue sunlight and down-converts it into NIR radiation that efficiently generates extra PV power in addition to the one produced by visible and NIR spectral components of sunlight.

alternative is polymer nanocomposites filled with the nanoparticles of down-converting compounds of rare-earth (RE) elements. RE compounds have recently found many applications ranging from up-conversion biomarkers for bio-imaging, agents for cancer diagnostics and treatment, additives in solar power materials, to various sensors [6–25]. The advantages of RE-filled polymer nanocomposites as spectral down-converters are three-fold: their RE-based phosphor constituents can have high down-converting efficiency [26–30], they are environment friendly, and the polymer matrix offers smooth coating/form shaping.

Currently, polymer nanocomposite down-converting films are made by applying phosphor nanocolloids in polymer solutions over LSC panels or PV cells using spin coating [2], spraying, or dip coating [26] followed by drying off the solvent. The major deficiencies include limited concentration of phosphor nanoparticles in the colloids, poor control of film thickness, and possible clustering of the nanoparticles in the initial colloids during storage or when they are drying after deposition. The rationale for this work was to investigate an alternative, new approach for making polymer nanocomposite down-converting films – the concurrent multi-beam multi-target pulsed laser deposition (CMBMT-PLD) in open air. PLD,

traditionally conducted in a vacuum chamber, uses a beam of a high-energy pulsed laser to ablate a target and transfer target material on a substrate. The thickness of the deposited film can be maintained with a sub-nanometre precision. Multi-beam multi-target PLD makes films composed of the materials of several targets, which could have quite different physical and chemical properties. The constituents can be combined at any desirable proportion. Accordingly, a polymer nanocomposite film can be loaded with a greater amount of down-conversion phosphor than in the case of traditional techniques of film making. The concentration of the phosphor in the polymer matrix can also be precisely controlled in the direction normal to the film as well as along the film's plane. Concurrent deposition provides more uniform mixing of the phosphor particles in the polymer matrix as compared to non-concurrent (sequential) PLD. However, the vacuum chamber puts severe restrictions on the size of the substrates that can be coated and negates the benefits of conventional PLD in vacuum. Open-air PLD lacks this restriction. It brings the capability to coat large-size substrates of complex shapes, flexibility, and low cost. The major limitations of open-air PLD are possible degradation of the deposited material due to laser-initiated chemical reaction with atmospheric oxygen and nitrogen and strong

scattering of the ejected target matter on its way toward the substrate due to collisions with air molecules. The authors, using their experience with CMBMT-PLD [31–47], close the gap of knowledge on the properties of polymer nanocomposite films deposited in open air and show that, despite limitations, they can potentially function as solar spectrum down-converters.

Section 2 of the article describes deposition setup, preparation of RE-based down-conversion phosphors and phosphor PLD targets, and deposition process. In Section 3, based on optical spectroscopy data, the solar spectrum down-conversion mechanisms in the RE phosphors are discussed. The section also contains the results and discussion of the morphology and chemical integrity of pure polymer films made by open-air PLD. The structure and optical properties of the polymer-phosphor composite films are also discussed. Finally, in Section 4, the conclusions are made on feasibility of the proposed approach of making solar spectrum down-converting coatings.

2 Materials and methods

2.1 Deposition setup

The experimental setup for open-air CMBMT-PLD is schematically presented in Figure 2. Two high-energy focused laser beams from a pulsed laser concurrently ablate polymer and phosphor targets. The targets might rotate to avoid rapid erosion and cracking due to ablation in single spot. The plumes of the ablated material propagate toward the substrate and condensate on it. Since the plumes intersect, the phosphor and the polymer mix in a composite film formed on the substrate. The substrate is moving in X – Y directions to coat over a broad area. The substrate can also be heated to fuse separate melted polymer droplets in uniform film and smoothen its surface by capillary forces.

2.2 Targets

The inorganic targets were made of two RE-doped fluorides: $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ and $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$. Justification of using groups of RE ions (Yb^{3+} , Er^{3+}) and (Yb^{3+} , Tm^{3+}) for efficient down-conversion is given, for instance, in ref. [48]. It will also be briefly discussed in the next section.

Figure 2: Schematic of open-air co-deposition of phosphor and polymer using CMBMT-PLD. Parameter t is the distance between the spot of target ablation and the substrate.

The selection of fluoride NaYF_4 as a host for RE ions is justified by its low phonon energy ($\sim 300 \text{ cm}^{-1}$) that makes multi-phonon-assisted non-radiative relaxation of excited ions negligible [49]. Powders of the phosphors were synthesized using the economical wet process, which in its essence is co-precipitation in the presence of Na_2 -ethylenediaminetetraacetic acid (EDTA). In a typical procedure, 2.1 g of NaF (0.05 mol) was dissolved in 60 mL of deionized water. Another solution was prepared by mixing together $a \times 16 \text{ mL}$ of 0.2 mol/L aqueous solution of YCl_3 , $b \times 16 \text{ mL}$ of 0.2 mol/L solution of YbCl_3 , $c \times 16 \text{ mL}$ ($c = 1 - (a + b)$) of 0.2 mol/L solution of XCl_3 (X stands for Er or Tm), and 20 mL of 0.2 mol/L EDTA aqueous stock solution to form the metal–EDTA complex. All the chemicals were acquired from Sigma-Aldrich. The complex solution was injected in the NaF solution quickly, and the mixture was stirred vigorously for 1 h at room temperature. After stirring, the mixture was allowed to stay overnight for the precipitate to settle. The precipitate was collected, washed several times with distilled water and anhydrous ethanol. In the second stage of the process, the precipitate was dried in open air for 48 h at 60°C to remove traces of water. The resulting powder had the doping rate according to the formula $\text{NaY}_a\text{F}_4:\text{Yb}_b^{3+}, \text{X}_c^{3+}$. Four samples of phosphor powders were made. There were two samples of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ type: $\text{NaY}_{0.94}\text{F}_4:\text{Yb}_{0.03}^{3+}, \text{Er}_{0.03}^{3+}$ and $\text{NaY}_{0.78}\text{F}_4:\text{Yb}_{0.2}^{3+}, \text{Er}_{0.02}^{3+}$; and two samples of $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$ type: $\text{NaY}_{0.88}\text{F}_4:\text{Yb}_{0.1}^{3+}, \text{Tm}_{0.02}^{3+}$ and $\text{NaY}_{0.78}\text{F}_4:\text{Yb}_{0.2}^{3+}, \text{Tm}_{0.02}^{3+}$. The freshly made crystalline powder had NaYF_4 host in the cubic α -phase. It was converted into more efficient hexagonal β -phase using heat treatment in an open-air furnace at a temperature in the range between 400 and 600°C for 1 h. These temperature

range and duration of heating were found to be optimal for crystalline phase change in ref. [50]. After that, the phosphor powder was reduced by ball-milling to nano-powder. Finally, the nano-powder was compressed in a solid PLD target using a 25-T manual hydraulic press.

