2013

Polymer Optical Fibers For Luminescent Solar Concentration

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POLYMER OPTICAL FIBERS
FOR LUMINESCENT SOLAR CONCENTRATION

by

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A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Electrical Engineering and Computer Science
in the College of Engineering and Computer Science
at the University of Central Florida
Orlando, Florida

Spring Term
2013

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ABSTRACT

Luminescent solar concentrators (LSC's) are promising candidates for reducing the cost of solar power generation. Conventional LSC's are slab waveguides coated or doped with luminescence materials for absorption and guiding of light to the slab edges in order to convert optical energy into electricity via attached photovoltaic (PV) cells. Exploiting the advantages of optical fiber production, a fiber LSC (FLSC) is presented in this thesis, in which the waveguide is a polymeric optical fiber. A hybrid fiber structure is proposed for an efficient two-stage concentration of incident light, first into a small doped core using a cylindrical micro-lens that extends along the fiber, and second to the fiber ends by guiding the fluoresced light from the active dopants. Flexible sheets are assembled with fibers that can be bundled and attached to small-area PV cells. Small dimensions and directional guiding of the fibers allow for approximately one order of magnitude geometrical gain improvement over that of existing flat LSC's. In addition, the undesired limit of LSC size is eliminated in one direction.

Modeling and optimization of an FLSC design is presented using polarization-ray tracing under realistic conditions with solar spectrum radiation and broad-band absorption and emission spectra of fluorescence materials with their inevitable self-absorption effect.

Methods and results of fabrication and accurate optical characterization of such FLSC using two off-the-shelf organic dyes and a commercially available polymer, COP, are discussed in detail. Fiber preforms, fabricated under optimized conditions for lowlight transport loss, are thermally

drawn into sub-millimeter-size fibers. Characterization of several samples with various concentrations of the two dyes shows an optical-to-optical conversion efficiency of 9.1% for a tandem combination of two 2.5-cm-long fibers with the efficiency gradually decreasing to 4.9% with increase in fiber length to 10 cm.

I lovingly dedicate this dissertation to my wonderful family. Particularly to my patient wife, Viyan, who has put up with these many years of research and has given me the strength to cope with difficult situations, and to our precious daughter Wanda, who is the joy of our lives and an extra motivation for hard work. I dedicate this work to my loving parents, Lili and Alireza, whose support throughout my life has been central to my success.

ACKNOWLEDGMENTS

I acknowledge my research advisor, Dr. Ayman Abouraddy, for his guidance and availability to discuss scientific and technical aspects of research throughout my almost 5 years in his group. I sincerely thank Drs. Sasan Fathpour and Patrick LiKamWa for their assistance during my last semesters when I switched from Optics program to Electrical Engineering program while still working at CREOL. I borrowed several pieces of equipment and materials from other groups at CREOL. I acknowledge the critical help from all those groups: Dr. Schoenfeld for giving me access to the quantum efficiency measurement device which was of great importance to producing useful experimental data in the solar fabric project; Dr. Martin Richardson for lending me vacuum parts that I used in the solar fabric project and the Opti-BPM software that I used for other projects not reported in this thesis; Dr. S.-T. Wu for allowing me to use the pulsed green laser in his lab for gain measurements for PT-symmetric fiber project which is not reported in the thesis either; Dr. Mike Bass for lending us up-conversion micro-particles; Dr. Ted Sargent of University of Toronto for sending us quantum dots; Drs. Van Stryland and Hagan from NLO group for access to their labs for fluorescence measurements.

During my time at UCF I had great support from many of the administrative staff at CREOL and CECS. I would like to extend special thanks to Richard Zotti who patiently tolerated over 1000 hours of my presence in CREOL's machine shop and taught me machining tricks that he had gained over years.

My teammates Joshua Kaufman and Soroush Shabahang with whom I shared an office too for over 4 years were great helps in many instances.

I must highly appreciate my wife, Viyan, for her patience during my PhD time when I had to spend most of the holidays and weekends at work with countless all-nighters in labs while she was either cultivating me for better performance or growing our precious daughter, Wanda, with best care ever possible. I consider her as a co-owner of this thesis although only my name appears on the cover.

Last, but not least, I thank my parents, Lili and Alireza, for their constant support at all times. Their loving efforts have led me to this point; and their financial support let me finish this PhD without extra stresses that could have otherwise existed in handling a family with a student stipend.

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CHAPTER 1: INTRODUCTION

Growing economic, environmental and geopolitical issues related to the use of fossil fuels along with ever-increasing demand for energy are motivating the exploration of alternative renewable energy resources such as sunlight [1]. Economy of solar power is still subject of controversy. But projections are promising that photovoltaic will be economically preferred over fossil fuels in a few years both for large-scale commercial power plants and for small-scale residential use. Tremendous progress in photovoltaic (PV) materials has been made over decades. The efficiency of traditional Silicon panels, however, reached a plateau with almost no appreciable improvement in about two decades [2]. Nevertheless, improvement in manufacturing and economy of scaling has continued. Alternative solid state materials such as group III-V [3] and CIGS (Copper Indium Gallium Selenide) [4] semiconductors have been exploited for higher-efficiency and thin-film cells. Organic semiconductors have offered lower price and more flexibility for PV modules. Their lifetime is still a challenge [5] though. Photon management in micro- and nano-scale has further assisted PV performance [6] by improving the light trapping probability for more efficient light-matter interactions and power conversion. Several variations of conventional solar concentrators have been invented to reduce the surface area of the required expensive semiconducting materials using lower-expense reflective, refractive and diffractive optics to collect and concentrate light from a larger area [7]. Particularly, refractive elements such as flat Fresnel lenses [8] and holographic films [9] have been used to reduce the size of the

modules in commercial scale. Solar concentrators have gone even further for applications such as solar pumped bulk [10] and fiber lasers [11] which combine ideas from multiple disciplines within optics. Recently, relatively compact concentrating modules were reported incorporating micro-lens arrays to focus sunlight onto an array of micro-deflectors attached to a transparent waveguide [12, 13]. A considerable portion of normally incident light gets deflected into waveguide modes for delivery to waveguide edges where PV cells can be attached. Most of these concentrating systems, however, require relatively accurate mechanical tracking systems in order to keep the concentrated light focused on the small-area PV cells.

An alternative route for solar-energy harvesting that obviates the need for tracking, especially in indirect or diffuse light, relies on luminescent solar concentrators (LSC's). Conventional LSC's are slab waveguides coated or embedded with an organic or inorganic luminescent material that absorbs sunlight from the surface and re-emits it into the waveguide that carries the light to the edges for optical-to-electrical power conversion [14]. LSC's allow for concentration of indirect and diffuse light, a quality that is not achievable with conventional concentrators. LSC concept can be tracked back to 1970's [15] while it became a subject of more active research in 2000's due to the advancement of luminescent materials [16] and geopolitical changes that necessitated exploitation of renewable energies. Various aspects of LSC's have been investigated widely. Wide absorption spectrum of quantum dots has allowed for better use of the incident sunlight spectrum [17, 18]. Inorganic rare-earth ions [19] and organic-inorganic compounds [20] have boosted the light transport efficiency in LSC's due to their large Stokes shift that minimizes self-absorption, a major loss mechanism that limits the efficiency of LSC's and stems from the inevitable overlap between absorption and fluorescence spectra of most organic luminescence

materials [21]. Currie, et al. [22] reported the use of advanced photo-physical effects such as Förster resonance energy transfer and phosphorescence in a tandem stack of two LSC slabs to demonstrate estimated 6.8% conversion efficiency for a relatively small LSC ($2.5 \times 2.5 \times 0.2 \text{ cm}^3$) with a reflective mirror backing. This record was soon changed to 7.1% for a single-plate LSC ($5 \times 5 \times 0.5 \text{ cm}^3$) with a diffuse backside reflector [23]. Later research reported alignment of organic dyes to minimize the emission into the scape cone [24-26], the range of sharp emission angles that do not experience total internal reflection for confinement in the waveguide. Patterned dye layers in conjunction with micro-lens arrays were also reported to reduce the surface covered by dyes to reduce the self-absorption effect [27]. New waveguide materials have been developed to reduce the linear background loss of the waveguide [28, 29]. Yoon et al. [30] reported high conversion efficiency at the center of a novel, millimeter-size flexible LSC device with interconnected arrays of micro-scale silicon solar cells embedded in a thin, flexible LSC to reduce the propagation path length, and hence self-absorption, for fluoresced photons before they reach the solar cells. Later the same year, Giebink et al. applied the concept of optical resonance shifting by forming and adjusting the layer thicknesses in a bilayer cavity in the LSC structure to circumvent reabsorption loss [31].

Recently, another distinct aspect of LSC's, the waveguide *form factor*, has become focus of attention for some research groups around the world. Departure from flat waveguide and its replacement with an array of cylindrical rods has shown improvement in light capture and concentration [32]. Individual cylindrical rods doped with organic luminescent dyes [33] or quantum dots [34] have been reported to have performance superior to that of flat LSC's. Along the same route, use of optical fibers for luminescent solar concentration purpose was recently

suggested and investigated, but without a reported efficiency measurement [35]. The convenient form factor of fiber was used in preceding years both for organic LED and organic photovoltaic devices coated on metal wires [36, 37]. Recently, He *et al.* reported on fabrication of Silicon p-i-n junction in the form of fiber fabricated with high pressure chemical vapor deposition up to 10 m [38].

It appears that the convenient form factor of fiber creates the possibility of making functional fabrics woven from flexible fibers. This has been exploited to make fabrics with electronic and acoustic functionalities [39, 40]. It is, nevertheless, conceivable that optical fibers that have been traditionally used for low-loss optical signal transmission may similarly serve other applications that require efficient light transport, such as luminescent solar concentration in which the luminesced light has to travel through the fiber length before it is converted to electric power. On the other hand, there seems to be a need for a solution to provide energy for remote applications for which flexibility and light weight can be central. For example, for personal outdoor activities or even military missions solar power is sometimes the only accessible source of energy. It is beneficial to such users to have access to electric power for charging their mobile devices from the abundant source of solar power by means of a solar cell or solar power converter that is not so prone to mechanical shock or inevitable situations such as high humidity.

The promise of optical fibers to be high-performance light guides and the need for a product that fills the above mentioned gap motivates the research outlined in this thesis.

This dissertation presents the results of our research on polymer optical fibers for light concentration application, methods of adding active materials to them, design and theoretical

optimization of a fiber luminescent solar concentrator (FLSC), fabrication methods and optical characterization of a series of fabricated FLSC. A novel form of Fiber-LSC's is introduced with a hybrid configuration that combines benefits of flat and cylindrical LSC's taking advantage of advances and flexibilities of fiber drawing technology. A FLSC with square fiber cross section topped with a cylindrical cap is investigated in detail. After investigation of other simulation methods such as beam propagation, the non-sequential polarization ray-tracing mode of ZEMAX in conjunction with MATLAB codes and macros developed in ZEMAX Programming Language (ZPL) were utilized to model this unconventional FLSC system thoroughly. Effects of all key physical and geometrical parameters were investigated in search for optimum set of parameters for highest concentration efficiency. Methods were also developed and improved for fabricating FLSC's with predetermined specification. Experiments are developed for optical characterization of such FLSC with their unique limitations for evaluation of their performance.

This dissertation is organized as following: This introductory chapter will be followed by Chapter 2 which reviews the overall state of solar energy technologies and recent developments. A brief overview of all sectors of this technology from solid-state solar cells to various solar concentration schemes is presented. Chapter 3 will focus on luminescent solar concentrators, theoretical bases of their operation and more detailed review of key advances in the field to address specific problems. Chapter 4 will be devoted to fiber fabrication technology and the recent advances in multi-material and multi-functional fibers. The subject of this thesis, Fiber Luminescent Solar Concentrator, is considered a technology that brings multiple disciplines involved in LSC technology alongside with fiber fabrication technology to provide a lower-cost solution to mobile energy needs. Therefore, it is necessary to briefly review the state of each

element. A relatively comprehensive simulation model is developed and explained in Chapter 5 for modeling and predicting the optical performance of a FLSC with arbitrary set of physical and geometrical parameters. This model covers all events involved in performance of a FLSC including absorption of the incident light from the ambient, isotropic re-emission of the light power inside the fiber waveguide and light transport along the fiber that experiences various wavelength-dependent and wavelength-independent losses such as self-absorption and linear loss of the fiber. The model is initially developed for simplified conditions with single-wavelength illumination, absorption and emission. These limits are later lifted and full simulation of the FLSC system under realistic conditions is presented. Chapter 6 is devoted to the experimental efforts in this project for fabrication and optical characterization of FLSC's. Methods that were developed in the course of this research will be explained for addition of organic luminescent materials into the fiber preforms in predetermined locations across the fiber cross section without considerably compromising the optical quality of fibers. Standard and custom-designed measurement methods are also explained for characterization of material ingredients, un-doped optical fibers and finally the completed doped FLSC samples. Finally, Chapter 7 will present a conclusion to this work and will discuss possibilities for further improvement of such FLSC systems.

Appendices are devoted more fabrication methods that were developed and explored for various classes of organic and in-organic materials to be used in fibers but not directly reported in previous chapters and our other publications. They also briefly touch on a few side projects that I have initiated beside the major theme of this thesis. These works include: (1) a method for thermally drawing large-scale sheets with maintained micro-structures for large-scale flexible

optical and electronic device applications; (2) hot embossing as a method for fabrication of devices on the tip of polymeric fibers for remote sensing uses; and (3) theoretical investigation of acoustic band structure in 1-D periodic stacks of layers with high elasticity contrast. These works are left for further development and publication in the future.

CHAPTER 2: APPROACHES TO HARNESSING THE SOLAR POWER

Introduction

There is an increasing demand for energy that has motivated development of economic ways of exploiting renewable sources of energy [1]. Due to its abundance, cleanliness and availability, solar energy has attracted enormous attention during the last decade although it has been subject of active research and development for over five decades after the first demonstration of a PV panel in 1954 [41, 42]. Cost of solar power using the first commercial version announced by Hoffman Electronics in 1955 was approximately \$1500/W [43]. The United States Department of Energy (DOE) estimates that one US Dollar (\$1) per watt of installed PV system (including installer margin) is required to make solar power competitive with the wholesale rate of electricity without any subsidies [44]. Currently, solar power is still a few times too expensive [45]. There is, nevertheless, great promise for this abundant source of energy to become the choice of near future [46]. Silicon solar panels are the most widely used in commercial and residential markets. There are, however, two major drawbacks with the conventional silicon-based solar panels: (1) Limited resources of silicon that has inevitably increased the price of silicon over years; (2) Efficiency of silicon cells that has approached its practical limit with no appreciable improvement for almost two decades [2]. These two combined have limited the applicability of silicon panels in large scales without subsidies. Other materials have been

identified with better performance and economy of scale [3, 4], but no PV technology alone has yet offered the competitive price for large-scale utilization of solar power without subsidies.

Approaches to reduction of solar power cost

Active research and development is taking place both in industry and in academia to realize methods for better utilization of solar energy. Several routes can be taken for reduction of solar power cost. Less expensive materials, simpler fabrication processes, lower-cost light collection schemes and better use of the sunlight spectrum are the major conceivable paths. These efforts can be categorized in four general approaches that are actively being pursued and will be outlined in this section.

Spectral splitting

Each semiconductor material has a given band gap that allows for efficient absorption in a range of wavelengths but not the whole solar spectrum. Photons with energy less than the band gap cannot be absorbed and while the excess energy of photons with energy higher than the band gap will be dissipated thermally in the material. There are two general ways of spectrally separating the sunlight in order to use each section of the spectrum in a semiconductor junction whose band gap is tuned for the given spectral range: (1) vertical splitting; and (2) lateral splitting. Reference [47] reviews comprehensively the spectral splitting methods (Figure 2- 1 below)

Vertical spectral splitting

Semiconductor junctions can be stacked vertically on the top of each other to form the so-called multi-junction PV cells. Each junction has a band-gap that is tuned for high performance for a

given range of wavelengths. Therefore, each junction efficiently absorbs one wavelength band from the solar spectrum and transmits the rest to the next junction which is tuned for the transmitted band [48-52]. A record efficiency of 44% was recently reported with such multi-junction cells in conjunction with a concentrating system (947 suns) [53]. Despite the success for high efficiency, there are fabrication difficulties for this method such as the obligation to match the lattice structure of all stacked materials and the requirement for equal current in the series connection of the junctions which cannot be efficiently maintained due to spectral changes during the day and more [54]. Elaborate fabrication also makes these multi-junction cells affordable only for certain applications such as space applications or high concentration CPV systems for large power plants.