The polymer target was cut from an acrylic microscope slide (UVT-UV Transmittable-pure poly(methyl methacrylate) or PMMA from Ted Pella, Inc.; Catalog # 260226).

2.3 Deposition

During open-air CMBMT-PLD both targets (Figure 2) were ablated with focused beams from a Continuum Surelite SL III-10 Q-switched Nd:YAG laser. Laser pulses had an energy of 0.45 J for each target at a wavelength of 1,064 nm; pulse duration ~ 5 ns. Laser beams were focused on the targets with convex lenses (50 mm focal length). Peak beam intensity on the target of $\sim 2.8 \times 10^{16}$ W/cm² was typical for open-air PLD [51]. Corresponding fluence of $\sim 1.38 \times 10^8$ J/cm² exceeded by many orders of magnitude threshold fluence of PLD of target materials (between 0.4 and 1.25 J/cm² [34,52]). This resulted in a deposition rate of ~ 12 nm/pulse, which was three orders of magnitude faster than for typical vacuum PLD [34]. Ablation of PMMA target at the same fluence as phosphor leads to a higher polymer deposition rate and mixing phosphor particles in the

polymer at a proportion of $\sim 0.024\%$ by weight. The substrate was a glass microscope slide (Ted Pella Catalog #260441). Distance between the spot of target ablation and the substrate t (Figure 2) was ~ 2 mm. Incidence angles of the laser beams to the targets were in the range 80–86°. Time of ablation was 5 min. With a pulse repetition rate of 10 Hz, PLD took $\sim 3,000$ laser pulses.

3 Results and discussion

3.1 Down-conversion

3.1.1 Down-conversion mechanisms

The down-conversion mechanisms in the synthesized phosphors NaYF₄:Yb³⁺,Er³⁺ and NaYF₄:Yb³⁺,Tm³⁺ can be illustrated by energy-level diagrams of the pairs of coupled RE ions (Er³⁺, Yb³⁺) and (Tm³⁺, Yb³⁺) proposed in refs. [30,53]. They are presented in Figure 3a and b, respectively. The mechanisms correspond to the concentrations of RE ions and possible impurities and defects like the ones occurring in this work. Ion of Er³⁺ (Figure 3a) acts as an energy donor and that of Yb³⁺ as an acceptor. Wavy horizontal arrow marked “Sunlight” indicates optical excitation of Er³⁺ with UV photons of sunlight at a wavelength of ~ 380 nm. The

Figure 3: Energy-level diagram explaining the mechanisms of down-conversion in groups of ions (a) Er³⁺ and Yb³⁺ [30] and (b) Tm³⁺ and Yb³⁺ [53].

reason to select (Er^{3+} – Yb^{3+}) pair is that, for efficient down-conversion, a donor should have an energy level above 20,000 cm^{-1} along with an intermediate energy level at approximately 10,000 cm^{-1} , whereas the acceptor should have a single excited-state $^2\text{F}_{5/2}$ above $^2\text{F}_{7/2}$ ground-state corresponding to NIR emission in the range 9,100–11,100 cm^{-1} (900–1,100 nm wavelength). During exposure to sunlight, the absorbed UV photon excites Er^{3+} ion (grey arrow up in Figure 3a). Excited Er^{3+} ion relaxes radiationlessly from level $^4\text{G}_{11/2}$ down to $^4\text{F}_{7/2}$. After that, two cross-relaxation processes (marked by sloping dashed arrows) occur. Er^{3+} ion returns to the intermediate level $^4\text{I}_{11/2}$ from the $^4\text{F}_{7/2}$ level (dark grey dashed arrow down), resulting in the excitation of neighbouring Yb^{3+} ion from ground-state $^2\text{F}_{7/2}$ to level $^2\text{F}_{5/2}$ as shown by dashed arrow up. Then Er^{3+} ion returns to ground-level $^4\text{I}_{15/2}$ from intermediate-level $^4\text{I}_{11/2}$ and its energy is transferred to the second Yb^{3+} ion. This overall sequence involves a single UV photon and produces two NIR photons. In the case of (Tm^{3+} – Yb^{3+}) pair (Figure 3b), Tm^{3+} is excited by a blue sunlight photon. The energy of Tm^{3+} transition $^1\text{G}_4 \rightarrow ^3\text{H}_6$ is approximately twice as high as the energy difference between $^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$ levels of Yb^{3+} . This fact makes the cooperative down-conversion possible. Corresponding mechanism (1) thus results in two NIR photons emitted by Yb^{3+} ions. Since tetravalent Tm does not exist, the cooperative down-conversion from Tm^{3+} to Yb^{3+} would not be influenced by the “metal-to-metal” charge-transfer state. In addition, the low phonon energy of NaYF_4 ($\sim 300 \text{ cm}^{-1}$) together with the large energy gap between $\text{Tm}^{3+}:^1\text{G}_4$ and $\text{Yb}^{3+}:^2\text{F}_{5/2}$ makes the $\text{Tm}^{3+}:^1\text{G}_4 \rightarrow \text{Yb}^{3+}:^2\text{F}_{5/2}$ multi-phonon-assisted nonradiative relaxation negligible. There is also a cross-relaxation energy-transfer mechanism (2) between transition $\text{Tm}^{3+}:^1\text{G}_4 \rightarrow ^3\text{H}_5$ and $\text{Yb}^{3+}:^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$.