Lateral spectral splitting

An alternative way to split the spectrum is to use diffractive optical elements such as gratings or holograms [9], prisms [54] or dichroic elements [55] to spatially separate different portions of the spectrum before the sunlight reaches the solar cell. Single-junction cells that are optimized for the specific bands can then be used for conversion.

Figure 2- 1: Examples of vertical and lateral spectral splitting

Thin-film Photovoltaics

Conventional techniques for making PV cells are based on slicing mono- or poly-crystalline bulk materials. This leaves the cells with a minimum achievable thickness (typically hundreds of microns) that is still not fully used. Such thick layers are sometimes even necessary due to low absorption of certain materials such as Silicon in certain sections of the spectrum. It is known that approximately 40% of the cost of conventional PV cells is the cost of semiconductor material [56]. Thin-film solar technologies reduce the cost of solar cell material by depositing semiconductor materials in thin layers (a few microns). However, simple geometrical optical concepts will no longer apply to light trapping in such thin layers. New photon management strategies are required for efficient absorption and trapping of incident light. Deposition techniques developed for this purpose can have been applied to both rigid and flexible substrates. Many materials such as amorphous silicon and Copper Indium Gallium Selenide (CIGS) have been used for thin-film PV's. In January 2013, scientists at Empa, the Swiss Federal Laboratories for Materials Science and Technology, reported a world record of 20.4% for a CIGS composition on a flexible polymer substrate [57, 58]. This efficiency is even higher than the previous records for CIGS on rigid glass substrates. Recently GaAs cells and modules with respective efficiencies of 28.8% and 24.1% were launched as commercial products at Alta Devices. In March 2013 Alta Devices broke its record with a new GaAs cell of 30.8% conversion efficiency [59]. It is however, unclear whether the price of such thin-film PV modules can reach to a point where users other than military may utilize this technology at high efficiencies. Commercial thin-film modules currently have efficiencies of approximately 5% based on amorphous Silicon.

Organic Photovoltaics

With the advent of organic semiconducting and conducting materials, Organic PV became a possibility [60]. Low-cost synthesis of organic compositions using abundant materials, easier processing of organic materials and thin films along with flexibility of organic-based PV modules made organic PV a field of very active research and development [61-64]. Efficiencies up to 12% are reported for laboratory tests [65] while modules approximately 4% efficient are commercialized. The limited life-time, low large-scale efficiency and yet the cost of OPV modules are major drawbacks of OPV systems that do not allow them to be used widely.

Concentrators

The idea of concentrating light power collected from a large area to create high peak intensities in small spots to burn objects has been used since ancient era (Figure 2- 2 - [66-68]). In past few decades, however, the same idea became popular for more modern applications such as laser pumping for remote applications [10, 11], and reducing the cost of solar energy by replacing expensive solar panels with a less expensive optical system to concentrate the light from a large area onto a much smaller solar cell for conversion into electric power [7] or even direct use as a lighting source [69] or direct heating for various purposes [70].

Figure 2- 2: Examples of historical concentrators

Solar concentrators can be categorized into two distinct classes: (1) Imaging; and (2) Non-imaging concentrators. Hybrid concentrators that employ partially imaging and partially non-imaging methods have also emerged. Since the focus of this thesis is on a class of hybrid concentrator driven from the non-imaging Luminescent Solar Concentrators (LSC's), the last section of this chapter will introduce some hybrid concentrator concepts and the next chapter will be entirely devoted to LSC's. The rest of this section will, nevertheless, review the state of the art of imaging concentrators.

Imaging solar concentrators

Imaging concentrators work based on direct imaging of the sun onto the PV cells using reflective or refracting optical elements. Although what such devices do is formation of an image of the sun, the quality of imaging is not a concern. The major concern is high concentration with lower-cost optical systems. Reflective solar concentrators are still being used very widely both as individual reflective dishes for roof top energy collection either for conversion to electricity or

direct use of the concentrated light for indoor lighting via fiber bundles (Figure 2- 3). Reflective concentrators can also be arranged in large solar fields (Figure 2- 4 - [71]) with arrays of individual dishes with converting PV cells attached to each dish or an array of reflectors focusing solar light onto a central conversion tower with large-area, high-efficiency solar cells and cooling systems [72].

Figure 2- 3: Examples of roof-top concentrators for residential use

Figure 2- 4: Examples of solar concentrator fields for commercial use

An alternative way of arranging solar concentrators is to make highly packed arrays of smaller concentrators to minimize the useless area left between the individual concentrators to avoid shadowing effects (Figure 2- 5 - [73]). Linear Fresnel reflector arrays have been also demonstrated for focusing light into lines for efficient heating of water pipes, etc.

Figure 2- 5: Reflective concentrator panel

Refractive solar concentrators, instead, use refractive lenses to focus sunlight. There are examples of concentrators using large, bulky lenses for this purpose. But arrays of smaller lenses concentrating light on an array of PV cells are more popular as they allow for thinner and lighter-weight modules. Such solar modules are even used in the commercial market. Figure 2- 6 [74] shows two examples of the commercial refractive concentrator panels demonstrated in Canada and the United States.

Figure 2- 6: Refractive concentrator panels with regular convex (left) and Fresnel (right) lenses

Research and development are focused on optimizing the design of the primary, secondary and even tertiary concentrating elements with which the ultimate focusing of the light is divided into two or three stages to achieve higher concentration levels using the least solar cell area [75-77]. Theoretical aspects of the concept have also been explored by means of thermodynamics and energy transfer equations for the optical energy flow and the ultimate limits of the concentration dictated by thermodynamics [78, 79].

Non-imaging solar concentrators

Despite the high power conversion efficiencies that can be achieved by imaging concentrators, there is a major drawback to such systems. Very accurate alignment of the optics and tracking of sun are required (sometimes with tolerance of less than 0.2°) to maintain the high conversion efficiency. This alignment is usually maintained with complex mechanical systems for tracking sun from day to day and from season to season. Misalignments in the optics and error in tracking the sun can cause the sun image fall outside of the aperture of the PV cells and therefore cause a sharp drop in efficiency.

In contrast, non-imaging solar concentrators are based on diffusive or luminescence mechanisms for redirecting the sunlight [80]. Most of such systems are insensitive to alignments and do not require any tracking. Some, however, need occasional angular adjustment for better performance. Figure 2- 7 below (from reference [77]) demonstrates one of the earliest non-imaging concentrators, so-called “compound parabolic concentrator” or CPC invented in 1979 [81]. This concentrator utilizes a parabolic reflector. As demonstrated in the figure it performs adequately for a range of incident angles. Therefore, there is no need for continuous, accurate tracking of the sun. Such non-imaging concentrators pushed the geometrical optical concentrators (e.g., those based on lenses or mirrors) to the so-called sine limit [80], which describes the fundamental tradeoff between the acceptance angle (θ_{acc}) and concentration ratio (CR) given by $CR \leq \left(\frac{1}{\sin \theta_{acc}}\right)^2$. This relationship dictates the use of a tracking system in all passive concentrators in order to maintain high concentration ratios.

Figure 2- 7: Schematic of a non-imaging concentrator with higher angular tolerance compared to imaging concentrators

This relationship makes it clear that most non-imaging concentrators have low concentration ratios as opposed to large, imaging concentrators whose concentration ratio can exceed 1000 suns in some cases. High concentration ratio, beside its advantages for potentially high power generation, requires expensive PV cells designed to tolerate the extensive heat generated at the cell. This requires careful heat transfer management in the backing of PV cells too. Non-imaging system, in contrast, can utilize the low-cost commercial cells because of the lack of such excessive heating.

Figure 2- 8 (from reference [82]) demonstrates another example of a non-imaging concentrator that takes advantage of conventional CPC concentrators (above) while minimizing the ray rejection by smoothly transitioning the elliptical geometry of the entry to the square shape of the

exit which matches the solar cell aperture geometry. Such a concentrator, called Square Elliptical Hyperbolic (SEH), was produced at Heriot-Watt University in 2012 [82]. SHE with a thickness of 10 mm has shown a rather constant optical collection efficiency of $\sim 40\%$ over a wide angular range of 120° (from -60° to $+60^\circ$). This, almost completely, obviates the need for sun tracking during the day.

Figure 2- 8: SEH non-imaging concentrator

In the latter system explained above, it is shown that the optical efficiency increases with increasing the SHE concentrator height for a fixed ellipse size [82]. In this case efficiency can go up to $\sim 70\%$ for a slightly narrower angular range if the module thickness is increased to 30 mm. One drawback of such systems is, therefore, their size and weight. It is ideal to have a non-imaging concentrator that does not require tracking and yet has lighter weight and smaller dimensions.

Another class of non-imaging concentrators relies on diffusive layers attached to transparent plates which are in contact with small-area PV cells [83]. Light incident on the transparent plate will be diffused and a part of it will remain trapped inside the transparent plate until it reaches the attached PV cell (Figure 2- 9, top [83]). While old versions of this type of concentrators had the PV cell attached to the bottom face of the plate, the wave guiding of the slab is utilized in a more efficient way in more modern versions. PV cells can be attached to the edges of the slab (Figure 2- 9, bottom [45]), instead [45]. Figure 2- 9 compares these two concentrators schematically.

Figure 2- 9: Non-imaging concentrators with diffused backing

In 1970's the concept of using fluorescent materials to scatter light in such solar concentrators was proposed in an unpublished proposal (see Ref. [14]). Luminescent materials can be embedded or coated on transparent waveguides to absorb the sunlight and re-emit it into the waveguide for transport to the edges where PV cells can be attached for power conversion. The concept of Luminescent Solar Concentrator (LSC) was later known through the work of Weber and Lambe in 1976 [15]. Several aspects of LSC's were investigated in early years of their advent from theoretical and experimental perspectives [14, 15, 84-86]. Limits of luminescent materials, however, caused a long period of inactivity in the field until more advanced material concepts allowed scientists to revisit this field of solar technology which is still subject of active research [17, 22, 87]. Various aspects of LSC's will be discussed in more detail in the next chapter with a review of recent advances.

Imaging/non-imaging hybrid solar concentrators

Recently, a new class of concentrators emerged in which imaging and non-imaging concentration concepts were mixed. This new concentrator configuration was demonstrated with an array of millimeter-size lenses on the top of a slab waveguide with micro-reflectors (prisms) on the bottom to redirect the light focused by the lens array at proper angles to guarantee total internal reflection trapping of light in a way that a considerable part of the normally incident light can be collected at the edges of the slab waveguide [12]. The micro-lens array performs as the imaging portion of the system as it images the light source (sun) onto small spots on the bottom face of the device. The transparent waveguide with the micro-deflectors, however, acts as

the non-imaging component since the information of the image will be completely lost after deflection and multiple total internal reflections inside the waveguide. Figure 2- 10 (from [12]) shows the operation of such a hybrid concentrating system.

Figure 2- 10: Hybrid concentrator based on micro-optics planar waveguide

This system has shown an estimated optical concentration efficiency of approximately 90% under optimized situations for normal incidence. Prototypes have also been developed with a measured efficiency of $\sim 32\%$ for normal incident light collection.

It is clear that any concentrator whose primary concentration mechanism is based on imaging would require precise tracking systems by bulky, expensive tracking platforms. Hallas *et al.* reported on the use of a two-axis micro-translation stage to track sun by micro-movements in deflector locations underneath the waveguide instead of tracking sun with the bulk of the concentrator [88]. To eliminate the need for such tracking systems in the micro-optics-based concentrators, self-tracking designs have been reported recently. In 2012, Baker *et al.* reported [13] the design and device concept for a reactive self-tracking concentrator incorporating a thin

layer of low index material between the bottom surface of the waveguide and the micro-deflectors. This low-index material experiences an index increase when exposed to focused light in a way that creates a local coupling point to couple into the waveguide the deflected light which would have otherwise remained outside of the slab waveguide. Similar concepts based on light-induced phase-change (and therefore index-change) of the thin bottom layer has been preliminarily investigated and reported too [89].

As it will be explained in more detail in next chapters, the luminescent solar concentrator investigated and reported in this thesis can also be considered as a hybrid system with some geometrical similarities with a hybrid bulky concentrator which was recently reported by Bouchard and Thibault [90].

CHAPTER 3: LUMINESCENT SOLAR CONCENTRATORS

LSC background

In 1976, two of the research staff at Ford Motor Company, W. H. Weber and John Lambe, published the first paper reporting the use of luminescent materials in conjunction with total internal reflection waveguide mechanism for solar light collection [15]. They named this device a “luminescent greenhouse collector” because of the so-called greenhouse effect which is the absorption of visible light and re-radiation in near infrared. Four advantages of this new light collection strategy were detailed which are still the major driving forces behind the research and development of more modern luminescent solar concentrators: (1) no need for tracking the sun, unlike in mirror-based concentrators; (2) unchanged performance under cloudy and diffuse light conditions; (3) heat dissipation distributed over a large area; (4) spectral concentration of light to frequencies of optimized performance.

An LSC is composed of a transparent slab doped with organic or in-organic luminescent materials. The flat surface of the LSC is exposed to the solar light so that the embedded fluorescent materials can absorb the incident light and re-emit it at longer wavelengths inside the slab. A portion of the re-emitted light gets trapped in the slab waveguide by total internal reflection and travels to the edges of the waveguide where small-area solar cells are attached to collect and convert the concentrated light power into electricity. Weber and Lambe used mirror on one edge of the slab to reduce the use of PV cells even further. It, however, turns out that

minimizing the propagation length of the fluoresced light in the waveguide is more beneficial since it reduces the self-absorption loss of power. Therefore, all four edges of LSC's can be covered by efficient solar cells. Such a system with right choice of materials has been demonstrated with a record power conversion efficiency of 7.1% [23].

LSC operation

Several processes are involved in operation of LSC. Some processes introduce losses which need be minimized to maximize the overall efficiency of LSC system. Compromise between various factors also becomes necessary in some cases. Overall efficiency of LSC is the product of efficiencies related to each step of the process. Figure 3- 1 schematically shows the processes involved. Following paragraphs will briefly discuss these processes with reference to the numbers in Figure 3- 1. Methods for improving each process will also be explained with reference to recent publications in the field.

Figure 3- 1: Processes involved in LSC operation

Luminescent materials have finite absorption bandwidth that does not cover the whole solar spectrum. Therefore, a portion of the sunlight cannot be absorbed by the dopants and will pass through the LSC system with no change (1 in figure). It is ideal to absorb as much of the incident spectrum as possible. Three methods are used to this end: (1) some luminescent materials such as quantum dots have broad absorption spectra. Most of such materials, however, have high self-absorption ratios or low average quantum yields. (2) Multiple luminescent materials with narrower absorption bands can be used with a cascaded absorption and emission in a way that emission from one gets efficiently absorbed by the other and therefore emitted at a longer wavelength [14]. This method suffers from multiple absorption-emission events that each has a non-unity yield. (3) The third method which is advantageous over the other two uses separate LSC's stacked on the top of each other in a tandem configuration [22]. This method allows for optimum use of each section of the spectrum in one separate LSC. Usually, the top LSC absorbs the shorter wavelengths and transmits the longer ones for absorptions in the second LSC and so on.

The part of the spectrum (2 in figure) that overlaps with the absorption spectrum of the luminescent material will partially reflect off the surface of the LSC (3 in figure). In order to minimize this effect, anti-reflection layer may be used. Transmitted light (4 in figure) will be absorbed by the luminescent material (filled orange circles in figure). A portion of the absorbed energy will be dissipated non-radiatively in the form of phonons and heat (5 in figure).

Fluorescent materials can be engineered in a way to minimize the non-radiative radiation. Many

organic dyes have quantum efficiencies exceeding 0.95. Fluoresced light is emitted isotropically in all directions. Some of the re-emitted light arrives at the LSC surface at such sharp angles that total internal reflection cannot take place (6 in figure). The range of angles where light does not remain trapped in the slab is called escape cone. This is a major source of loss in LSC's. To maximize the light trapping efficiency, one can use plates with very high refractive index. This limits us to very expensive specialty glasses that are not economic choices for large-scale LSC's. Another method that has been applied to LSC's is based on alignment of dye molecules so that their radiation is directed at angles that do not fall in the escape cone [24, 25]. This method has shown improvement in trapping efficiency. But alignment of dyes makes their absorption polarization dependent. That's, not all of the sunlight can be absorbed.