3.1.2 Optical absorption

Diffuse reflectance spectra of the phosphor powders (Figure 4) were taken with a Shimadzu UV-2600-ISR-2600 Plus UV-VIS-NIR spectrophotometer with integrating sphere (measurable spectral range 220–1,400 nm). Dynamic light-scattering measurement of the powder suspensions in water with a Malvern Zetasizer revealed that the dominating size of the powder particles was between 5 and 10 μm . The samples were prepared by compressing the micro-powders into pellets with a 25-T manual hydraulic press. Following [54], the absorption peaks in the diffuse reflectance spectra were related to some transitions in pairs of ions (Er^{3+} , Yb^{3+}) (curve A) and (Tm^{3+} , Yb^{3+}) (curve B) as presented in Figure 4

Figure 4: Diffuse reflectance spectra of the powder samples of down-conversion RE phosphors. Curve A corresponds to phosphor $\text{NaY}_{0.94}\text{F}_4:\text{Yb}_{0.03}^{3+},\text{Er}_{0.03}^{3+}$ baked after synthesis for 1 h at 500°C; B – $\text{NaY}_{0.78}\text{F}_4:\text{Yb}_{0.2}^{3+},\text{Tm}_{0.02}^{3+}$ baked for 1 h at 500°C. Absorption peak 1 corresponds to transition in ion of $\text{Er}^{3+}:^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}$ (380 nm); 2 – $\text{Er}^{3+}:^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$ (488 nm); 3 – $\text{Er}^{3+}:^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ (520 nm); 4 – $\text{Er}^{3+}:^4\text{I}_{15/2} \rightarrow ^4\text{S}_{3/2}$ (540 nm); 5 – $\text{Er}^{3+}:^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$ (653 nm); and 6, 6' – $\text{Yb}^{3+}:^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ (980 nm).

caption. The strongest peaks (6 and 6') correspond to the optical absorbance of the ion of Yb^{3+} due to transition $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ ($\sim 980 \text{ nm}$). The ion was responsible for down-conversion NIR emission when relaxing back from excited to ground state. The strength of peaks 6 and 6' is similar in magnitude. The absorption peaks 1 through 5, attributed to Er^{3+} , are less strong than peak 6, but still significant (curve A). But the absorption peaks that could be attributed to Tm^{3+} are not noticeable as compared to peak 6' in curve B. This can be explained by different concentrations of Yb^{3+} . In phosphor $\text{NaY}_{0.94}\text{F}_4:\text{Yb}_{0.03}^{3+},\text{Er}_{0.03}^{3+}$ (curve A), the concentration of Yb^{3+} is equal to that of Er^{3+} , while in $\text{NaY}_{0.78}\text{F}_4:\text{Yb}_{0.2}^{3+},\text{Tm}_{0.02}^{3+}$ the concentration of Yb^{3+} is ten times greater than that of Tm^{3+} . This correlates with findings in ref. [54].

3.1.3 Light sources simulating sunlight

Down-conversion luminescence spectroscopy of the phosphors was conducted using three light sources imitating UV-blue components of sunlight: (a) Insect Killer Bulb (40 W UV black light; fits UVB45 and UV40 units; intensity in close vicinity of the bulb $\sim 8.8 \text{ mW/cm}^2$; spectral peak $\sim 369 \text{ nm}$; FWHM $\sim 20 \text{ nm}$; emission spectrum is shown in Figure 5a); (b) UV301 LED flashlight from Shenzhen Lightfe Lighting Co., Ltd, China (intensity $\sim 25.6 \text{ mW/cm}^2$; peak of

the spectrum is at 368 nm; FWHM ~ 20 nm; Figure 5b), and (c) Ar-ion laser. The first UV source produced ~ 1.76 times radiation of UV spectral component of sunlight at the air mass coefficient AM1.5 [55]. The second source produced 5.12 times radiation. Maximum power of 80 mW of 488-nm spectral line of the Ar-ion laser was ~ 1.6 times the visible sunlight at AM1.5. Sharp peaks in the spectrum of the Insect Killer Bulb (Figure 5a) at 365.4 and 404.7 nm belonged to the mercury-vapour light leaking through the UV fluorescent coating of the bulb.

3.1.4 Down-conversion and down-shifting emission

All the down-conversion spectra presented below were taken with a spectrometer SP2500i from Teledyne Princeton Instruments equipped with uncooled InGaAs photo-detector ID-441. Figure 6a presents down-conversion emission spectra of phosphors (1) $\text{NaY}_{0.94}\text{F}_4:\text{Yb}^{3+}_{0.03},\text{Er}^{3+}_{0.03}$ and (2) $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+}_{0.2},\text{Er}^{3+}_{0.02}$ pumped with UV LED flashlight (Figure 5b). Apparently, the NIR emission from phosphor (2) with seven-fold greater concentration of Yb^{3+} ions (its diffusive reflectance spectrum was presented by curve A in Figure 4) was ~ 2.5 times stronger than that of phosphor (1). Besides NIR, the phosphors had a visible down-shifting emission. The spectrum of such an emission was taken with the Princeton SP2500i spectrometer equipped with photo-multiplying tube R928. The spectrum (presented for phosphor 2 in Figure 6a) has spectral peaks corresponding to the absorption peaks in

Figure 4 (curve A) that were attributed to various energy transitions in the diagram in Figure 3a. These visible emission spectral peaks have green (520 and 540 nm) and red (653 nm) colours.

Figure 7 presents down-conversion emission spectra of phosphors (a) $\text{NaY}_{0.88}\text{F}_4:\text{Yb}^{3+}_{0.1},\text{Tm}^{3+}_{0.02}$ and (b) $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+}_{0.2},\text{Tm}^{3+}_{0.02}$ pumped with Ar-ion laser at 488 nm (power ~ 75.5 mW). One can see that the intensity of this emission is much stronger than that of the phosphors based on (Er, Yb) pair presented in Figure 6. This can be explained by strong down-shifting radiation (Figure 6b) competing more significantly with the down-conversion process in (Er, Yb) pair as compared to (Tm, Yb). Down-shifting emission from (Tm, Yb) pair pumped with blue light occurs in 650–660 nm and 800–816 nm bands (Figure 3b). As will be shown later (Figure 17), the radiation in the first, red band was much weaker than the radiation in the second, short-wavelength NIR band. Moreover, the second band was also directly involved in the cross-relaxation energy-transfer mechanism (2) between transition $\text{Tm}^{3+}:^1\text{G}_4 \rightarrow ^3\text{H}_5$ and $\text{Yb}^{3+}:^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ (Figure 3b) that contributed significantly to down-conversion. In each NIR down-conversion spectrum, Stark splitting peak structure of Yb^{3+} emission (during transition $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$, Figure 3b) could not be well distinguished. A dominating spectral peak at 980 nm could be observed for phosphor (a) and 1,100 nm – for phosphor (b) with double content of Yb^{3+} . The latter phosphor had a diffusion reflectance spectrum presented in Figure 4 (curve B) with a strong absorption peak corresponding to Yb^{3+} transition $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$. This

Figure 5: Emission spectra of UV sources used to simulate UV component of sunlight in the experiments with down-conversion materials: (a) Insect killer UV black light (intensity ~ 8.8 mW/cm²). (b) UV LED flashlight (intensity ~ 25.6 mW/cm²).