A part of the light that remains trapped in LSC may get re-absorbed by the same species (7 in figure) that has emitted it. This is due to the inevitable overlap between absorption and emission spectra of luminescent materials. Re-absorbed light will experience some red-shift and will be emitted again isotropically. Therefore, this self-absorption can be a major source of loss if the overlap between the two spectra is considerable or photons go through multiple absorption-emission events. In addition to development of engineered materials with minimum spectral overlap, several other methods have been reported to minimize the negative effect of self-absorption in the device.

There might be scattering centers in the waveguide body that can scatter the trapped light (8 in figure). Also the intrinsic loss of the waveguide bulk material can attenuate the emitted power (9 in figure). These can be avoided or minimized to some extent by using high quality optical

materials. Optical quality glasses exist with very low impurity levels. However, polymers are preferred materials for LSC fabrication due to their lower cost, ease of processing and lighter weight. Polymeric materials have been developed with short polymeric chains and low loss levels to reduce scattering and loss in LSC waveguides. Another source of loss in LSC's can be impurities and dust particles on the surface of LSC that can out-couple the trapped light (10 in figure). Finally, a portion of the light reaches the waveguide edges where the PV cells are attached (11 in figure). This light power is available for conversion to electric power except for some power loss due to imperfect coupling from LSC to the PV cell.

All processes explained above are formulated in Chapter 5 in more quantitative details. Next few paragraphs will briefly touch on some approaches to improving FLSC performance from various perspectives based on publications in recent years.

Materials for LSC

LSC's are composed of two major material elements: The host waveguide material and the luminescent materials.

Host waveguide materials

Traditionally, PMMA was the material used widely for such applications as LSC. PMMA has very high transparency in the visible and is an easy material to process [14]. A major drawback with PMMA is the high humidity absorption rate and low thermal stability that makes it degrade fast in humid, hot environments [91]. Therefore, materials such as PolyCarbonate have been used. PolyCarbonate has, however, slightly lower transparency compared to PMMA [92]. In

recent years new classes of polymeric materials have been synthesized and characterized for optical applications such as LSCs [28]. In order to make LSC materials more environmental friendly, materials such as silk have also been employed for LSC application [29].

Luminescent materials

From the material perspective to luminescent solar concentrators the major focus has been on the active ingredients of LSC's, that's, the luminescent materials. An ideal candidate for this application must have broad absorption band to utilize as much of the solar spectrum as possible. It should have high thermal and photo-stability to survive harsh outdoor conditions. It must have no to very little overlap between its absorption and emission spectra. Its luminescent quantum yield (efficiency) must be high to minimize the amount of energy dissipated in other forms than radiation. As in most cases in complex situations, not all ideal properties can be found in one material. Therefore, various research groups have investigated different classes of materials for LSC application including organic dyes [93], quantum dots [34], rare-earth ions [19], metal oxides, metal complexes, semiconductor polymers and dye-sensitized C₆₀. Here, only organic dyes and quantum dots that are the most popular classes of materials used for LSC's will be listed and briefly discussed.

Organic dyes

Organic dyes were the first natural candidates for LSC application at the time LSC concept was introduced. Chemistry of mixing organic dyes with polymers was very well known. Therefore, polymer slabs were selected as the host to organic dyes for this application. Luminescent materials were unfortunately the limiting factor in the 70's. This resulted in a downtime in

research on LSC after the initial flurry of research on the topic in 70's. During the last years of the second millennium several classes of luminescent materials were developed. Organic dyes were not an exception. They were also subject to active research and development. One major drawback of organic dyes was their life-time. Another problem was the high self-absorption due to small Stokes shift. On the other hand, desired large Stokes shift inevitably goes with low quantum yield since the spectral shift is the result of non-radiative relaxations. Trade-off between these two was investigated through development of new dye compositions for other purposes such as bio-labeling and microscopy that would require similar qualities for the luminescent dyes. Molecular engineering of dyes molecules has also allowed for dye structures with considerably higher photo and thermal stabilities. Applications such as Organic Light Emitting Diodes (OLED's) were the major motivation for such improvements and developments in organic luminophores. Organic dyes have also been developed with metallic nano-particles attached to the molecular structure in a way that the organic bonds absorb the photon energy and transfer that non-radiatively to the metallic nano-particle that instead has sharp resonance frequencies. This has proven to be an efficient way of reducing self-absorption to almost zero. The price is the low quantum yield of such compound materials, however.

Quantum dots

Quantum dots (QD's) are semiconductor nano-crystals that have different properties compared to their bulk counterparts due to their small size. Electron-hole pairs have a characteristic dimension known as exciton Bohr radius which is a measure of the natural radius of the pair. In bulk semiconductors the Bohr radius is much smaller than the crystallite bulk size and there is a continuum of electron and hole states. When the crystal size becomes smaller than Bohr radius

many properties such as optical absorption and emission of the nano-crystal change and discrete transitions will appear. Bohr radius is approximately 7 nm for CdTe, 5 nm for CdSe and 3 nm for CdS [94]. If the bulk material size is reduced to such a range in one, two or three directions, a *quantum well*, *quantum wire* or *quantum dot* is formed, respectively. There is a simple relationship between quantum dot size and its emission wavelength. The smaller the crystal size the shorter the emission wavelength because of tighter confinement of electrons and holes and further separated levels that allows only higher energy transitions. Semiconductor band gap of these materials can be adjusted by their size and shape [95]. Their thermal properties will change by size too. For example, the melting temperature of CdSe increases from 400 to 1600°C with decrease in size.

Reference [18] reviews QD's as candidates with several favorable properties for LSC application. QD's generally have broad absorption spectrum with relatively high absorption coefficients that can be adjusted by their size. Luminescent quantum yield should be high for LSC application. QD's with luminescent quantum yield exceeding 80% have been reported. QD's have been reported even with quantum yield above unity due to Multiple Exciton Generation (MEG). It is ideal for LSC materials to have little or no overlap between absorption and emission. This depends on the broadness of the spectral peaks and the Stokes shift. Stokes shift in QD's depend on their semiconductor material, their size and the surface states. A balance should be found between favorable large Stokes shift and quantum yield that decreases with increase in Stokes shift due to thermal relaxation of excitons. Width of the absorption and emission peaks strongly depends on the size distribution of QD's. It is ideal to have anisotropic emission in LSC in order to decrease the light that is lost in the escape cone. QD's with slightly

elongated shape (called quantum rods) have shown anisotropic emission due to their shape without compromising absorption that would have otherwise mandated higher doping concentration. Finally, QD's have shown the highest photo-stability among all luminophers which is very important for long operation of LSC without performance degradation. Core-shell QD's have even mitigated the oxidation issue of single-material quantum dots. Further details and references for QD's and their applications can be found in reference [18].

Review of recent progress in flat LSC

Since the advent of Luminescent Solar concentrators (LSC's) several aspects of LSC's have been investigated widely. Wide absorption spectrum of quantum dots has allowed for better use of the incident sunlight spectrum [17, 18]. Inorganic rare-earth ions [19] and organic-inorganic compounds [20] have boosted the light transport efficiency in LSC's due to their large Stokes shift that minimizes self-absorption, a major loss mechanism that limits the efficiency of LSC's and stems from the inevitable overlap between absorption and fluorescence spectra of most organic luminescence materials [21]. Currie, et al. [22] reported the use of advanced photo-physical effects such as Förster resonance energy transfer and phosphorescence in a tandem stack of two LSC slabs to demonstrate estimated 6.8% conversion efficiency for a relatively small LSC ($2.5 \times 2.5 \times 0.2 \text{ cm}^3$) with a reflective mirror backing. This record was soon changed to 7.1% for a single-plate LSC ($5 \times 5 \times 0.5 \text{ cm}^3$) with a diffuse backside reflector [23]. Later research reported alignment of organic dyes using a liquid crystal host to minimize the emission into the scape cone [24-26], the range of sharp emission angles that do not experience total

internal reflection for confinement in the waveguide. Patterned dye layers in conjunction with micro-lens arrays were also reported to reduce the surface covered by dyes to reduce the self-absorption effect [27]. There is, however, a trade-off between amount of absorption that is lost because of reduction in dye-covered surface and the improved self-absorption as a result of the same change. Yoon et al. [30] reported high conversion efficiency at the center of a novel, millimeter-size flexible LSC device with interconnected arrays of micro-scale silicon solar cells embedded in a thin, flexible LSC to reduce the propagation path length, and hence self-absorption, for fluoresced photons before they reach the solar cells. Later the same year, Giebink et al. applied the concept of optical resonance shifting by forming and adjusting the layer thicknesses in a bilayer cavity in the LSC structure to circumvent reabsorption loss [31]. Debije and Dekkers demonstrated improvement in LSC performance by adding some YAG:Ce phosphor to the scattering layer backing under the LSC [96]. In addition to the role of scattering transmitted light back into the LSC slab, this phosphor-added layer converts some of the unused light into useful light that can be trapped in LSC. Different types of filters such as Cholesteric-liquid-crystal filters have been reported to increase the trapping efficiency of fluoresced light when adjusted for efficient reflection of the fluoresced wavelength and applied to the top surface of LSC [97]. Plasmonic resonance of silver nano-particles added to quantum dot mix into the LSC has helped enhancing local light intensity that instead has enhanced light LSC conversion efficiency [98]. Menéndez-Velázquez *et. al.* recently reported on adding luminescence functionality to polarizers of an LCD display for absorbing the light that is otherwise wasted in inevitable polarizer and recycling it in the form of luminescence that can be used at the edges of LCD device for generating electric power that can instead be used for driving LCD [99].

CHAPTER 4: POLYMER OPTICAL FIBERS, MULTIMATERIAL FIBERS AND THEIR APPLICATION FOR SOLAR ENERGY

Introduction

Optical fibers are integrated part of daily lives of people all over the world for their application in telecommunication among others. The profound influence of the invention of optical fibers led to 2009 Nobel Prize in physics which was awarded in part to Charles Kao for his pioneering contribution to low-loss optical fibers development that paved the way for long-distance high-speed communication. Optical fibers have been exploited for numerous other applications such as lighting [100], medical instrumentation [101], sensors [102], fiber lasers [103], etc. beside constant improvements and inventions in their application for telecommunication and data communication. Several different classes of fibers have emerged including glass optical fibers, polymer optical fibers, multi-material fibers. Various guiding mechanisms are used such as regular index guiding in step-index fibers, graded-index guiding, Bragg reflection in Bragg fibers and photonic crystal fibers and index guiding in suspended-core fibers with air holes surrounding a solid core for reduction of the effective index in cladding.

Polymer optical fiber (POF)

Optical fibers are usually known because of Glass Optical Fibers (GOF) although chronologically Polymer Optical Fibers (POF) were made first in late 1960's by DuPont [104].

With the advent of glass optical fibers, POF's were pushed to a side since their transmission loss was not competitive with glass fibers. Multi-mode polymer optical fibers made with the popular material Polymethyl methacrylate (PMMA) had loss levels close to 1000 dB/km initially with that approached later to approximately 150 dB/km. Glass optical fibers, on the other hand, show optical loss of down to 0.2 dB/km for single-mode fibers, and ~ 3 dB/km for multi-mode fibers [104]. Therefore, GOF rapidly dominated markets for fast-growing application of long-distance communications. Even to date POF's are not applicable to long-distance communications. Nevertheless, lower material cost, easier processing, flexibility and lighter weight of POF's compared to GOF's have made them promising candidates for applications that require short-distance signal transmission [105, 106]. Here, major applications of POF's are discussed briefly.

POF applications

Industrial control systems

POF's are currently very widely used in numerous industrial control applications. Many processes across several industries require data links that can resist electromagnetic interference caused by high-voltage or high-current devices and machine that work in the same environment. For such applications, industries have found POF's as the major solution since they are inexpensive, prone to electromagnetic fields in their surrounding and flexible.

Illumination, lighting and imaging

POF's are used for illumination purpose in several forms [107]. One popular illumination application is local illumination of objects with light transported to the object using single or bundled POF's. This is widely used in art galleries and more importantly for endoscopic surgeries where POF's play dual role of illuminating body interior and picking up images

directly from the inside of body. In addition, POF's have been used in solar concentrator systems that use reflective dish-like collectors. Collectors focus light onto a small spot where a fiber bundle is mounted. The coupled light can then be transmitted through the fiber bundle to remote locations in buildings with no or little access to natural light. This is a method for bringing natural visible light to rooms with the harmful UV light and the heat generating IR light being filtered on the way in the fibers.

Automotive and aerospace industries

Ever increasing complexity of devices and facilities in modern automobiles has made internal communication between parts of cars very complex. This has led to complex wiring and wire networks that used to be unique and proprietary to automobile companies. Since 2000 many such companies have started serious research and development of internal optical communication systems with global standards using polymer optical fibers to not only reduce the complexities but also give higher bandwidth compared to copper wiring for modern audio, video and high-speed feedback systems in cars. High-speed communication using POF with critical elements such as airbag sensors is one out of many examples. Automotive companies have gone even further in application of POF's by using them as friction-free replacement for some mechanical links. For example, the mechanical link between brakes and brake pedal is now being replaced by an optical link in a way that pressing the brake pedal creates an optical signal in the fiber with its intensity proportional to the strength of pressing pedal. This signal is transmitted optically to the actuators connected to brakes to actuate them with the required strength.

Aerospace industries also enjoy from POF's for their short-distance internal communications. For aerospace applications such as aircrafts, tanks, ships, helicopters, missiles and spacecraft POF are ideal solutions due to their light weight, small size, resiliency to shock and vibration and high bandwidth capability over short distances.

Computer interconnects

Companies like Intel are heavily investing on making optical circuits on computer motherboards in order to increase the data processing rate in computers. While the current processor speeds are on the order of 1 GHz, it is expected that computers of the next decade would require tens of GHz which is impossible to achieve without optical circuits. Communication between components can be done with POF since the dimensions of computer boxes allow use of POF with no concern about their attenuation and bandwidth for such short distances as a few feet at most. Similarly, large data centers, server farms and supercomputers continue to develop. Such systems also require high-speed communication between hundreds of thousands of computers in several hundreds of racks. Number of racks and computers continue to increase in this growing industry. POF are best candidates to provide the fast communication as low-cost.

Sensors

Optical fibers, in general, have been very widely used for sensing. POF's are especially useful for applications such as structural health monitoring, medicine, environment and biology sensing [108]. Polymer optical fibers have been applied to several classes of fiber sensors based on all mechanisms including interferometry, Bragg fiber sensors and intensity modulation sensors in reflective or transmissive modes.

Local Area Networks (LAN's)

It is known that the widely spread network of glass fibers in global optical fiber networks can go from nations to nations, from continents to continents. But they fail to meet all requirements for the last few hundreds of meters of the optical networks when signal has to enter neighborhoods, commercial buildings or homes [106]. For local area networks, several qualities such as flexibility, easy installation and low-cost become critical. Local networks inevitably have several bending points around buildings. Such bending can cause significant loss in single-mode glass fibers. Plus, brittle glass material in glass fibers does not allow bending beyond a level which is not enough for local network needs. Sing-mode glass fibers that carry signal for long distances require very accurate couplers and connections because of the very small core diameter ($\sim 10 \mu\text{m}$). While accurate alignment in optical fiber connection centers is possible, it becomes very costly and impractical for local networks because of the large number of nodes in local networks. Plus, maintenance and installation of such connectors in every home or building requires expertise and expensive equipment that are not available to final users. On the other hand, large-core multimode glass fibers that are easier to align and connect cannot be used because of the rigidity of glass fibers in large diameters. Therefore, POF seems to be the solution to replace copper wires and optical-to-electronic signal conversions that limit the speed of data communication in local networks. This has been a major focus and driving force for development of POF's for many decades and it is projected that POF will soon become an option for LAN service providers. Data rates of up to 1 Gb/s for local networks have been demonstrated with large-core multimode fibers that are easy to install [106].

POF materials

Most popular polymers for traditional polymer optical fibers are Polymethyl methacrylate (PMMA), Polystyrene (PS) and Poly Carbonate (PC). Figure 4- 1: Attenuation of multi-mode polymer optical fibers below from reference [105] shows the progress in attenuation of POF fiber materials.

Figure 4- 1: Attenuation of multi-mode polymer optical fibers

Recently, a newly commercialized polymer, Cyclo Olefin Polymer (COP) and its co-polymer derivative, Cyclo Olefin Co-polymer (COC) have been used for micro-structured optical fibers due to their high transparency. COC and COP have been also used as substrate for lab-on-the-chip applications because of their capability to maintain sharp embossed structures at micro-scale.

Micro-structured POF's

Transmission loss of step-index POF's has been a major challenge since their invention. After years of improvement in PS, PC and PMMA polymer optical fibers, best attenuation level was still at approximately 150 dB/km. Japanese researchers developed a new class of perfluorinated polymeric compounds (CYTOP) that brought the single-mode POF attenuation down to 50 dB/km. Graded-index POF's are also known for lower loss and lower dispersion compared to step-index counterparts. Their preforms are, however, made with complicated polymerization processes to obtain the graded index profile. Such processes also put extreme limits on the choice of fiber materials. Immediately after the invention of glass photonic crystal fibers, micro-structured polymer optical fibers were also reported. Micro-structured POF's allowed for large-core fiber that operated essentially like single-mode fibers with dispersion that can be engineered.

Multi-material fibers

Although traditional silica fibers and polymer fibers were dominant in the market as well as in academic research, in mid-1990's Photonic Crystal Fibers (PCF's) and Photonic Bandgap Fibers (PBG's) that combined a second material, air, in the fiber design opened eyes for a new class of fibers: Multi-material fibers. Multi-material fibers are defined as fibers comprising multiple distinct classes of materials. These can include polymers, glasses, metals, etc. integrated in a single fiber in order to give new functionalities and properties to fibers. Emergence of this new field in the last decade has introduced several new functionalities into fibers that were conventionally not available in the fiber form. Examples are fibers that produce electrical signal when their external surface is illuminated by light, or when ambient temperature changes, self-

monitoring fibers, fibers that can see or detect optical field distributions in their surrounding and fibers that produce or detect ultrasound signals.

CHAPTER 5: DESIGN OF A POLYMER OPTICAL FIBER LUMINESCENCE SOLAR CONCENTRATOR

5.1. Introduction

This chapter will describe the design, detailed numerical simulation, and optimization of a fiber luminescent solar concentrator (FLSC) in which a *polymer* optical fiber judiciously impregnated with luminescent dopants absorbs sunlight incident externally on its outer surface.

The fiber then plays the role of a waveguide for transmission of this luminescence to the fiber end where PV cells are placed. Figure 5- 1 depicts schematically the overall FLSC system configuration. A multiplicity of individual parallel FLSC's are assembled on a surface and their ends are bundled and connected to a small-area PV cell. Each fiber is an independent LSC and their juxtaposition enables covering a large surface area. The geometric gain [22], defined as the ratio of the area covered by the LSC to the area of the PV cells required, is approximately the ratio of the fiber length to its diameter, which can be considerably high. Such structures may potentially lead to wearable solar-harvesting fabrics for mobile energy.

Figure 5- 1: Overall design of a FLSC system with individual fibers assembled in a fabric.

The specific class of fibers we investigate here has a non-traditional structure: its cross section comprises a rectangle with an axially symmetric cylindrical cap on the top surface designed to focus externally incident light into the fiber (see Figure 5- 2c). Luminescent dopants, located at the focal spot (extending axially along the fiber) absorb incident sunlight and re-emit light into the fiber, which is then guided to the fiber end. Fiber-based LSC's with uniform luminescent doping results in high self-absorption, while coating the dopants on the fiber surface, as is usually done in flat LSC's, eliminates the benefits accrued by the curved fiber surface. The FLSC design investigated here harnesses the focusing capabilities of the curved fiber surface to minimize the amount of dopants needed, thereby reducing self-absorption. To the best of our

knowledge, this is the first time an FLSC design has been systematically investigated and optimized for efficient luminescent solar concentration. Furthermore, the feasibility of producing such non-traditional fiber structures is demonstrated experimentally (see Chapter 6) using the traditional process of thermal fiber drawing from a scaled-up model called a ‘preform’ (see Figure 5- 2) [40].

Previous theoretical studies have examined LSC performance from various viewpoints, such as microscopic level models based on molecular light-matter interactions [109], thermodynamic approaches based on radiative transfer theory from a macroscopic perspective [87], and system-level design and optimization using Monte Carlo ray-tracing. Here primarily the ray tracing method is employed for optical system design, analysis, and optimization (see Section 5.3 for details).

This chapter is organized as follows. After providing an overview of the general strategy in Section 5.2 and details of the simulation method in Section 5.3, the rationale for choosing the rectangular fiber with an integrated cylindrical lens cap is elucidated in Section 5.4 by comparing it with two simpler structures, rectangular and cylindrical waveguides, along with the experimental progress on controllably fabricating ‘cold’ polymer fibers (i.e., undoped) with cross-sectional structures similar to those studied theoretically here. Section 5.5 examines the first stage of the concentration process, absorption of incident sunlight, and evaluates the dependence of absorption efficiency on the fiber geometrical and physical degrees of freedom. In Section 5.6 the capture of the luminescence in the fiber via total internal reflection (TIR) is investigated, while Section 5.7 focuses on the important issue of self-absorption as a limiting factor for increasing the length of FLSC’s (and hence setting a limit on the geometrical gain).

Section 5.7 concludes with a simple empirical model of the dependence of self-absorption on the fiber degrees of freedom, allowing for rapid evaluation of multiple designs. Section 5.8 presents results on optimizing the performance of the proposed FLSC over the full parameter space of the FLSC structural and physical degrees of freedom. Up to this point, the analysis is carried out using a fixed pair of absorption and emission wavelengths.

This restriction is lifted in Section 5.9, where an analysis is presented that takes into consideration the solar spectrum and the wavelength dependence of absorption and luminescence by a dopant. This chapter is concluded by summarizing the potential advantages of FLSC's with respect to traditional LSC designs.

5.2. Overall Strategy

Although optical glasses may attain superior optical properties with respect to polymers, thereby making them useful in the construction of LSC's, polymers have the positive attributes of easier processing and machining, lower price, higher mechanical flexibility and robustness, and lower weight. Optical polymers thus offer a compromise between these useful attributes and optical performance. Polymers, such as cyclic olefin polymer (COP) are highly transparent in the visible and can demonstrate high photo-stability with low absorption in the ultraviolet [110]. A subset of optical polymers, typically *thermoplastic* polymers such as COP, may be thermally drawn into fibers, and they are natural candidates for fabricating FLSCs.

From the schematic depiction in Figure 5- 1, the operation of an FLSC may be divided into three distinct steps:

(1) *Absorption of sunlight in the fiber.* Sunlight incident on the external surface of the FLSC is focused by its curved outer surface into a preselected spot inside the fiber where luminescent dopants are placed. The fraction of incident sunlight absorbed in the fiber may be maximized through optimizing the fiber surface geometry, transverse structure, and concentration and spatial distribution of the luminescent dopants (Sections 5.4 and 5.5).

(2) *Luminescence capture by the fiber.* A fraction of the isotropically emitted luminescence is captured by total internal reflection (TIR), depending on the refractive index and structure of the FLSC (Section 5.6).

(3) *Optical emission delivery.* The captured luminescence undergoes absorption as it propagates along the fiber, mainly due to self-absorption. This issue is investigated in Section 5.7 where the effects of the FLSC degrees of freedom on light transport efficiency are examined. The distribution and concentration of the luminescent dopants must be chosen to strike a compromise between increasing optical absorption and decreasing the self-absorption, which sets the limit on luminescence propagation along the fiber to the PV cell. We carry out this optimization in Section 5.8. Finally, optical-to-electric energy conversion occurs at the fiber tips which are coupled to a PV cell optimized with respect to the luminescence spectrum and not the full solar spectrum. The mechanical flexibility and robustness of polymer fibers allows bundling them together at their ends, which facilitates interfacing them to PV cells (Fig. Figure 5- 2h).

5.3. Ray-Tracing Simulation

The modeling and optimization simulations are carried out using the Monte Carlo ray-tracing software package ZEMAX[®] in the non-sequential mode in conjunction with MATLAB[®].

I employ ray-tracing in lieu of the beam propagation method, for instance, because of the large bandwidth of the radiation in k -space in conjunction with the typical sizes of FSLC's under investigation ($\sim 10^6 \lambda^2$), which makes beam propagation methods computationally prohibitive.

I account for the effects of the angles of incidence and polarization on reflection and refraction at interfaces through the use of the 'polarization ray-tracing' method.

The fiber structures are defined by either overlapping simple geometrical shapes or extruding objects through user-defined apertures. This allows us to set the *geometric* parameters of the cross section, such as width W and height H of the rectangular section, the cylindrical cap height h , and diameter D and location l of the core. The *physical* parameters of the fiber, such as the wavelength-dependent refractive index $n(\lambda)$, the optical absorption coefficient $\alpha(\lambda)$ of the luminescent dopants, are also adjusted. The polymer refractive index throughout the visible was fixed at its value at 550 nm, thereby in effect neglecting material dispersion for the polymer. Furthermore, ray-tracing calculations over a set of fiber structures in which a geometric or physical parameter is scanned over a range of values is carried out in a loop using macros written in the ZEMAX programming language (ZPL).

The incident light throughout the paper is assumed to be spatially incoherent and unpolarized.

The source is a rectangle of dimensions $500 \times 100 \mu\text{m}^2$ producing collimated rays with unity radiation power illuminating the fibers vertically from the top. Simulations to estimate the percentage of incident sunlight absorbed by the fiber make use of a source producing 10,000

rays. Increasing the number of rays to 200,000 in these simulations changes the estimated absorption percentage by less than %0.01.

To estimate the power absorbed by the ‘cold’ fiber (Figure 5- 3), we place flat detectors surrounding all sides of the fiber to detect light emerging from it. The percentage of absorbed light is the difference between the source and the detected signal. In order to obtain the intensity distribution inside the fibers, we place a detector normal to the fiber axis at the location of interest tilted 1° with respect to that normal. The detector intercepts the rays at the plane of interest while introducing minimal distortion in the acquired distribution. To isolate the desired absorption by the luminescent dopants from background absorption of the host polymer, all materials in the doped fibers except the luminescent dopants were assumed lossless for the simulations, and the host material absorption was subsequently added separately. For the case of doped cores, we utilize the ‘bulk scattering’ feature of ZEMAX[®], which simulates fluorescence in ray-tracing.

5.4. General fiber design

I start by comparing three broad classes of polymer fiber structures: (1) rectangular fibers (dimensions $W \times H$) that resemble traditional flat LSC’s (Figure 5- 2a); (2) cylindrical fibers with outer diameter W (Figure 5- 2b); and (3) hybrid fibers consisting of a rectangular cross section ($W \times H$) with an axially extending cylindrical cap of height h and radius of curvature $r = \frac{h}{2} + \frac{W^2}{8h}$ on top (Figure 5- 2c). In all three fibers, the luminescent dopants are located in a ‘core’ of diameter D , whose center is at a height l in the hybrid structure and is located at the geometric

center in the rectangular and cylindrical structures. The refractive index is uniform over the cross-section and the doped-core differs only in that it has an optical density of α_d (in absorbance units per cm). I consider a generic polymer with refractive index $n=1.53$ and optical absorption losses 1 dB/m [111]. Such parameters are comparable to those of typical optical polymers such as COP [110] or polycarbonate (PC) [112]. We compare the focusing capabilities of the fiber external surfaces by examining the ‘cold’ fiber structures, i.e., in absence of luminescent dopants. In Figure 5- 3 we plot the results of ray-tracing simulations of light incident vertically with respect to the horizontal axis of cold fibers suspended in air (see Section 5.3 for details).

Figure 5- 2: Schematic and microscopic image of cross sections of three FLSC structures and an assembled ‘cold’ fabric

The rectangular fiber (Figure 5- 3a; $500 \times 500 \mu\text{m}^2$) does not focus incident light, and the fraction of sunlight intercepted by the core is at best D/W . In the cylindrical fiber (Figure 5- 3b; $W = 500 \mu\text{m}$), the external curved surface focuses incident rays to the opposing side of the fiber, and the percentage of rays intercepted by the core is now larger than D/W . This outcome is *independent* of the fiber diameter: the focal point is *always* at the opposite side of the fiber (for typical values of n). In the hybrid fiber structure (Figure 5- 3c), a cylindrical cap is provided on the top which focuses incident light to a point inside the fiber determined by its curvature. For example, if the

cap is a half cylinder of diameter W , $h = \frac{W}{2}$, then incident light is focused into the core (Figure 5-3c; $W=H=500\text{ }\mu\text{m}$). This structure therefore allows one to choose the location of the spot at which externally incident light is focused by judiciously choosing W , H , and h , in contradistinction to the cylindrical fiber where the location of the focal spot is predetermined. In addition, using such a structure facilitates assembling the fibers on a surface while maintaining correct orientation, enables a large fill-factor, and potentially allows placing a back reflector beneath the FLSC assembly.

It is useful to consider the effect of adding a reflector under the three fiber structures (Figure 5-3d-f). We model the reflector as an aluminum coating with complex refractive index $n=0.7-7.0i$ giving a 94.6% reflectivity for normal incidence. The mirror is separated from the fiber by a thin air gap ($1\text{-}\mu\text{m}$ -thick; results are not sensitive to the gap thickness). In this way, by varying the cap height h , it may be arranged for incident light to pass through the core twice.

Figure 5- 3: Ray-tracing simulations of normally incident light in the three 'cold' (undoped) structures

With our understanding of the trajectories of the light rays in the 'cold' structures, we proceed to determine the fraction of incident light absorbed by luminescent materials in doped cores ($\alpha_d = 100 \text{ cm}^{-1}$). Figure 5- 4 shows that the fraction of incident light absorbed is strongly dependent on the surface geometry. In the square fiber (Figure 5- 4a), the amount of captured light is approximately $D/W=0.4$, as expected. The absorption is highest in the capped fiber (Figure 5- 4c). Although it is conceivable that more complex surface structures may outperform this one, we limit ourselves here to fibers having axial symmetry, since they can be drawn from a macroscopic preform by traditional thermal drawing [40] and do not require post-processing.

Note that the geometric gain G in a traditional flat LSC of dimensions $L \times L$ and thickness H is

defined as the ratio of the LSC area to the area of the needed PV cells, $G = \frac{L^2}{4LH} = \frac{L}{4H}$.

Considering a FLSC of equal area ($\frac{L}{W}$ fibers of length L and width W each, such that the total area

is $L \times L$), we have $G \sim \frac{L}{2H}$, where a factor of 2 improvement is achieved due to the directional guiding along the fibers. This consequence of the fiber form factor is one of the advantages of polymer FLSC's in addition to others that I describe below.

Figure 5- 4: Ray-tracing simulations of normally incident light in the three 'hot' structures

5.5. Impact of FLSC geometrical and physical parameters on absorption

After establishing the superior absorption performance of the hybrid capped fiber design with respect to the cylindrical and square fibers and also the feasibility of fabricating such a fiber structure, I proceed to examine the impact of the following structural and physical degrees of freedom on its performance: (1) the cylindrical cap curvature, or alternatively its height h ; (2) the optical density of the luminescent dopants α_d ; (3) the doped core diameter D ; (4) the fiber aspect ratio $W : H$; and (5) the location of the doped core in the fiber l (Figure 5- 2c).

We first investigate the effect of each degree of freedom separately and then carry out optimization over the full five-dimensional parameter space in Section 5.8. This investigation is carried out assuming a single incident wavelength and a single emission wavelength. The effect of the incident, absorption, and emission spectra is considered in Section 5.9.

Impact of cap height h and doping concentration α_d

Fibers with smaller h are easier to fabricate, but absorption in the core is reduced because of the resulting weaker focusing. Similarly, lowering α_d reduces the absorption of incident light, but lower values of α_d are easier to implement and also result in lower self-absorption. I assess quantitatively the impact of h and α_d on the absorption efficiency η_{abs} , defined as the fraction of incident light absorbed by the FLSC, by determining the difference between the incident optical power and the total power emerging or reflecting from the fiber.

Figure 5- 5: (a) Dependence of η_{abs} on the optical density α_d for different cap heights.