Figure 6: (a) Down-conversion emission spectra of phosphors (1) $\text{NaY}_{0.94}\text{F}_4:\text{Yb}^{3+},\text{Er}^{3+}$ and (2) $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+},\text{Er}^{3+}$ pumped by UV flashlight (Figure 5b). (b) Visible (down-shifting) emission spectrum of phosphor $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+},\text{Er}^{3+}$ pumped by UV bulb for insect killer (Figure 5a). Group of peaks 1 corresponds to the transition of excited ion $\text{Er}^{3+}:^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (520 nm); group 2 – $\text{Er}^{3+}:^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (540 nm); group 3 – $\text{Er}^{3+}:^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (653 nm). Dashed line is the tail of the spectrum of the UV bulb.

Figure 7: (a) Down-conversion emission spectra of phosphors (a) $\text{NaY}_{0.88}\text{F}_4:\text{Yb}^{3+},\text{Tm}^{3+}$ and (b) $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+},\text{Tm}^{3+}$ pumped with Ar-ion laser at 488 nm (power ~ 75.5 mW).

intensity of down-conversion emission of this phosphor was also ~ 5 times greater than that of phosphor (a).

Figure 8a presents the intensity of down-conversion emission at 980 nm of phosphor $\text{NaY}_{0.88}\text{F}_4:\text{Yb}^{3+},\text{Tm}^{3+}$ plotted versus the wavelength of the pump (different spectral lines of Ar-ion laser). The intensity was re-calibrated to account for different pump powers at various wavelengths. One can see that NIR emission response of the phosphor remains basically “flat” within the spectral band of the pump from 457.9 to 514.5 nm. Quantum yield (QY) of down-conversion emission of the phosphor, defined as

the ratio of number N_{NIR} of produced NIR photons to number N_{488} of pump blue (488 nm) photons $\text{QY} = N_{\text{NIR}}/N_{488}$ [56], was roughly (neglecting reflectance of pump radiation) estimated in the following way. N_{488} was proportional to the power of incident 488-nm laser beam (~ 80 mW), $N_{488} = T \times 80$ mW (T – time interval). N_{NIR} was computed based on the ratio of the intensity of NIR emission I_{NIR} , as measured by spectrometer SP2500i, times its spectral band Δ_{NIR} to intensity I_{980} of the spectral peak of a reference 980 nm laser diode with known power (1.6 mW) times its spectral band Δ_{980} , $N_{\text{NIR}} = T \times [(I_{\text{NIR}} \times$

Figure 8: Intensity of down-conversion emission at 980 nm of phosphor $\text{NaY}_{0.88}\text{F}_4:\text{Yb}^{3+}, \text{Tm}^{3+}_{0.02}$ (a) versus the wavelength of the pump (different spectral lines of Ar-ion laser) and (b) versus the power of pump from Ar-ion laser spectral line at 465.8 nm. Solid red line is the linear fit of the experimental plot.

$\Delta_{\text{NIR}}/(I_{980} \times \Delta_{980})] \times 1.6 \text{ mW}$. QY was found to be $\sim 5\%$ – of the same order as in ref. [56]. As an example of the phosphor response to variable pump power of the Ar-ion laser spectral lines, Figure 8b presents the intensity of down-conversion emission at 980 nm peak plotted versus the power of the 465.8 nm pump from Ar-ion laser. Linear fit of the plot suggests that down-conversion is a linear process [54]. Accordingly, this makes it possible to reach high conversion efficiencies independent of the incident power and allows for the use of non-concentrated sunlight.

with polymer coating was placed on a hot plate heated to a temperature of $\sim 90^\circ\text{C}$ as measured by a thermocouple thermometer touching the surface of the hot-plate. Heating the substrate for 2 min melted isolated polymer islands and forced some of them to coalesce (Figure 10). In the centre of the coating (Figure 11), coalescence produced a continuous polymer film. The film was separated from the substrate and its thickness was measured with a micrometer to be $35 \pm 5 \mu\text{m}$. Poorly controlled and rather rapid heat influx induced boiling and formed air bubbles in some spots.

3.2 Pure polymer film after deposition

3.2.1 Morphology

Since the polymer target was exposed to intense laser radiation in ambient air, our concern was preservation of polymer integrity during PLD. The morphology of pure PMMA coatings was investigated using optical microscopy with an optical AmScope M400 monocular compound microscope (WF10 $\times$ eyepiece; 40 $\times$ to 400 $\times$ magnification; tungsten bulb illuminator; brightfield, Abbe condenser; coarse and fine Focus) with Mu 400 CCD camera. The microscope images of the coatings are presented in Figures 9–11. Images taken on the edge of the coating (Figures 9 and 10) show that the deposited material was in the form of separate polymer islands brought to the substrate more likely by the process of laser-induced catapulting of the droplets of melted target [57]. Glass transition temperature of PMMA is known to be between 85 and 165 $^\circ\text{C}$ [58]. The substrate

3.2.2 Chemical integrity

To verify if the polymer molecules disintegrated after deposition, we compared FTIR absorption spectra of the coating against unexposed target (Figure 12a). FTIR spectra were taken with Nicolet iS5 FTIR spectrometer from Thermo Fisher Scientific with iD7 ATR diamond anvil attachment. Apparent similarity of two FTIR spectra indicated that there was no noticeable decomposition of the deposited polymer. Figure 12b presents FTIR spectra of (1) virgin target (unexposed PMMA slide) and (2) target material on the edge of the cavity made in the target by the laser ablation. Three new absorption peaks can be attributed to the stretch vibration modes of terminal alkynes $\text{R}-\text{C}\equiv\text{C}-\text{H}$ (2,140–2,100 cm^{-1}), $\text{R}-\text{N}=\text{C}-\text{S}$ (2,140–1,990 cm^{-1}), $\text{R}-\text{N}-\text{C}$ (2,165–2,110 cm^{-1}), or cyanide $\text{C}\equiv\text{N}$ (2,109 cm^{-1}) [59]. Based on the FTIR data, the following assumptions can be made with regard to the sequence of events during open-air PLD of the polymer (Figure 13): (1) laser beam heated and melted the polymer; (2) volatile products of decomposition of the

Figure 9: Microscope images of PMMA coating on glass substrate right after open-air PLD. The images were taken with (a) $\times 40$ magnification (dimensions: $X = 2,257 \mu\text{m}$, $Y = 1,674 \mu\text{m}$) and (b) $\times 100$ magnification (dimensions: $X = 903 \mu\text{m}$, $Y = 670 \mu\text{m}$). Dark band on the right in image (a) is the mark made by microscope objective that occasionally touched the coating. The images were taken on the edge of the deposition zone, where deposited material did not cover whole surface.