The interplay of h and α_d is depicted in Figure 5- 5a. We use a monochromatic, spatially incoherent, unpolarized optical beam of uniform intensity (see Section 5.3) incident normally on a hybrid fiber structure with $W=H=500 \mu\text{m}$, $D=200 \mu\text{m}$, and $l=250 \mu\text{m}$. One expects that increasing α_d for fixed h will increase η_{abs} . This intuition is borne out in Figure 5- 5a. Note that the maximum absorption at large α_d is ultimately limited by the focusing effect of the cap.

Adding a back-reflector increases η_{abs} by offering a longer effective interaction length with the dopants (Figure 5- 5b). Surprisingly, the relation between η_{abs} and h is no longer monotonic for fixed α_d , as it is in absence of the back-reflector. In fact, a smaller h (e.g., 100 μm) may result in a higher η_{abs} than a larger h (150 μm) when the back-reflector is added. The corresponding intensity profiles (Figure 5- 5b, inset) offer the explanation: while light is initially focused weaker with the lower-curvature cap, the folded-back beam has its focal point at the core, thereby increasing η_{abs} after two passes.

Finally, we plot in Figure 5- 6 the full dependence of η_{abs} on both α_d and h in absence and presence of a back-reflector, showing that high absorption may be achieved over a wide range of values of α_d and h . Figure 5- 5a and Figure 5- 5b are one-dimensional sections through this two dimensional distribution.

Figure 5- 6: η_{abs} in the hybrid FLSC structure as a function of cap height h and the optical density α_d .

Impact of fiber aspect ratio

It is advantageous to design a FLSC with a large aspect ratio $W:H$ by decreasing H , that is, a high-aspect-ratio rectangle. Such a structure requires less material, which reduces the weight and cost per unit area, while simultaneously increasing the flexibility of the FLSC (Figure 5- 2h).

Figure 5- 7: (a) Fraction of sunlight absorbed by an FLSC as a function of h and H .

We evaluate the effect of H on η_{abs} while holding W and D fixed. For each value of H we choose the location of the core l that maximizes η_{abs} . We first perform ray tracing for a cold fiber structure, determine the point with highest intensity, center the core at that point, and then carry out the ray-tracing simulation again with the doped-core included. We plot in Figure 5- 7 η_{abs} versus h and H while holding the following parameters fixed: $D = 200 \mu\text{m}$, $W = 500 \mu\text{m}$, and

$\alpha_d=100 \text{ cm}^{-1}$. The vacant part in the plot corresponds to incommensurate values of H and h , since we choose $H+h>D+150$ to maintain a minimum of 75- μm -thick undoped polymer both below and above the doped core. We find that high absorption is achieved when large values of H and h are chosen simultaneously, and maintaining high η_{abs} while reducing H necessitates using large h .

Impact of doped-core diameter

The interplay between the effects of the doped-core diameter D and α_d on η_{abs} is shown in Figure 5- 8. High absorption can be achieved by either increasing D or α_d in absence or presence of a back-reflector. A large core captures a wider range of focused rays for fixed α_d , and a higher α_d results in stronger absorption for fixed D . Unfortunately, configurations that result in the highest η_{abs} , such as those with large D or high α_d , usually also induce high self-absorption, as we shall see shortly. Thus, in choosing the values of such degrees of freedom, a compromise must be struck between improving η_{abs} and self-absorption, which reduces the luminescence reaching the FLSC end.

Figure 5- 8: Impact of D and α_d on η_{abs} for FLSC's with and without back-reflector

5.6. Luminescence capture in fiber

A fraction of the absorbed optical energy is lost due to the luminescence quantum efficiency of the dopants (non-radiative decay of the excited state) and the quantum defect (the Stokes shift between the absorbed and emitted wavelengths). These two effects are captured in the parameter η_Q , the quantum conversion efficiency, which is the fraction of absorbed optical energy that is re-emitted into the fiber. In this section I determine the fraction of the *emitted* radiation that is confined in the fiber via total internal reflection (η_{TIR}). The remaining fraction, emitted in the so-called ‘escape cone’, leaks out. This captured fraction depends on the refractive index and the fiber geometry. While analytic formulae for η_{TIR} have been derived for simple geometries such as slab and circular waveguides [32], I estimate η_{TIR} in our hybrid FLSC geometry by ray-tracing simulations. I compare η_{TIR} in the square, cylindrical and hybrid FLSC’s by scanning a luminescent point source (1- μm radius) emitting isotropically 50,000 rays/ μm^2 ($\sim 157,000$ rays per point source) and determine the remaining fraction of rays confined in the cold fiber after the unguided rays have leaked out, which typically occurs in less than 1 mm. Although dye molecules in a solid matrix (for example) may retain the memory of the optical excitation, and hence signatures of the dipole molecular emission may be observed [113, 114], the incoherence and unpolarized nature of solar radiation justifies the assumption of isotropic emission. For a rectangular waveguide with $n = 1.53$, we find that $\eta_{\text{TIR}} \approx 50.8\%$ independently of the emission position of the point source and of the aspect ratio $W : H$ (see Ref. [32]). In a cylindrical waveguide of the same refractive index, η_{TIR} for a point source that is scanned in the radial direction changes from $\approx 34.6\%$ for an on-axis emitter to $\approx 75.5\%$ for a point source located at the surface. In the hybrid FLSC, η_{TIR} changes with h from 50.8% when $h = 0$ (rectangular fiber)

and drops rapidly to 34.6% when $h=50\text{ }\mu\text{m}$, and remains so with increase in h to a maximum value of $h = 250\text{ }\mu\text{m}$ (here $W=H=500\text{ }\mu\text{m}$).

Figure 5- 9: Intensity profile of incident sunlight and luminesced light in FLSC's

Crucially, η_{TIR} is independent of position in the hybrid FLSC, similarly to the rectangular fiber and in contradistinction to the cylindrical fiber. This allows us to implement a very useful simplification: there is no need to simulate the propagation along each structure with its distinct non-uniform luminescence emission profile, which is proportional to the intensity of light absorbed locally. Two examples of such spatially varying emission profiles are shown in Figure 5- 9. Instead of using directly these profiles, we may replace an arbitrarily shaped emission pattern with an isotropically emitting *uniform disc* having the same diameter as the doped core,

with the proviso that *the total luminescence power of this uniform disc is equal to that of the original spatially varying emission profile*. We hereon use this simplification, which enables us to reach general conclusions in the next Section with regards to self-absorption.

5.7. Impact of self-absorption

Self-absorption is the suppression of the useful output signal resulting from the unavoidable overlap between the absorption and emission spectra of the luminescent dopants, and it typically sets the upper limit on useful LSC size and performance [14, 22]. Two material properties help quantify self-absorption: (1) the Stokes shift $\Delta\lambda_s$, which is the difference between the peak absorption λ_A and the peak emission $\lambda_{PL}=\lambda_A+\Delta\lambda_s$ wavelengths, and (2) the self-absorption ratio S , the ratio between the absorption coefficient values at peak absorption and peak emission wavelengths $S = \frac{\Phi_a(\lambda_A)}{\Phi_a(\lambda_{PL})}$, where $\Phi_a(\lambda)$ is the absorption spectrum. In an ideal LSC, $\Delta\lambda_s$ and S should be as large as possible. In this section, we use the parameters typical of a typical laser dye in a solid matrix as a model luminescent material ($S=100$).

While simplified analytical models for self-absorption in planar [22] and cylindrical [20] LSC's have been developed, the unusual cross section of our FLSC necessitates the use of simulations to evaluate the impact of self-absorption. We consider here only the first generation of luminescent photons; that is, re-emission after self-absorption is neglected. Consequently, the spectral red-shift resulting from multiple emission/re-absorption events is ignored.

It is expected that self-absorption increases with propagation distance z along the FLSC, with α_d , and with the doped area in the FLSC cross section. We define a figure of merit η_{sa} , which is the

fraction of emitted luminescence that reaches the fiber end after undergoing self-absorption. We have performed simulations in the four-dimensional parameter space of H , h , D , and α_d , and the results reveal that η_{sa} may be accurately modeled by an exponential function of the form

$$\eta_{sa}(z) = e^{-\kappa \cdot \alpha_d(\lambda_e) \cdot A_r \cdot z}, \quad (1)$$

where A_r is the fraction of the cross-sectional area that is (uniformly) doped, α_d is the optical density of the doped region at the *emission* wavelength λ_e , and z is the axial position along the FLSC away from the point where incident radiation is absorbed. Here $\kappa=3.064$ is an empirical fitting parameter that results in an average error in estimating η_{sa} of $\sim 1\%$ averaged over all the examined configurations.

5.8. Optimum FLSC performance

The overall optical conversion efficiency η_O is a product of the efficiencies of the consecutive processes we have discussed thus far,

$$\eta_O = (1 - R) \times \eta_{abs} \times \eta_Q \times \eta_{TIR} \times \eta_{prop}(z), \quad (2)$$

here z is the distance along the fiber measured from the position of incident light confined to a point; R is the fraction of sunlight reflected from the fiber outer surface (Section 5.4); η_{abs} is the fraction of sunlight absorbed by the luminescent materials (Section 5.5); η_Q is the quantum conversion efficiency, which incorporates the luminescence quantum efficiency and the quantum

defect (Section 5.6); η_{TIR} is the fraction of luminescence confined by total internal reflection (Section 5.6); and η_{prop} is the fraction of trapped luminescence delivered to the fiber tip after absorption by the host, waveguide losses due to surface roughness, and self-absorption (Section 5.7),

$$\eta_{prop}(z) = \eta_{host}(z) \times \eta_r \times \eta_{sa}(z). \quad (3)$$

The three factors in $\eta_{sa}(z) = e^{-\kappa \cdot \alpha_d(\lambda_e) \cdot A_r \cdot z}$, (1) all typically have the form of an exponential function, but the exponent of η_{sa} (Eq. 1) usually dominates.

The overall optical conversion efficiency is obtained by integrating $\eta_O(z)$ over the length of the fiber L :

$$\eta_O = (1 - R) \times \eta_{abs} \times \eta_Q \times \eta_{TIR} \times \int_0^L dz \eta_{prop}(z). \quad (4)$$

This formula corresponds to integrating the amount of light reaching the fiber ends from a set of incident points distributed uniformly along its length.

Now that we have in place all the elements of a full model of our FLSC, we carry out an optimization of its performance with respect to its degrees of freedom. We simulate more than 52,000 FLSC configurations using the full model in search of the maximum optical concentration efficiency η_O , defined as the fraction of normally incident optical energy that is delivered to the fiber end in the form of luminescence. We fix the following FLSC parameters: length is $L=30$ cm, $S=100$ (a conservative value; e.g., DCJTB has $S \sim 180$ in a typical solid matrix), and $W=500$ μm . The FLSC parameters we vary are (1) α_d in the range 0 to 400 cm^{-1} ,

(2) D in the range 8 to 200 μm , (3) h in the range 4 to 250 μm , and (4) H in the range $D - h + 150$ to W .

We find a maximum efficiency of $\eta_O = 13.92\%$ for a configuration with $\alpha_d = 340 \text{ cm}^{-1}$, $D = 24 \mu\text{m}$, $H = W = 500 \mu\text{m}$, $h = 250 \mu\text{m}$. When the FLSC is provided with a reflective mirror, a maximum efficiency $\eta_O = 14.16\%$ occurs for a configuration with $\alpha_d = 280 \text{ cm}^{-1}$, $D = 24 \text{ m}$, $W = H = 500 \mu\text{m}$, $h = 100 \mu\text{m}$. Although the optimal efficiencies are similar in presence and absence of the mirror, the optimal value in the former requires a smaller cap height h and a lower doping concentration α_d , which ease fabrication constraints.

5.9. Integration over solar and luminescence spectra

The ray-tracing simulations reported above are carried out assuming incident radiation at a single wavelength and a single emission wavelength. We now move to a more realistic model where three relevant spectral distributions are incorporated: (1) the incident radiation has a spectral distribution $\Phi_i(\lambda)$, taken to be AM 1.5 solar spectrum; (2) the absorption spectrum of the luminescent dopants is $\Phi_a(\lambda)$; and (3) their emission spectrum is $\Phi_e(\lambda)$. We normalize these three spectra such that $\int d\lambda \Phi_j(\lambda) = 1$, where $j = i, a, e$.

We now generalize the results in the previous sections by integrating η_O over all three spectra using the formula

$$\eta_O = (1 - R) \times \eta_{TIR} \times \eta_Q \times \int d\lambda_i \eta_{abs}(\lambda_i) \Phi_i(\lambda_i) \times \int_0^L dz \int d\lambda_e \eta_{prop}(\lambda_e, z) \Phi_e(\lambda_e), \quad (5)$$

where λ_i and λ_e are the incident and emitted wavelengths.

This formula captures a very general model of a FLSC with both the parameters of the incident light, the fiber, and the luminescent materials included. Note that both η_{prop} and η_{abs} are now wavelength-dependent at the absorption and emission wavelengths through $\alpha_d(\lambda) = \alpha_d^{(\text{peak})} \Phi_a(\lambda)$, where $\alpha_d^{(\text{peak})}$ is a scaling factor for the normalized distribution $\Phi_a(\lambda)$. We ignore the wavelength dependence of η_{TIR} , which amounts to neglecting the polymer material dispersion in the wavelength range of interest, which is a minor effect.

In performing this spectral integration, we use a simplified model for $\Phi_a(\lambda)$ formed by the superposition of two Gaussian spectra

$$\Phi_a(\lambda) = \frac{1}{2\sqrt{2\pi}\sigma_a^2} \left\{ \exp\left(-\frac{(\lambda-\lambda_1)^2}{2\sigma_a^2}\right) + \exp\left(-\frac{(\lambda-\lambda_2)^2}{2\sigma_a^2}\right) \right\}, \quad (6)$$

with peaks at $\lambda_1 = 400$ nm and $\lambda_2 = 550$ nm, and full width half-maximum (FWHM) bandwidths of 120 nm each. This model represents the absorption spectrum of a broadband absorbing fluorescent dye or a compound fluorescent material. We take $\Phi_e(\lambda)$ to have a Lorentzian distribution,

$$\Phi_e(\lambda) = \frac{1}{2\pi} \frac{\sigma_e}{(\lambda-\lambda_3)^2 + \frac{1}{2}\sigma_e^2}, \quad (7)$$

with emission peak at $\lambda_3 = 730$ nm and FWHM bandwidth $\sigma_e = 15$ nm; see Figure 5- 10a. In designing an ideal LSC in general, the goal is to choose materials with the broadest spectral

distribution for $\Phi_a(\lambda)$ to capture the solar spectrum, while minimizing the overlap between $\Phi_a(\lambda)$ and $\Phi_e(\lambda)$ to reduce self-absorption.

Figure 5-10: Spectral distributions for efficiency integration and η_0 as a function of $\alpha_d^{(\text{peak})}$ for different FLSC lengths L

Using the optimal geometrical configuration in the previous Section ($H = W = 500 \mu\text{m}$, $D = 24 \mu\text{m}$, no back-reflector), we searched for the optical density of luminescent dopants $\alpha_d^{(peak)}$ that maximizes η_O when the full spectral integration is carried out. We extended the range of $\alpha_d^{(peak)}$ to 2000 cm^{-1} since the increase of absorption at higher $\alpha_d^{(peak)}$ outstrips the increase in self-absorption after spectral averaging beyond the value 400 cm^{-1} we used in Section 5.8. Figure 5-10b depicts the dependence of η_O on $\alpha_d^{(peak)}$ and FLSC length. For this FLSC geometry, maximal values for two different fiber lengths $L=2.5$ and 30 cm are η_O of 7.2% and 6.2% , which occur at $\alpha_d^{(peak)} = 1670$ and 967 cm^{-1} , respectively. I further multiply these values by 0.7 to account for several factors that contribute to reduction in overall FLSC system efficiency.

(1) Power-conversion efficiency at the PV cells attached to the FLSC ends. I assume PV cells selected such that their peak conversion efficiency occurs in a spectral band that overlaps with the emission spectra of the luminescent dopants. Close-to-unity conversion efficiency may be achieved in this fashion; see Ref. [115].

(2) Coupling losses from the fiber ends to the PV cell. These losses can be minimized using clear index matching optical glues.

(3) Non-unity η_Q for real luminescent dopants. η_Q greater than 0.95 is common in fluorescence dyes and quantum dots.

The conservative multiplicative factor of 0.7 reduces the potential optical-to-electrical power conversion efficiencies to $\eta_{\text{conv}}=5.0\%$ and 4.3% for FLSC lengths of 2.5 cm ($G=18$) and 30 cm ($G=220$), respectively.

For comparison with conventional flat slab LSCs, we use Ref. [22] where $\eta_{\text{conv}}=6.8\%$ was estimated from measurements of η_{O} on a small-area, thick LSC of dimensions $25 \times 25 \times 2 \text{ mm}^3$ ($G=3$). Currie *et al.* [22] projected a reduction to $\eta_{\text{conv}}=6.1\%$ for a LSC having $G=45$ (surface area of $36 \times 36 \text{ cm}^2$). The values in Ref. [22], however, were obtained using a high-index glass (SF10, $n=1.8$), which improves η_{TIR} by 27% over the polymer FLSC here ($n=1.53$). By incorporating this effect, we find that the calculated values of η_{conv} here for a FLSC and reported values for a slab LSC are comparable, albeit while achieving much larger values of G in the FLSC having the same area as the slab LSC.

5.10. Summary and conclusion

While the proposed polymer FLSC structure yields comparable values of η_{conv} to those of state-of-the-art glass-based slab LSC's, there are nevertheless several advantages that suggest the usefulness of FLSC's. First, polymer-based FLSC's are lighter-weight than glass based LSC's. For example, the density of SF10 glass (used in Ref. [22]) is 4.8 g/cm^3 , compared to 1.02 g/cm^3 for COP. Using the dimensions $W = H = 500 \text{ }\mu\text{m}$ and $h=250 \text{ }\mu\text{m}$ for the FLSC and the dimensions in Ref. [22], the weight of the FLSC per unit area is reduced by a factor of ≈ 13.5 . The FLSC fabric is projected to weigh only $\approx 700 \text{ g/m}^2$. The superior mechanical properties of polymers versus glasses with respect to bending forces further suggest the usefulness of FLSC's in mobile applications.

Finally, FLSC's may improve the economics of solar energy since the cost of unit power generated by a concentrator is directly proportional to the cost of collector system and inversely proportional to the product $G \times \eta_{\text{conv}}$; see Eq. (1) of Ref. [22]. The larger G for the FLSC's

designs investigated here (but with comparable η_{conv}) means both that smaller-area PV cells are required and a smaller quantity of polymer is needed in constructing the FLSC compared to a glass-based slab LSC of the same area. The cost is reduced on all three counts, thereby potentially reducing the cost by an order of magnitude.

Future investigations will examine the performance of these FLSC's with respect to diffuse incident light, and the potential of combining both down-conversion and up-conversion materials to harness the full solar spectrum.

In conclusion, I have presented a full investigation of the design of a luminescent solar concentrator having the form-factor of a fiber, a FLSC. I have examined the impact of the geometric and physical degrees of freedom of the FLSC on its performance. Such FLSC's may be readily fabricated using the traditional and scalable process of thermal drawing. These new concentrators offer several unique advantages in terms of weight and flexibility without sacrificing the performance in comparison to state-of-the-art glass-based slab LSC's.

CHAPTER 6: EXPERIMENTAL REALIZATION OF A FIBER LUMINESCENT SOLAR CONCENTRATOR FABRIC

6.1. Introduction

As detailed in Chapter 3, in addition to recent advances in LSC materials and construction, another design degree-of-freedom is the LSC geometric/structural form-factor itself that may be exploited to further improve its utility. Specifically, it is now appreciated that cylindrical LSC's offer unique advantages in terms of light-capture and concentration with respect to traditional flat slabs [32], as demonstrated recently using individual bulky doped cylindrical rods [34]. The salutary features of the cylindrical form-factor suggest the usefulness of optical fibers as realizations of LSC's. Lately, fibers have been utilized in constructing one-dimensional organic PV cells [36, 37] and multimaterial fibers may potentially lead to silicon-based PV's [38, 116]. Nevertheless, in these contexts the fiber is not used to transmit light along its length – a task for which optical fibers are particularly well-suited. Instead, the fiber serves the role of a structural scaffold that is coated with organic PV materials [36, 37] or that hosts silicon within it [38, 116]. Therefore, the unique and useful attributes of optical fibers viewed as photonic devices – such as the long producible lengths that have enabled global internet connectivity – have yet to be put to use in harnessing solar energy.

In this Chapter the new LSC form-factor (a robust and flexible polymeric fiber LSC, or FLSC) which was introduced earlier in this thesis is investigated experimentally. The scalability

inherent in the fiber drawing process [117] is harnessed. Precise control is exercised over the transverse geometry of fiber to produce extended lengths of uniform polymer fiber drawn from a macroscopic preform having a specially designed external morphology and precisely located luminescent dopants. Polymer fibers are drawn with a non-traditional cross-sectional geometry: a square with a half-cylinder cap. Several functionalities are integrated monolithically in these FLSC's with no need for post-drawing processing. First, the curved fiber surface provides an axially extended cylindrical micro-lens that focuses externally incident sunlight into the core along the whole fiber length. Second, sunlight absorption is achieved with a variety of potential dopants that are controllably concentrated and judiciously placed in the fiber cross section. Third, the fiber naturally provides optical guidance of the captured fraction of the emitted luminescence. A multiplicity of such FLSC's may be arranged in a flexible yet robust non-woven fabric that may be used for mobile energy needs where flexibility and robustness are critical. The use of flexible yet robust polymer fibers in lieu of potentially brittle glass fibers may enable the incorporation of FLSC's into fabrics. Figure 6- 1 shows an assembled FLSC fabric that is constructed by placing FLSC fibers on an adhesive tape for demonstration.

Figure 6- 1: FLSC fabric assembled from fabricated FLSC fibers

6.2. Overall approach

The overall approach of a FLSC is shown schematically in Figure 6- 2 where multiple parallel-aligned FLSC's assembled on an extended curved surface are depicted. Sunlight incident on the curved FLSC surfaces is focused into the doped core within each individual FLSC, and a percentage of the essentially isotropically emitted luminescence is captured and guided via total internal reflection to the fiber ends coupled to PV cells where optical-to-electric energy conversion takes place (Figure 6- 2, inset). Figure 6- 3 shows ray-tracing simulations results for total internal reflection trapping of the isotropic emission in fiber.

Figure 6- 2: FLSC fabric system concept

Figure 6- 3: TIR light trapping in FLSC fiber

A portion of the useful luminescence may be lost during propagation along the FLSC via self-absorption determined by the strength of the absorption tail of the dopants at the emission wavelength. These mechanisms are illustrated schematically in Figure 6- 4.

Figure 6- 4: Operation of a FLSC

The transverse fiber structure proposed here represents a dramatic departure from traditional LSC's that are shaped as flat slabs with luminescent dopants forming a thin film on its surface extending across the area of intercepted sunlight. The proposed FLSC has a hybrid cross section comprising a square section that allows for easy arrangement and alignment of fibers beside giving a high fill-factor. The square section is topped with a cylindrical micro-lens that runs along the fiber for concentration of incident light onto a core doped with luminescent materials. The FLSC combines elements from flat LSC's (the square section) and optical fibers (the top half-cylinder cap). The motivation for adopting this hybrid geometry may be appreciated by examining the focusing effect of the curved surface of a cylindrical fiber, shown in Figure 6- 5 for a fiber having refractive index $n = 1.53$ (typical of silica glass and optical polymers) and diameter $500\text{ }\mu\text{m}$ – the focused spot is a point on the opposite side of the fiber. This result is

scale-free and independent of the fiber diameter. The range of values for refractive indices of solid optical materials that are transparent in the visible ($n \sim 1.4 \rightarrow 3$) does not result in a strong focusing effect. The design pursued here thus decouples the location of the focal point from the opposite curved wall of the fiber. By changing H and h we may arrange for the focal spot to be at any height within the fiber, where we then place the needed dopants, thereby allowing for locating the dopants at specific locations to maximize absorption and potentially reduce self-absorption. Furthermore, the broken cylindrical symmetry of this fiber design and the flat bottom surface facilitate placement and alignment of the fibers on a surface (Figure 6- 1), while the flat side surfaces improve the fill-factor.

Figure 6- 5: Comparison of focusing power in circular and hybrid FLSC's

One important LSC figure of merit is its geometric gain G defined as the ratio of the LSC area to that of the required edge PV cells. The cost-effectiveness of LSC's is determined by the concentration ratio $C = G \times \eta_0$, i.e., increasing G has the same impact as improving the efficiency. It is immediately clear that transverse optical confinement in FLSC's doubles G compared to a slab LSC of equal area. While an LSC of transverse dimensions $L \times L$ and

thickness t has $G_{\text{LSC}} = \frac{L^2}{4tL} = \frac{L}{4t}$, a FLSC of length L , width W , and thickness t has $G_{\text{FLSC}} = \frac{LW}{2tW} = 2G_{\text{LSC}}$. Arranging $\frac{L}{W}$ such FLSC's to cover the same area $L \times L$ does not change G .

A theoretical model is constructed and described in Chapter 5 for the operation and performance of a FLSC. This model uses ray-tracing calculations to incorporate the focusing effect of the curved fiber surface on incident rays, the absorption of focused light within a core of diameter D and optical density α_d , isotropic emission of red-shifted luminescence from the doped core, and optical guidance by TIR assuming a polymer refractive index $n = 1.53$. Assuming incident sunlight with AM1.5 solar spectrum absorbed by the organic dye DCM, the impact of self-absorption through the overlap of the absorption and emission spectra of the dye is incorporated. Figure 6- 6 plots the optical conversion efficiency η_o of a FLSC while varying the core diameter D and the optical density α_d while holding fixed the geometry of the fiber cross section: $W = H = 500 \text{ } \mu\text{m}$ and $h = 250 \text{ } \mu\text{m}$ (i.e., a half-cylinder cap). The core is assumed to be located at the center of the square portion of the fiber at a height $250 \text{ } \mu\text{m}$ from the bottom flat surface. Efficiency calculation in this figure assumes a DCM-doped core with absorption and emission spectra as shown in Figure 6- 7(e). FLSC length is chosen to be 10 cm. It is shown in this figure that there is not one unique solution for high concentration efficiency. A relatively wide range of the two parameters (core diameter and optical density) can result in high optical efficiencies. This is suitable because various fluorescent materials may have different solubility values in the host polymer or may experience concentration quenching (fluorescence efficiency that reduces beyond a certain level of concentration) to different levels that impose some limits on the achievable optical density.

Figure 6- 6: Optical efficiency variations with core diameter and optical density for 10-cm-long FLSC with DCM core

6.3. FLSC Fabrication

Overview of fabrication

An important question to be addressed is the feasibility of fabricating these non-traditional fiber structures vis-à-vis the scalable process of thermal fiber-drawing from a macroscopic scaled-up preform, as is typical of telecommunications fiber production. An outline of the consecutive steps followed in fabricating such a fiber is presented in Figure 6- 7a that illustrates the procedure.

Figure 6- 7: FLSC fabrication and material characterization overview

Process start with extruding an optical polymer rod (cyclic olefin polymer, COP [110]) having the desired fiber cross section. Thermoplastic COP granules are heated above their glass-transition temperature (T_g) and extruded under pressure in vacuum through a die whose shape

dictates the morphology of the rod produced. A typical example is shown in Figure 6- 7a-i where the preform cross section is that depicted in Figure 6- 5 – a square with a half-cylinder cap. A cylindrical hole is then drilled at the desired location (Figure 6- 7a-ii) into which a doped COP core rod is inserted (Figure 6- 7a-iii). The doped COP core is produced by co-dissolution of the polymer granules with the luminescent dopant of interest (here an organic dye). The solvent (chloroform) is evaporated and the resulting porous dye-impregnated polymer is heated above its T_g and extruded under vacuum to form a solid doped cylindrical rod of diameter 4.7 mm (Figure 6- 7b). The preform is subsequently consolidated above the polymer softening temperature under vacuum to eliminate gaps at the core/cladding interface (Figure 6- 7a-iv) and drawn thermally into an extended fiber (Figure 6- 7a-v); see next sections for the details of each fabrication step. Rods are extruded incorporating multiple concentrations of one of two organic dyes – DCM and FHI5868 – chosen to absorb different segments of the solar spectrum. The doping concentration (in %wt) is correlated to the optical density α_d in cm^{-1} of these bulk samples before incorporation into the preforms (Figure 6- 7c,d) and also their absorption and fluorescence spectra are measured for use in the theoretical model to calculate the expected conversion efficiency (Figure 6- 7e,f). Section 6.4 describes further details of the spectral measurements.

The preforms are thermally drawn into fibers with width typically 500 μm , chosen to ensure the ruggedness and flexibility of the drawn fibers while reducing their weight, while maintaining the cross section built into the preform after transverse scale-reduction and axial elongation (Figure 6- 8a).

Figure 6- 8: FLSC preform to fiber images

Progress in synthesis of organic dyes has resulted in higher photo and thermal stability of dyes in certain classes of materials. Nevertheless, with the flexibility of our fabrication process it can be conceived that a layer of UV-absorbing material can also be added on the top of doped cores to protect the dyes and even the host polymer. Large-Stokes-shift materials are reported that are capable of exploiting this UV light by re-emitting it at longer wavelengths to contribute to the concentration efficiency. FHI6058 is an example of such compound dyes that is used in this work.

Preform fabrication

The overall steps for preparing a fiber preform from which a FLSC is produced via thermal drawing (as shown in Figure 6- 7a) are as follows: (1) polymer cladding extrusion and drilling; (2) impregnating the polymer with an organic dye and core polymer extrusion; and (3) preform consolidation.

Cladding preparation

The optically clear polymer cyclo-olefin polymer (COP) was used to prepare the FLSC cladding. The polymer is used in the form of as-received granules or pellets from Zeon Chemicals L.P. (Louisville, KY, USA); see Figure 6- 9a. The polymer COP was chosen since it is among the most transparent optical polymers in the visible and near IR [118]. The COP pellets were cleaned using IPA solution (VWR, 99%), baked at 100 °C under vacuum for 12 hours, and then extruded under pressure at elevated temperature in vacuum in a custom-built system shown in Figure 6- 9b. The pellets are packed in a stainless steel sleeve that is placed inside a cylindrical furnace. The sleeve is connected from one end to a vacuum pump and sealed from both ends to produce a pressure of ~ 0.5 Torr throughout the extrusion process, which facilitates the extraction of air and moisture from the pellets. The sleeve is heated to 245 °C and evacuated before a piston extrudes the material through a die using ~ 600 lbs of force.

Figure 6- 9: FLSC cladding extrusion

The shape of the die dictates the morphology of the extruded rod. When using a circular die, a cylindrical rod is extruded [Figure 6- 9-c]. To produce the cladding rod with the non-traditional cross-sectional geometry shown in Figure 6- 8-a, we have used two approaches. In the first approach, we extrude a cylindrical polymer rod and then machine it to the desired shape. While this process is simple, it results in the waste of a considerable fraction of the polymer material

and leaves a rough external surface. In the second approach, we directly extrude a polymer rod with the geometry shown in Figure 6- 7-a. The custom-made die shown in Figure 6- 10-a is designed and machined to reproduce the desired fiber cross sectional shape in a single step. It consists of a square ($19 \times 19 \text{ mm}^2$) with a semi-circle of diameter 19 mm on the top, and the extrusion produces optically clear rods of the desired shape [Figure 6- 10-b]. There is a slight deviation in the extruded rod shape from the perfect square and semi-circle. This bulge is due to the softness of the polymer at the exit of the die. As explained in section 6.4, this has negligible effect on light transport efficiency of the final fiber. Further optimization of the die design is possible to implement pre-compensation of post-extrusion deformation that occurs during quenching.

Figure 6- 10: FLSC cladding extrusion die and rod

After extrusion, a hole is drilled down the center of the square part of the rod's cross section (Figure 6- 11) where the doped core is to be placed, followed by polishing the inner surface of the hole to remove extraneous material and improve the surface smoothness. Alternatively, we may extrude the rod with a hole in it directly, which may potentially yield a smoother surface along the hole compared to the drilling approach.

Figure 6- 11: Extruded cladding after hole drilling

Preparation of the dye-doped core

The dye-doped core rods were prepared by solution processing. The host polymer is the same COP used in the cladding [Figure 6- 12-a]. Two dyes were used in this work: (1) DCM was used as-received from Exciton (Dayton, OH, USA) and (2) FHI5868 was used as-received from Fabricolor Holding Int'l LLC (Paterson, NJ, USA). Chloroform is a common solvent for the host polymer and the dyes [Figure 6- 12-b]. Therefore, in the case of each dye, we dissolved in chloroform both the dye and the polymer pellets.