Figure 10: Microscope images of PMMA coating presented in Figure 9 after melting on a hot plate at $\sim 90^\circ\text{C}$ with (a) $\times 40$ and (b) $\times 100$ magnification. The images were taken on the edge of the deposition zone, where deposited material did not cover whole surface.

Figure 11: Microscope image of PMMA coating right after melting on a hot plate at $\sim 90^\circ\text{C}$ taken with (a) $\times 40$ and (b) $\times 100$ magnification. The images were taken in the centre, where deposited material covered whole surface. Small circles are air bubbles in the boiling melt.

Figure 12: (a) FTIR absorption spectra of PMMA slide used as a PLD target and deposited film (Figures 9 through 11). (b) FTIR spectra of (1) PMMA slide (target) and (2) the material on the edge of the cavity created in the PMMA slide by the laser beam during ablation. Three new absorption peaks in the box can be attributed to the stretch vibration modes of terminal alkynes $R-C\equiv C-H$ ($2,140-2,100\text{ cm}^{-1}$), $R-N\equiv C-S$ ($2,140-1,990\text{ cm}^{-1}$), $R-N\equiv C$ ($2,165-2,110\text{ cm}^{-1}$), $C\equiv N$ (cyanides, $2,019\text{ cm}^{-1}$) [59].

polymer escaped; (3) shock wave pulverized and sputtered (catapulted) droplets of melted polymer on the substrate; (4) polymer target material around the cavity edges underwent pyrolysis and photo-chemical modification; (5) polymer droplets solidified on the substrate; and (6) deposited coating preserved the chemical structure of the polymer target.

3.3 Polymer nanocomposite film

Down-conversion polymer–phosphor composite films made by CMBMT-PLD were further investigated to verify if the

Figure 13: Schematic illustrating the open-air PLD of polymer coating.

phosphor particles retained the properties of the target and to find the average size of the particles and the way they were embedded in the polymer. Figure 14a presents the X-ray diffraction (XRD) spectrum of PMMA + NaYF₄:Yb³⁺,Er³⁺ film taken with a Bruker D2 Phaser diffractometer. The sample was prepared by separating the film from the substrate and pulverizing it with a mortar. Observed diffraction peaks can be attributed to the hexagonal β -phase of NaYF₄ (JCPDS No 28-1192) identical to the crystalline structure of the target. As for the effect of Yb³⁺ or Er³⁺ (Tm³⁺) dopants on the XRD spectrum of the NaYF₄ matrix in the phosphors, small variations might be detected in the lattice parameters due to differences in ionic radius size between the Y³⁺ and the dopants taking its place in random locations in the crystalline matrix [60,61]. Randomness of the dopant locations brings disorder in the matrix and variations of the local crystal field for the second-nearest neighbours of the dopant ions. This imposes a slightly different crystal field environment for each subset of the dopant ions. Such differences imply an inhomogeneous broadening of the bands corresponding to the transitions in the photoluminescence spectra unlike those from ordered crystals that exhibit narrow bands. Detailed investigation of such phenomena was out of scope of this work. High-resolution scanning-electron-microscope (SEM) image of the film taken with a JEOL JSM-7100FA microscope (Figure 14b) shows phosphor particles (white spots) of a size between 10 and 50 nm dispersed in the polymer matrix. Analysis of the SEM images showed that the mean concentration of nanoparticles n was 526 per square micron. The uniformity of their

Figure 14: (a) XRD spectrum of the polymer nanocomposite film made of PMMA and the nanoparticles of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ with the diffraction peaks attributed to the hexagonal β -phase of NaYF_4 . (b) High-resolution SEM image of the polymer nanocomposite film of PMMA + $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ deposited on glass substrate at magnification $\times 100\text{k}$.

dispersion U , defined as $U = (1 - \text{SD}/n) \times 100\%$ [62] (SD is the standard deviation of the concentration of nanoparticles), was 76%. Further improvement of uniformity could be achieved by randomized translation of the substrate during the deposition. Based on average nanoparticle diameter $d_a \sim 30$ nm and two-dimensional concentration of the nanoparticles in the film, the effective share of sunlight photons captured by a 30 nm-thick nanocomposite sub-layer S_c could be estimated as $S_c = n(\pi d^2/4) = 0.546$. The share of sunlight photons passing freely through the sub-layer was thus $P_f = 1 - S_c = 0.454$. For a 300 nm-thick nanocomposite film made of ten 30 nm-thick sub-layers the share of passing sunlight photons would be $(P_f)^{10} = 3.4 \times 10^{-4}$. So almost all the photons were captured. QY $\sim 5\%$ of the phosphor determined earlier could thus be applied to a nanocomposite film of a thickness >300 nm as an estimate of its down-conversion efficiency as well.

One convenient way of checking preservation of optical properties of the phosphor target in deposited nanoparticles could be observation of visible up-conversion radiation from a polymer nanocomposite film illuminated with a 980 nm laser diode. Here we consider nanoparticles of $\text{NaYF}_4:\text{Yb}^{3+},\text{Tm}^{3+}$. Energy-level diagram explaining mechanisms of up-conversion in coupled ions of Yb^{3+} and Tm^{3+} is presented in Figure 15 [63]. Solid, dotted, and wavy arrows represent photon absorption/emission, energy transfer, and non-radiative relaxation processes, respectively. Four ions of Yb^{3+} are excited by NIR pump radiation and transfer energy of their NIR photons via a multi-step excitation process to an ion of Tm^{3+} . During relaxation to the ground state Tm^{3+} ion can emit blue, green, red, or short-wavelength NIR photon. We illuminated the deposited and melted PMMA + $\text{NaY}_{88}\text{F}_{12}:\text{Yb}_{10}\text{Tm}_{20}$

film with a 980-nm laser diode and were able to see up-conversion emission from illuminated spots in the form of blue strips having the shape of the laser beam (Figure 16). Furthermore, spectroscopy of up-conversion emission from the film

Figure 15: Energy-level diagram of Yb^{3+} and Tm^{3+} ions explaining the mechanism of up-conversion. Solid, dotted, and wavy arrows represent photon absorption/emission, energy-transfer, and non-radiative relaxation processes, respectively [63].

Figure 16: Optical microscopic images of PMMA+ $\text{NaY}_{0.88}\text{F}_4:\text{Yb}_{0.1}^{3+}\text{Tm}_{0.02}^{3+}$ nanocomposite film made by open-air CMBMT-PLD and heated at $\sim 90^\circ\text{C}$ at magnification (a) $\times 40$ and (b) $\times 100$. The film was illuminated with a 200 mW 980 nm laser. Blue strip is produced by up-conversion emission of the embedded phosphor nanoparticles initiated by the infrared pump.