Figure 6- 12: FLSC dye-doped core fabrication steps

Figure 6- 13: Extruded rods with various concentrations of two organic dyes

The dye is first dissolved in chloroform at room temperature. The solution is filtered before mixing with COP to produce the different concentrations (and hence different optical densities

α_d ; see Figure 6- 7-c) used in our study. The solution containing the polymer and the dye was homogenously mixed and then dried under vacuum at 100 °C to evaporate the chloroform, leaving behind dried dye-impregnated polymer in the form of porous chunks, such as that shown in Figure 6- 12-c. The polymer was cut into small pieces before being loaded into the extrusion sleeve. The sleeve was heated to 240 °C under vacuum and we extruded the polymer through a 6.5-mm-diameter die at 600-1000 lbs of force to produce clear dye-doped polymer rods [Figure 6- 12-d]. The diameter of the extruded rod is adjusted by controlling the speed at which the extruded rod is pulled from the extruder. Multiple rods are extruded for different concentrations of each dye; see Figure 6- 13. These rods are used to characterize the absorption and emission spectra of the dye-impregnated polymer, as discussed in the next section 6.4.

Preform consolidation

After a cylindrical hole is drilled and its inner surface is smoothed, the extruded dye-doped core is then carefully inserted into the hole in the cladding rod within a clean laminar flow station. This process is analogous to the traditional rod-in-tube insertion technique often used in conventional step-index fiber preform fabrication [119]. The assembled preform is then thermally consolidated under vacuum at 185 °C to remove air from the interface between the doped core and the clear cladding, as shown in Figure 6- 14.

Figure 6- 14: Preform assembly

FLSC drawing

Using the structured preforms described above, FLSC's are thermally drawn in a custom-built fiber draw tower shown in Figure 6- 15-a. The fibers were typically drawn at a speed of ~ 0.5 m/min at a tension equivalent to ~ 40 -60 g. The draw tower contains a three-zone tube furnace for heating the preform, and we set the temperatures in the three zones – from top to bottom – at 170 °C, 245 °C, and 25 °C, respectively. This temperature combination, along with the other drawing parameters, allows us to maintain the non-circularly symmetric geometry of the preform in the final FLSC fiber despite transverse size reduction and axial elongation.

Figure 6- 15: FLSC fiber drawing

6.4. Characterization methods and results

Overview of Characterizations

The optical performance of the FLSC confirms to match the theoretical prediction and the fiber structural characterization. First the focusing effect due to the curved fiber cap is examined. This is achieved by measuring the optical intensity distribution resulting from a normally incident beam (Figure 6- 26) after polishing the bottom flat FLSC surface at a slight angle ($\sim 2^\circ$) with respect to the fiber axis. As a result, measuring the intensity distribution along the fiber axis gradually reveals the optical distribution inside the fiber. Figure 6- 28 presents the measured and calculated intensity distributions at three locations along the fiber: (i) below the intact FLSC,

which reveals the divergent field after passing through the focal point inside the FLSC; (ii) the field after removing half of the square, which reveals the location of the focal spot peak; and (iii) the field after removing the square leaving only the half-cylinder cap, which reveals the converging field through the focal spot and subsequent divergence. See next section for details of the measurements and the simulations. The agreement between the experimental data and the simulations indicate the usefulness of the cap in delivering focused sunlight to the designated axial locus along the fiber length. In addition, the linear transmission losses of the fibers are characterized by cutback measurements. It is found that a cold (un-doped) fiber with the hybrid cross-sectional shape and dimensions of the FLSC described here has transmission loss of approximately 5 ± 1 dB/m, which is relatively low for such a large-core fiber with air cladding and is a negligible source of loss compared to other sources of loss such as self-absorption. In addition, applications such as FLSC rarely need lengths exceeding a meter for individual fibers. This low level of loss is achieved through material preparation and fabrication under clean conditions in a laminar flow station. It is expected to achieve even lower loss values if material preparation and processing take place in a cleanroom.

After characterizing the passive optical characteristics of an FLSC, the optical conversion efficiency η_0 of seven FLSC's with various concentrations of two dyes are measured. Using a solar simulator, η_0 is measured as a function of FLSC length (Figure 6- 34 and Figure 6- 34). Since the two dyes used in this research cover distinct portions of the visible spectrum it is intuitive from the tandem LSC's reported in the literature [22] that a tandem stack of two FLSC's with different dopants should improve the optical conversion efficiency. Samples with the highest efficiencies from the dyes are then stacked vertically on the top of each other with the

bottom of the top FLSC almost in touch with the top of the curved cap of the bottom FLSC. This combination showed optical-to-optical concentration efficiency of 9.1% and 4.9% for FLSC lengths of 2.5 cm and 10 cm, respectively. Theoretical fits assume an exponential decay of η_0 with fiber length. The theoretical model is applied to the fabricated FLSC's to compare the results. While both experiments and simulations agree in the overall trends in efficiency variations, there is a considerable difference between predicted and measured values. Measured values are higher than expected. This can be attributed to the following three simplifying assumptions in the theoretical model: (1) model considers first-generation photons only. In practice, higher-generation photons experience a considerable red-shift during consecutive self-absorption and re-emissions. This red-shift very quickly reduces the deteriorating effect of self-absorption while our model assumes constant self-absorption all along the propagation path of photons. (2) Another effect that is not taken into account in the theoretical model is the non-linear changes in absorption and fluorescence quantum yields with variations in dye concentration. (3) Third effect that can also be considerable is the spectral shifts observed for various dyes when doped into polymer hosts. This spectral shift is observed to be highly dependent on dye concentration in polymer while we have used a fixed fluorescence spectrum for all concentrations. It is noticeable, nevertheless, that shifts in fluorescence spectrum are usually accompanied by changes in quantum yield due to non-radiative relaxations that cause the spectral shift.

Materials characterization

Spectroscopic characterization

The absorption and emission spectra are measured for the dyes at different concentrations in both solution and in solid form after incorporation into the COP matrix. For absorption measurements in the dye solution, chloroform is used as a solvent and the solution is placed in a quartz cuvette. For absorption measurements in dye-doped COP, the solid samples used were in the form of thin disks of diameter 4 – 6 mm and sub-millimeter thickness that were sectioned from the extruded dye-doped rods (Figure 6- 13) and polished. In both the dye solution and solid samples, the absorption spectra were obtained using a spectrophotometer (Varian CARY 500 Scan). Figure 6- 16 and Figure 6- 17 show the absorption spectra of DCM and FHI5868 dyes in solution and solid forms.

Figure 6- 16: Absorption spectrum of DCM in solution and solid bulk with various concentrations

Figure 6- 17: Absorption spectrum of FHI5868 in solution and solid bulk with various concentrations

The absorption spectra shown in Figure 6- 7 were recorded in a different manner. They are not the direct linear absorption curves measured by the spectrophotometer, as shown here. Instead, in Figure 6- 7 we plot the ‘effective’ absorption spectra, i.e., the absorption spectrum that contributes to fluorescence through radiative transitions, which excludes the UV absorption tail in Figure 6- 16 and Figure 6- 17 that does not contribute to fluorescence. This spectrum is obtained from the optical conversion efficiency measurements described below, where the total emission power from a solid sample for each incident wavelength is measured.

The fluorescence spectra were captured with a fiber-based spectrometer (Ocean Optics, Jaz EL 200-XR1), as depicted schematically in Figure 6- 18. In the case of the dye solutions, the solution was excited in the cuvette from one face and the fluorescence was collected from the orthogonal side. In the case of the solid samples, short rods were cut from the extruded dye-doped rods (Figure 6- 13), the samples were excited normally to the curved surface and the

fluorescence was collected from the end facet. The excitation beam was approximately incident of the rod 5 mm away from the sample flat end facet. In both cases (solution and solid samples), a laser at 532 nm wavelength was used.

Figure 6- 18: Fluorescence measurement arrangements

Fluorescence spectra of the two dyes in solution and in COP matrix are shown in Figure 6- 19 and Figure 6- 20 for various concentrations. It is shown in the figures that emission spectrum experiences some red-shift with increase in concentration. This concentration-dependent red-shift is a known effect that applies to fluorescence from organic and in-organic materials either

in solutions or polymeric matrices [120-122]. This effect is widely studied even in biological systems [123] and industrial petroleum products [124].

Figure 6- 19: Fluorescence spectrum of DCM in solution and in solid bulk for various concentrations

Figure 6- 20: Fluorescence spectrum of FHI5868 in solution and in solid bulk for various concentrations

Thermal processing characterization

A major concern for applying organic dyes to FLSC fibers is the thermal stability of dye molecules during the thermal processes involved in core extrusion, preform assembly and fiber drawing. In order to quantify the amount of molecular degradation during the processes fluorescence strength of dye-doped polymer samples that have undergone heating at various temperatures for various time intervals is measured and compared as an indirect measure of degradation. Heating temperatures (100, 130, 160 and 190) and durations (0.5 h, 1 h, 1.5 h, 2 h, 2.5 h, 3 h, 6 h and 12 h) were chosen based on the knowledge of the temperatures and durations involved in the fabrication processes. Dye-doped polymer rods with square cross-sectional shape were extruded in the same way as core rods were made (section 6.3) except for the extrusion die which was replaced by a home-made die with square opening. Extruded rods were sliced into 2-mm-thick square-shaped pieces with parallel faces. Sliced samples were coded carefully and were thermally annealed in a vacuum furnace for various amounts of time at various temperatures in a stainless steel mold which was made in house to evenly distribute heat to the samples without deforming their square shape. Figure 6- 21 shows fabrication steps in the order they were performed from the top to the bottom.

Square cross section was chosen so that fluorescence emission from differently annealed samples can be measured from the sides of the square. Direct measurement of the fluoresced light from the edges turned out to be very inaccurate due to the difficulty of perfect sample alignment with respect to the collection fiber that takes the fluoresced light to the measurement device.

Figure 6- 21: Sample fabrication steps for thermal effect test

Therefore, samples were further polished down to approximately 0.5 mm and were placed inside an integrating sphere with a custom-made samples holder made out of white Teflon™ in order to minimize the interference of the sample holder presence with integration geometry of the sphere. Figure 6- 22 shows the schematic and the actual arrangement for this measurement. 32 samples of each dye (total of 64) were tested using this setup and a few unreliable samples were removed from the list. Figure 6- 23 shows a sample of the direct raw data measured in this setup for 6 FHI5868-doped samples thermally annealed at 190°C for various time intervals.

Figure 6- 22: Experimental arrangement for thermal effect test

Figure 6- 23: Raw spectral data for thermal effect test

After the thermal treatment samples are polished to the target thickness of 0.5 mm. In order to obtain a consistent surface quality all sample surfaces were scratched with the same fine sand paper (grit size: 1200) to create the same roughness. Polishing all such thin samples to an optical quality level to minimize scattering could not be achieved in a reasonable time with consistency since quarter wavelength accuracy in the visible cannot be easily achieved. Nevertheless, this experiment has several sources of error including slightly different surface roughness or sample mounting that leads to different levels of light scattering into the sphere. In order to cancel this effect all measured spectra were leveled to the same level of green light that is scattered from the same sample surface under identical situations with the fluoresced light. For analysis collected power density detected at peak fluorescence spectrum of each dye was tabulated versus annealing time and temperature. Standard deviation divided by average value of several trials on DCM-doped and FHI5868-doped samples treated at 100°C was used and averaged as the error bar size for this experiment. Figure 6- 24 and Figure 6- 25 on the next page show the processed data for all reliable samples. It is clear that the experiment does not have enough accuracy for drawing accurate quantitative conclusions. It can be, however, seen that no sample at any temperature is showing considerable drop in fluorescence strength with prolonged heating even up to 12 hours. Samples annealed at 160°C and 190°C are not heated for more than 3 hours since heating to such high temperatures only occurs during the extrusion and fiber drawing that do not take more than 2-3 hours under any circumstance. Given that the melting temperature for the two dyes are reported to be above 200°C, we can, loosely speaking, conclude that the two dyes used in this research are not appreciably degraded during the thermal processes involved.

Figure 6- 24: Thermal effect test results for DCM-doped COP

Figure 6- 25: Thermal effect test results for FHI5868-doped COP

Cold fiber characterization

Cold fibers are the test fibers that are made in a similar way to the FLSC samples, but with no active materials embedded in them. These passive fibers are used for investigation of the fiber shape on its focusing effect as the first concentration stage, measurement of the background loss that stems from intrinsic and impurity losses in the polymer matrix as well as waveguide radiative loss. Since the FLSC's and corresponding cold fibers investigated here are air cladding fibers dust and humidity in the ambient also contribute to the losses. Now, further details of such cold fiber characterizations are discussed in the following paragraphs.

In-fiber focusing test

Purpose of this experiment is testing the effectiveness of the curved cylindrical cap of the FLSC in focusing incident light to the theoretically predicted location, which depends on the curvature of the cap. To determine the intensity distribution inside the FLSC resulting from an incident collimated beam, the arrangement shown in the Figure 6- 26 is used. First the cold hybrid fiber samples are prepared in a special way. A 20-mm-long fiber section is embedded in an epoxy. The bottom flat surface of the FLSC is then polished while maintained a 2° tilt angle with respect to the fiber axis. As a result, the internal sections in the fiber from the bottom flat surface upwards to the cylindrical cap are gradually exposed. The resulting structure is shown schematically in Figure 6- 26 (not to scale). The epoxy was then carefully removed without damaging the fiber surfaces, leaving behind the tapered hybrid fiber structure free-standing in air. Figure 6- 27 also depicts side-view optical microscopic image of the tilt-polished fiber with more specifics about the locations the measurements were taken at. This image is combination of

23 microscopic images from short sections of the sample put together artificially to construct the image of the full fiber that does not fit in one microscopic frame.

Figure 6- 26: Experimental arrangement for in-fiber focusing test

Figure 6- 27: microscopic side-view of tilt-polished FLSC fiber

Using the setup depicted in Figure 6- 26, the fiber was illuminated from the lens side with a collimated laser beam (532 nm). Light intensity distribution was then locally captured across the sample fiber width with a GRIN Silica fiber. Collection fiber was scanned across the sample fiber which was kept stationary and normal to both laser beam and the collection fiber. Measurement was repeated at three locations along the fiber with proportionally increasing fiber thickness from only full cap to full cap with half square and finally full cap with full square. The wedged shape of the fiber after tilt polishing made this possible. Figure 6- 28 below compares simulation predictions for light intensity distribution at the three tested locations with the actual measurement results. Simulations were performed with ZEMAX ray-tracing with the same setting as described in Chapter 5 for transverse intensity captures. The only difference is the object that is constructed in ZEMAX to replicate the exact shape of the actual fiber at the three locations in question free-standing in air. “E” and “T” in this figure represent experimental and theory, respectively.

Figure 6- 28: In-fiber focusing test results – cap height: 250 μm

To further prove that the focal spot can be adjusted judiciously with the fiber design and the curvature of the cylindrical lens, the experiment outlined above is repeated for a similar fiber with a lens cap height of 100 μm instead. Figure 6- 29 shows the close match between theoretical prediction and the experimental measurement with some perturbations due to imperfection of experimental conditions.

Figure 6- 29: In-fiber focusing test results - cap height: 100 μm

Transmission loss measurement

The optical transmission losses of three ‘cold’ fibers (i.e., undoped) were measured by the cut-back method at a wavelength of 650 nm chosen to be close to the emission wavelengths of the two fluorescent dyes. These three fibers are: (1) Hybrid ($500 \times 500 \mu\text{m}^2$ square with 250- μm -height lens cap) with bulged sides as produced by direct extrusion; (2) Hybrid ($500 \times 500 \mu\text{m}^2$ square with 250- μm -height lens cap) with flat sides obtained by machining of bulges in the preform; (3) Circular fiber (diameter: 500 μm) drawn from a circular preform extruded under the

same conditions as those of the hybrid fibers except for the shape of the extrusion die. A diode laser with built-in collimating lens is used as the light source. The almost collimated beam of ~1mm diameter is coupled directly into the fibers such that the whole fiber facet is illuminated. Fibers are held in a standard fiber chuck with black jaws that eliminate the light that is not coupled into fiber along its 5-cm length. Start length of the fibers is 1 meter. Then fibers are cut with a sharp surgical-grade razor blade by 75 millimeters several times from the detection end while the input end is carefully kept firm and unchanged. The output power is measured at each length with a visible power meter (Ophir). Figure 6- 30 plots the normalized output power versus with fiber length for the three fibers mentioned above. The three fibers (hybrid with bulged sides, hybrid with flat sides and circular) show attenuation rates of 6 dB/m, 5 dB/m and 4 dB/m, respectively, within the measurement error of our experiment which is ± 1 dB/m on average and increases with decrease in the intrinsic loss of the fiber since the air-clad fiber becomes more sensitive to the ambient.