Figure 17: Upconversion emission spectrum of PMMA + $\text{NaY}_{0.88}\text{F}_4:\text{Yb}_{0.1}^{3+}\text{Tm}_{0.02}^{3+}$ nanocomposite film made by open-air CMBMT-PLD. The film was pumped with a 200 mW 980 nm laser.

(Figure 17) revealed the presence of blue (488 nm), weak (slightly higher than noise) red (658 nm), and strong 802 nm NIR peak in agreement with the energy diagram (Figure 15) and literature data [63]. This confirmed that the phosphor nanoparticles retained the optical properties of the target after PLD process and were evenly distributed in the deposited polymer film.

4 Conclusions

RE-based phosphors $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$ and $\text{NaYF}_4:\text{Yb}^{3+}, \text{Tm}^{3+}$, synthesized by the wet method, were found to be

suitable for polymer nanocomposite sunlight spectrum down-converters with a Stokes shift between the spectrum of absorption and fluorescence as large as 620 nm (from 360 to 980 nm) minimizing the effect of re-absorption. The latter phosphor was more efficient in down-converting blue light in NIR with a QY of $\sim 5\%$. Polymer nanocomposite down-converters were successfully deposited on glass substrates by co-deposition of polymer PMMA and the phosphors using the open-air CMBMT-PLD process. The polymer was found to preserve its chemical integrity during deposition that more likely occurred as catapulting polymer droplets from the melted target. Post-heating of the substrate at $\sim 90^\circ\text{C}$ led to fusion of melted polymer islands into uniform coating. The phosphor nanoparticles with a size ranging from 10 to 50 nm were evenly embedded in the polymer matrix during the co-deposition. The nanoparticles retained the crystalline structure and optical properties of the phosphor target. QY of the down-conversion polymer nanocomposite film was estimated to be not less than 5%. The proposed deposition method thus demonstrated its feasibility and potential for making commercial-size thin-film sunlight down-converters for PV solar power applications.

Acknowledgments: Dillard team appreciates the financial support from US Air Force Office of Scientific Research Grant FA9550-18-1-0364 AFOSR and Army Research Office Grant No W911-NF-19-1-0451 and the partial support from DU Minority Health and Health Disparity Research Center MHHDR. Research of Dr. Patel was sponsored by the Army Research Office and was accomplished under Grants Number W911NF-18-1-0446 and W911NF-19-1-0506. The

views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Office or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein. Additionally, Dr. Patel's research was supported by the grant from UNCF, Henry C. McBay Research Fellowship 2019.

Conflict of interest: The authors declare no conflict of interest regarding the publication of this paper.

References

- [1] Debije M. Luminescent solar concentrators. Luminescent solar solutions. *Semiconductor solutions*. Nat Photonics. 2017;11:143–4.
- [2] Ho W-J, Yang G-C, Shen Y-T, Deng Y-J. Improving efficiency of silicon solar cells using europium-doped silicate-phosphor layer by spin-on film coating. *Appl Surf Sci*. 2016;365:120–4.
- [3] Krumer Z, Pera SJ, van Dijk – Moes RJA, Zhao Y, de Brouwer S, et al. Tackling self-absorption in luminescent solar concentrators with type-II colloidal quantum dots. *Sol Energ Mat Sol C*. 2013;111:57–65.
- [4] Pietryga JM, Park Y-S, Lim J, Fidler AF, Bae WK, Sergio Brovelli S, et al. Spectroscopic and device aspects of nanocrystal quantum dots. *Chem Rev*. 2016;116:10513–622.
- [5] Giebink NC, Wiederrecht GP, Wasielewski MR. Resonance-shifting to circumvent reabsorption loss in luminescent solar concentrators. *Nat Photonics*. 2011;5:694–701.
- [6] Bhattacharya S, Alkharfy KM, Janardhanan R, Mukhopadhyay D. Nanomedicine: Pharmacological perspectives. *Nanotechnol Rev*. 2012;1:235–53.
- [7] Huang Y-Y, Sharma SK, Dai T, Chung H, Yaroslavsky A, Garcia-Diaz M, et al. Can nanotechnology potentiate photodynamic therapy? *Nanotechnol Rev*. 2012;1(2):111–46.
- [8] Le Trequesser Q, Seznec H, Delville M-H. Functionalized nanomaterials: Their use as contrast agents in bioimaging: mono- and multimodal approaches. *Nanotechnol Rev*. 2013;2(2):125–69.
- [9] Youkhanna J, Syoufjy J, Rhorer M, Oladeinde O, Zeineldin R. Toward nanotechnology-based solutions for a disease: Ovarian cancer as an example. *Nanotechnol Rev*. 2013;2(4):473–84.
- [10] Sheeba CJ, Marslin G, Revina AM, Franklin G. Signaling pathways influencing tumor microenvironment and their exploitation for targeted drug delivery. *Nanotechnol Rev*. 2014;3(2):123–51.
- [11] Yao L, Xu S. Detection of magnetic nanomaterials in molecular imaging and diagnosis applications. *Nanotechnol Rev*. 2014;3(3):247–68.
- [12] Rai M, Birla S, Ingle AP, Gupta I, Gade A, Abd-Elsalam K, et al. Nanosilver: An inorganic nanoparticle with myriad potential applications. *Nanotechnol Rev*. 2014;3(3):281–309.
- [13] Li J, Liu H, Deng Y, Liu G, Chen Y, Yang J. Emerging nanostructured materials for the catalytic removal of volatile organic compounds. *Nanotechnol Rev*. 2016;5(1):147–81.
- [14] Zoghbi ME, Altenberg GA. Membrane protein reconstitution in nanodiscs for luminescence spectroscopy studies. *Nanotechnol Rev*. 2017;6(1):33–46.
- [15] Song C, Zhang S, Zhou Q, Hai H, Zhao D, Hui Y. Upconversion nanoparticles for bioimaging. *Nanotechnol Rev*. 2017;6(2):233–42.
- [16] Yang Y, Qina Z, Zenga W, Yanga T, Cao Y, Mei C, et al. Toxicity assessment of nanoparticles in various systems and organs. *Nanotechnol Rev*. 2017;6(3):279–89.
- [17] Malekzad H, Zangabad PS, Mirshekar H, Karimi M, Hamblin MR. Noble metal nanoparticles in biosensors: Recent studies and applications. *Nanotechnol Rev*. 2017;6(3):301–29.
- [18] Zhoua Q, Zhanga L, Wua H. Nanomaterials for cancer therapies. *Nanotechnol Rev*. 2017;6(5):473–96.
- [19] Fan R, Lu F, Li K. Fabrication and simulation of 1,540 nm transmission by 532 nm excitation in photonic crystal of Er:ZnO film. *Nanotechnol Rev*. 2017;6(6):497–503.
- [20] Li J, Yao M, Shao Y, Yao D. The application of bio-nanotechnology in tumor diagnosis and treatment: A view. *Nanotechnol Rev*. 2018;7(3):257–66.
- [21] Jia F, Li G, Yang B, Yu B, Shen Y, Cong H. Investigation of rare earth upconversion fluorescent nanoparticles in biomedical field. *Nanotechnol Rev*. 2019;8:1–17.
- [22] Sawicki K, Czajka M, Matysiak-Kucharek M, Fal B, Drop B, Męczyńska-Wielgosz S, et al. Toxicity of metallic nanoparticles in the central nervous system. *Nanotechnol Rev*. 2019;8:175–200.
- [23] Miao Y, Lu J, Yin J, Zhou C, Guo Y, Zhou S. Yb³⁺-containing chitosan hydrogels induce B-16 melanoma cell anoikis via a Fak-dependent pathway. *Nanotechnol Rev*. 2019;8:645–60.
- [24] Godlewski MM, Kaszewski J, Kielbik P, Olszewski J, Lipinski W, Słowska A, et al. New generation of oxide-based nanoparticles for the applications in early cancer detection and diagnostics. *Nanotechnol Rev*. 2020;9(1):274–302.
- [25] Nakamura M. Biomedical applications of organosilica nanoparticles towards theranostics. *Nanotechnol Rev*. 2012;1:469–91.
- [26] Wang T, Zhang J, Maa W, Luo Y, Wang L, Hua Z, et al. Luminescent solar concentrator employing rare earth complex with zero self-absorption loss. *Sol Energy*. 2011;85:2571–9.
- [27] Park WJ, Oh SJ, Kim JK, Heo J, Wagner T, Strizik L. Down-conversion in Tm³⁺/Yb³⁺ doped glasses for multicrystalline silicon photo-voltaic module efficiency enhancement. *J Non-Cryst Solids*. 2014;83:181–3.
- [28] Melvin ten Kate O, Krämer KW, Van, der Kolk E. Efficient luminescent solar concentrators based on self-absorption free, Tm²⁺ doped halides. *Sol Energ Mat Sol C*. 2015;140:115–20.
- [29] Xia W, Jin X, Yang X, Xiao S. Down conversion of Er³⁺-Yb³⁺ couple in Y₂BaZnO₅. *Opt Mater*. 2016;54:294–9.
- [30] Verma A, Sharma SK. Down-conversion from Er³⁺-Yb³⁺ co-doped CaMoO₄ phosphor: A spectral conversion to improve solar cell efficiency. *Ceram Inter*. 2017;43:8879–85.
- [31] Darwish A, Sarkisov S. Method and apparatus for open-air pulsed laser deposition. US Patent No. 10316403 B2. June 11, 2019.

- [32] Darwish AM, Sagapolutele MT, Sarkisov S, Patel D, Hui D, Koplitz B. Double beam pulsed laser deposition of composite films of poly (methyl methacrylate) and rare earth fluoride upconversion phosphors. *Compos Part B - Eng.* 2013;55:139–46.
- [33] Darwish AM, Wilson S, Sarkisov S, Patel D. Double pulse laser deposition of polymer nanocomposite $\text{NaYF}_4:\text{Tm}^{3+},\text{Yb}^{3+}$ films for optical sensors and light emitting applications. In: Yin S, Guo R, editors. *Photonic fiber and crystal devices: advances in materials and innovations in device applications VII*. Proceedings of SPIE 8847; 2014 Sept 28; San Diego, CA. Bellingham, WA: SPIE; 2013. p. 884702.
- [34] Darwish AM, Burkett A, Blackwell A, Taylor K, Sarkisov S, Patel D, et al. Polymer-inorganic nano-composite thin film upconversion light emitters prepared by double-beam matrix assisted pulsed laser evaporation (DB-MAPLE) method. *Compos Part B-Eng.* 2015;68:355–64.
- [35] Darwish AM, Burkett A, Blackwell A, Taylor K, Walker V, Sarkisov S, et al. Efficient upconversion polymer-inorganic nanocomposite emitters prepared by the double beam matrix assisted pulsed laser evaporation (DB-MAPLE). In: Yin S, Guo R, editors. *Photonic fiber and crystal devices: advances in materials and innovations in device applications VIII*. Proceedings SPIE 9200; 2014 Sept 5; San Diego, CA. Bellingham, WA: SPIE; 2014. p. 92000C.
- [36] Patel D, Lewis A, Wright III D, Lewis D, Sarkisov S, Darwish AM. Optical properties and size distribution of the nano-colloids made of rare-earth ion-doped NaYF_4 . In: Jiang S, Digonet MJF, editors. *Optical components and materials XII: Proceedings of SPIE 9359*; 2015 March 16; San Francisco, CA. Bellingham, WA: SPIE; 2015. p. 93591L.
- [37] Darwish AM, Wilson S, Blackwell A, Taylor K, Sarkisov SS, Patel DN, et al. Ammonia sensor based on polymer-inorganic nano-composite thin film upconversion light emitter prepared by double-beam pulsed laser deposition. *Am J Mater Sci.* 2015;5(3A):8–15.
- [38] Darwish AM, Wilson S, Blackwell A, Taylor K, Sarkisov S, Patel D, et al. Polymer-inorganic nanocomposite thin film emitters, optoelectronic chemical sensors, and energy harvesters produced by multiple-beam pulsed laser deposition. In: Yin S, Guo R, editors. *Photonic fiber and crystal devices: advances in materials and innovations in device applications IX: Proceedings of SPIE 9586*; 2015 Aug 26; San Diego, CA. Bellingham, WA: SPIE; 2015. p. 958602.
- [39] Darwish AM, Wilson S, Blackwell A, Sarkisov S, Patel D, Mele P, et al. Multi-beam pulsed laser deposition: New method of making nanocomposite coatings. In: Yin S, Guo R, editors. *Photonic fiber and crystal devices: advances in materials and innovations in device applications IX: Proceedings of SPIE 9586*; 2015 Aug 26; San Diego, CA. Bellingham, WA: SPIE; 2015. p. 958605.
- [40] Darwish AM, Moore S, Muhammad A, Sarkisov SS, Patel DN, Mele P, et al. Organic-inorganic nano-composite films for photonic applications made by multi-beam multi-target pulsed laser deposition with remote control of the plume directions. In: Yin S, Guo R, editors. *Photonic fiber and crystal devices: advances in materials and innovations in device applications X: Proceedings of SPIE 9958*; 2016 Sept 15; San Diego, CA. Bellingham, WA: SPIE; 2016. p. 995802.
- [41] Darwish AM, Moore S, Muhammad A, Sarkisov S, Patel D, Mele P, et al. Polymer nano-composite films with inorganic upconversion phosphor and electro-optic additives made by concurrent triple-beam matrix assisted and direct pulsed laser deposition. *Compos Part B Eng.* 2017;109:82–90.
- [42] Darwish AM, Sarkisov SS, Patel DN. Concurrent multi-target laser ablation for making nano-composite films. Chapter 6. In: Yang D, editor. *Applications of laser ablation – Thin Film Deposition, Nanomaterial Synthesis and Surface Modification*. Rijeka, Croatia: InTech; 2016. p. 129–48.
- [43] Darwish AM, Sarkisov SS, Patel DN, Muhammad A, Thompson K, Johnson M, et al. Polymer nanocomposite luminescent films for solar energy harvesting made by concurrent multi-beam multi-target pulsed laser deposition. In: Yin S, Guo R, editors. *Photonic fiber and crystal devices: advances in materials and innovations in device applications XII: Proceedings of SPIE 10755*; 2018 Sept 4; San Diego, CA. Bellingham, WA: SPIE; 2018. p. 107552.
- [44] Darwish AM, Sarkisov SS, Patel DN. Nanocomposite luminescent solar concentrators: Optics for green energy. *Asian J Phys.* 2018;27(9–12):625–36.
- [45] Darwish AM, Sarkisov SS, Wilson J, Muhammad A, Thompson K, Patel DN, et al. Luminescent solar concentrators based on polymer nanocomposite films made by open-air pulsed laser deposition. In: Yin S, Guo R, editors. *Photonic fiber and crystal devices: advances in materials and innovations in device applications XIII: Proceedings of SPIE 11123*; 2019 Sept 9; San Diego, CA. Bellingham, WA: SPIE; 2019. p. 1112302.
- [46] Darwish AM, Sarkisov SS, Patel DN. Nanocomposite windows converting solar power into electricity for self-sustaining buildings. In: Bumajdad A, Bouhamra W, Alsayegh OA, Kamal HA, Alhajraf SF, editors. *Gulf Conference on Sustainable Built Environment*. Cham, Switzerland: Springer Nature Switzerland AG; 2020. p. 367–82.
- [47] Husainat A, Warsame A, Cofe P, Attia J, Fuller J, Darwish A. Simulation and analysis method of different back metals contact of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cell along with electron transport layer TiO_2 using MBMT-MAPLE/PLD. *Am J Opt Photonics.* 2020;8(1):6–26.
- [48] Van der Ende BM, Aarts L, Meijerink A. Lanthanide ions as spectral converters for solar cells. *Phys Chem Phys.* 2009;11:11081–95.
- [49] Baker CC, Fontana J, Kim W, Bowman SR, Sanghera J, Ballato J, et al. Nanoparticle doping for high power fiber lasers at eye-safer wavelengths. *Opt Express.* 2017;25(12):13903–15.
- [50] Patel D, Sarkisov SS, Darwish A, Ballato J. Optical gain in capillary light guides filled with $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanocolloids. *Opt Express.* 2016;24(18):21147–58.
- [51] Konov VI, Kononenko TV, Loubnin EN, Dausinger F, Breitling D. Pulsed laser deposition of hard coatings in atmospheric air. *Appl Phys A.* 2004;79:931–6.
- [52] Torrisi L, Lorusso A, Nassisi V, Picciotto A. Characterization of laser ablation of polymethylmethacrylate at different laser wavelengths. *Rad Eff Defects Solids: Incorpor Plasma Sci Plasma Technol.* 2008;163(3):179–87.
- [53] Lin H, Zhou S, Hou X, Li W, Li Y, Teng H, et al. Down-conversion from blue to near infrared in $\text{Tm}^{3+}-\text{Yb}^{3+}$ codoped Y_2O_3 transparent ceramics. *IEEE Photon Tech Lett.* 2010;22(12):866–88.
- [54] Aarts L, Van der Ende BM, Meijerink A. Downconversion for solar cells in $\text{NaYF}_4:\text{Er}$, Yb . *J Appl Phys.* 2009;106:023522.

- [55] Sunlight. Wikipedia [Internet] 2020 July [cited 2020 August 23]. Available from https://en.wikipedia.org/wiki/Sunlight#cite_ref-6.
- [56] Zhydachevskyy Y, Tsiurma V, Baran M, Lipinska L, Sybilski P, Suchoki A. Quantum efficiency of the down-conversion process in Bi^{3+} – Yb^{3+} co-doped Gd_2O_3 . *J Lumin.* 2018;196:169–73.
- [57] Vogel A, Loretz K, Horneffer V, Huttman G, von Smolinski D, Gebert A. Mechanisms of laser-induced dissection and transport of histologic specimens. *Biophys J.* 2007;93:4481–500.
- [58] Poly(methyl methacrylate). Wikipedia [Internet] 2020 August [cited 2020 August 28]. Available from https://en.wikipedia.org/wiki/Sunlight#cite_ref-6.
- [59] Larkin P. *Infrared and Raman Spectroscopy: Principles and Spectral Interpretation*. Waltman, MA: Elsevier; 2011.
- [60] Deng K, Gong T, Hu L, Wei X, Chen Y, Yin M. Efficient near-infrared quantum cutting in $\text{NaYF}_4:\text{Ho}^{3+},\text{Yb}^{3+}$ for solar photovoltaics. *Opt Express.* 2011;19(3):1749–54.
- [61] Barranco J, Mendez-Blas A, Calixto ME. Structural, morphology and optical properties of NaYF_4 thin films doped with trivalent lanthanide ions. *J Mat Sci: Mat Electron.* 2019;30:4855–66.
- [62] Prokhorov AV, Hanssen LM. Numerical modeling of an integrating sphere radiation source. In: Wooley CB, editor. *Modeling and Characterization of Light Sources: Proceedings of SPIE 4775*; 2002 August 16; Seattle, WA. Bellingham, WA: SPIE; 2002. p. 106–18.
- [63] Arppe R, Hyppänen I, Perälä N, Peltomaa R, Kaiser M, Würth C, et al. $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ and $\text{NaYF}_4:\text{Yb}^{3+},\text{Tm}^{3+}$ nanophosphors by water: The role of the sensitizer Yb^{3+} in non-radiative relaxation. *Nanoscale.* 2015;7:11746–57.