Figure 6- 30: Cut-back transmission loss measurement

FLSC characterization

Optical conversion efficiency measurement

The optical conversion efficiency η_0 of the FLSC's (as reported in Figure 6- 34 - Figure 6- 35) was measured using a quantum efficiency measurement kit (Newport QE-PV-SI) with Oriel MS260i monochromator and Oriel 500-W Hg arc source. Light from the source was first coupled into the monochromator and the collimated light beam emerging from it impinged normally on a 12-cm-long FLSC section that is held horizontally in the beam path such that the beam is incident on the curved surface of the fiber. The fiber is held straight in a home-built housing that grasps the fiber from its two ends with transparent polycarbonate holders. Each holder is in

contact with the FLSC fiber only on the two flat sides of the square section of the fiber cross section, with the contact length between the holder and fiber being less than 1 mm. We kept the contact area at a minimum to avoid light leakage at the holder positions to minimize perturbations to the measured values of η_0 . The FLSC sample and the holder are positioned on a rotation stage for fine adjustment of the incident beam angle with respect to the FLSC. The 5-mm-wide incident beam is scanned along the fiber in 5-mm steps. Figure 6- 31 shows the setup schematically, while Figure 6- 32 depicts a photograph of the setup.

Figure 6- 31: Optical efficiency measurement setup - Schematic

Figure 6- 32: Optical efficiency measurement setup

At each incidence location along the fiber, the spectral power density of light emerging from one fiber end is recorded and normalized with respect to a reference. This reference is taken to be the spectral power density of the incident beam itself as measured by a detector whose exposure area is equal to the area of the beam intercepted by the FLSC [i.e., $5\text{-mm} \times W$; see Figure 6- 5].

Incident beam is scanned in from 300 to 800 nm with 1 nm steps while the FWHM of the monochromator output was 4 nm as measured directly by a spectrometer.

Figure 6- 33 below shows a sample plot of the data directly obtained from this measurement normalized to incident power density, but before integrations over length and wavelength as described below. This is the measurement result for the tandem configuration that shows absorption peaks from both dyes.

Figure 6- 33: Optical efficiency spectrum with local excitation

This measurement and normalization together yield $\eta_o(z, \lambda)$ corresponding to each illumination location (Figure 6- 33). Integrating $\eta_o(z, \lambda)$ along the FLSC length L and over the wavelengths scanned by the monochromator weighted by AM 1.5 solar spectrum,

$$\eta_o = \int S(\lambda) d\lambda \int_0^L dz \eta_o(z, \lambda),$$

yields the overall η_o of the FLSC corresponding to incident radiation with the solar spectrum and uniform intensity along the fiber. To maintain the consistent measurements, all FLSC samples lengths were equal and the facets were prepared in as similar a manner as possible by polishing them with the same speed and pressure for the same

length of time. Figure 6- 34 and Figure 6- 35 below plot variations in optical conversion efficiency as a function of FLSC length for a total of seven FLSC samples with the two dyes used in this research, DCM and FHI 5868. The solid black curve in Figure 6- 34 shows the measured efficiency for a tandem combination of two FLSC's, one with each dye, held on the top of each other in the same measurement setup. The FLSC's with the highest measured efficiency with each dye was selected for this tandem configuration. The DCM-doped FLSC was placed on the top of the FHI5868-doped one to absorb and convert shorter-wavelength section of the spectrum first. The two FLSC's are carefully stacked with no glue in a way that the bottom of the top FLSC is almost in contact with the top of the curved cap of the bottom FLSC with the two fibers carefully aligned. The longer-wavelength parts of the spectrum are transmitted through the first FLSC and get absorbed by the second one which is doped with FHI-5868.

Figure 6- 34: Optical conversion efficiency vs. length of DCM-doped FLSC

Figure 6- 35: Optical conversion efficiency vs. length of FHI5868-doped FLSC

Exponential curves are fitted to the experimental data points with high correlations. This rather good fit with the exponential function confirm the validity of the empirical exponential function for self-absorption and propagation effects that were described in detail in Chapter 5. The decay rate (slope) of the exponential curves increase gradually with increase in dye concentration, that's, the peak absorbance as marked on the plots. This is due to the increasingly deteriorating self-absorption effect. This increase in the slope is slower for DCM than for FHI5868, however, due to its smaller overlap between emission and absorption spectra.

It is also seen in this figure that the optical efficiency of the tandem configuration is slightly lower than the sum of the two individual FLSC's. This is related to the following: (1) there is some overlap between the absorption spectra of the two dyes. Therefore, a portion of the

spectrum that could have been absorbed with the second FLSC is filtered by the first one and converted with different quantum efficiency. (2) Although long-wavelength portion of the incident spectrum is not absorbed by the first FLSC, it still converges onto the doped core and diverges rapidly by the point it exits the top FLSC. Therefore, the beam incident on the second FLSC is not collimated and does not get focused efficiently onto the doped core of the second FLSC. A simple solution around this is to weave the two FLSC's in two orthogonal directions so that the beam exiting the first FLSC is only diverged in the direction that experiences linearly symmetric cylindrical lens of the second FLSC. In other words, the incident beam gets focused in one direction with the top FLSC without any distortion in the other direction and the second FLSC focuses the un-distorted wavefront while the initial distortion in the other direction does not affect the performance of the second FLSC due to its uniformity along that axis.

Figure 6- 36 and Figure 6- 37 below show the theoretical prediction for efficiency variations as a function of core material concentration for various FLSC lengths with the two dyes. Added to these figures are the corresponding experimentally measured data points that are taken from Figure 6- 34 and Figure 6- 35 above. There is a considerable discrepancy between our experimental results and the simulation prediction in favor of the real experimental measurements. This discrepancy is attributed to simplifying assumptions made in the theoretical model: (1) first-generation emitted photons are considered in the model whereas several absorption-emissions occur before a photon reaches the fiber end; (2) absorption and fluorescence strength of the dyes are assumed to scale linearly with concentration, while concentration quenching is a known phenomenon that varies from one material to another; (3) fixed fluorescence spectrum is assumed for all concentrations of dyes whereas a considerable

spectral shift is observed in reality. These points are discussed in further detail in the conclusion of this chapter. It is, nevertheless, noticeable that the discrepancy is larger in the case of FHI5868-doped FLSC's than that of DCM-doped FLSC's. Given that more dramatic spectral shift and larger absorption/emission spectral overlap is observed in FHI5868, it is confirmed that the above mentioned simplifying assumptions are the origins of the mismatch between our simulation prediction and the experimental measurements.

Figure 6- 36: Optical conversion efficiency of DCM-doped FLSC

Figure 6- 37: Optical conversion efficiency of FHI5868-doped FLSC

6.5. Conclusion and discussion

In conclusion, methods are developed for fabrication of FLSC fibers with an unconventional cross section for a two-stage concentration system. Fabrication procedures are optimized for reduction of impurity to enable low-loss transport of generated light along the fibers. Two commercially available organic dyes in conjunction with a popular optical polymer were used for absorption of distinct sections of the solar spectrum. Materials, passive (un-doped) fibers and active FLSC's are characterized both for device performance prediction and for verification of their first- and second- stage concentration performance. First stage of concentration which is the focusing of normally incident light onto the active region of fiber showed very close agreement with ray-tracing simulations. Second stage of concentration is a relatively complicated process that includes absorption, fluorescence, TIR trapping, propagation along fiber, self-absorption by active materials and linear absorption by polymer. Experimental measurements show performance superior to simulation predictions. This superiority is attributed to the following simplifying assumptions that may suppress the FLSC performance in simulation compared to reality. (1) Theoretical model considers first-generation photons only. In practice, higher-generation photons experience a considerable red-shift during consecutive self-absorption and re-emissions. This red-shift very quickly reduces the deteriorating effect of self-absorption while our model assumes constant self-absorption all along the propagation path of photons. (2) Another effect that is not taken into account in the theoretical model is the non-linear changes in absorption and fluorescence quantum yields with variations in dye concentration. (3) Third effect that can also be considerable is the spectral shifts observed for various dyes when doped into polymer hosts. This spectral shift is observed to be highly dependent on dye concentration in

polymer while we have used a fixed fluorescence spectrum for all concentrations. It is noticeable, nevertheless, that shifts in fluorescence spectrum are usually accompanied by changes in quantum yield due to non-radiative relaxations that cause the spectral shift.

These assumptions cannot be lifted from the theoretical model without knowledge about the behavior of the specific dyes in the specific host medium. Therefore, our model is pursued in a general way that can be altered for specific materials in the future.

CHAPTER 7: CONCLUSION AND FUTUTRE WORK

Conclusion

In conclusion, a new route is presented in this thesis that proves to be a great leap forward toward an economically viable luminescent solar concentrator. Benefits that the convenient fiber form factor provides, alongside the unconventional dual-function fiber cross-sectional shape, allow for an order of magnitude improvement in concentration ratio of luminescent solar concentrators. This becomes more advantageous from economic standpoint due to the low-cost, scalable technology of fiber preform fabrication and fiber drawing. It is noticeable that work presented in this thesis solely proves the concept with off-the-shelf materials, and yet efficiencies comparable to state-of-the-art planar luminescent concentrator are obtained with an unprecedented concentration ratio. Optical-to-optical efficiency of 9% and 5% are experimentally measured for 2.5- and 10-cm FLSC's comprising a tandem of two individual FLSC's each designed for absorption and conversion of a portion of the solar spectrum. A simulation model is developed based on polarization ray-tracing that takes into account all major processes involved in FLSC operation from incident light absorption to fluorescence and light transport in fiber. Comparison of the experimental measurements and theoretical predictions using our model is made. It appears that some of the simplifying assumptions should be removed and the model needs to take more specifics of the active materials for better match between theory and experiment.

In summary, the feasibility of producing LSC in the advantageous form of optical fibers is demonstrated and several paths for improving the performance of such concentrators by translating existing and novel configurations from flat LSC to fiber LSC are envisioned as described in more detail in the next section.

Future work

I suggest that many approaches to improvement of planar LSC's can be readily applied to FLSC's. Several simple steps to this end are envisioned here: (1) Simplest improvement can be made by optimizing the doped core size and location; (2) fabrication process used in this research has been performed under laminar flow station in regular labs. Material preparation in cleanroom before fabrication can be a simple step that can improve the light transport efficiency of fibers considerably; (3) While fluorescent dyes that we had easy access to are used in this research, one can utilize more efficient dyes with tailored spectra or even materials with more advanced energy transfer concepts such as phosphorescence and FRET; (4) Instead of simply stacking two FLSC samples to demonstrate a tandem FLSC configuration, to reduce the thickness of the assembly it is straightforward to integrate multiple domains of active materials in an individual fiber with low-index layers separating them to mimic a tandem LSC with air gaps, but without difficulties of maintaining the air gaps over large areas; (5) We have produced (not reported here) LSC's doped with organic-inorganic compounds with high photo-stability that convert UV light into red fluorescence with a large stokes shift. Such materials can be added to the top layers of FLSC preform and therefore fiber to serve two purposes: One, utilization of

the UV section of the spectrum; Two, protection of polymer and dye materials underneath; (6) organic materials capable of photon up-conversion through multiple photon absorption from non-coherent light have been investigated and developed recently with estimated average quantum yield of 25% in NIR. We estimate that realistically such materials may raise the FLSC efficiency by up to 1% utilizing a portion of spectrum which is usually ignored; (7) a novel method of resonant shifting was recently reported for reduction of self-absorption effect by engineering bi-layer cavities of various thicknesses along a LSC. It is conceivable that a similar configuration across the fiber may equally serve FLSC's too.

APPENDIX A:

ADDITIONAL FABRICATION METHODS

Doping methods

Depending on the type, physical and chemical properties of dopant materials, various techniques were used for doping.

Quasi-dip-coating of thin films with organic dyes and quantum dot solutions

In some cases it is desired to have a method for surface impregnation of the polymer films with luminescent materials. For example, quantum dots are known for their aggregation problem when they are mixed with polymers in solutions. This aggregation results in changes in the effective size of dots (now clusters of dots) and therefore their emission spectrum. Randomness of the aggregation process results in the appearance of a broad range of cluster sizes which instead leaves us with a broadened emission spectrum which is not desired in many applications such as LSC due to the increased overlap with absorption. To avoid this problem, a method of doping was invented in which polymer films are quasi-dip-coated with a solution of quantum dots. Polymer films are fed into a very narrow bath of a solution that includes quantum dots mixed with a solvent that slowly dissolves the polymer. Surface of the polymer films is exposed to the reactive solvent for a brief period of time during which a small amount of the solution will penetrate into the film without dissolving the film entirely. Coated film gets dried as it comes out of the bath and gets rolled on a roller whose speed is controlled with a stepper motor. Figure A- 1 shows a schematic of such a quasi-dip-coating machine and the computer-controlled machine that was constructed in-house for this purpose.

Figure A- 1: Quasi-dip film coating machine

Figure A- 2 shows flat samples doped with an organic dye under various coating speeds and number of coatings to gain control over doping process. It also shows doped films that are tightly rolled, consolidated and extruded *without* vacuum and used for FLSC preform fabrication.

Figure A- 2: Quasi-dip coating for dye-doped preforms

Figure A- 3 shows another example of a rolled Poly Carbonate billet doped using the quasi-dip coating machined with an organic-inorganic luminescent compound with large Stokes shift from UV to red. The rolled and consolidated billet was extruded without vacuum, rolled with COP films to a preform and drawn into a fiber that shows fluorescence confinement in fiber core due to index-guiding of PC/COP fiber. The large Stokes shift, and therefore the small self-absorption, is what allows for efficient fluorescence light transport in the doped core.

Figure A- 3: Preform and fiber doped with UV absorbing dye

Figure A- 4 below shows an example of small samples doped with PbS quantum dots and their fluorescence measurements that shows successful doping of polymer matrix with quantum dots without appreciable aggregation using the quasi-dip coating method.

Figure A- 4: QDOT-doped flat samples with their linear absorption and fluorescence spectra

Figure A- 5 shows a fabricated fiber preform and drawn fiber heavily doped with quantum dots.

Figure A- 5: QDOT-doped preform and fiber

Micro-particle doping and post-processing

As explained in Chapter 3, a class of luminescent materials is based on crystalline host materials doped with rare-earth ions. Such materials cannot be dissolved in solvents for mixing with polymer. Instead, polymer films with rough surfaces were carefully cleaned with IPA and micro-powders of crystals doped with rare-earth ions were physically spread over the sheets in a uniform way so that pores on the rough polymer surface were filled with micro-particles that could no longer be separated from the sheets. Then, the polymer films that are contaminated with the micro-powders are rolled very tightly and thermally consolidated under vacuum after proper baking. This consolidation could then be continued for a long period of time to allow for all

voids around the micro-particles to be filled with the polymer matrix. In some cases the refractive index of the polymer and that of host crystal were so close that after this thermal post-processing scattering was reduced considerably.

Figure A- 6 shows preforms doped with this method before and after the thermal post-processing. Samples of three drawn fibers are also shown in the right panel illuminated with a laser beam at 980 nm emitting Red, Green and Blue with three different up-conversion crystals.

Figure A- 6: Fibers and preforms doped with up-conversion micro- and nano-crystals

Solution-based doping of polymers with organic materials

Solution-based mixing of polymers and dye is a very common method that has been used for decades. Polymer and dye are simply mixed in a common solvent or a mixture of two solvents with compatible polarity one dissolving the polymer and the other dissolving the dye. Details of this method and the process of extrusion under vacuum are explained in Chapter 6.

Manual press as a first step toward vacuum extrusion

In the process of exploring methods for high-optical-quality core and cladding fabrication, several manual methods of pressing porous materials under vacuum were tested. Figure A- 7 shows examples of home-made pressure chambers that were placed inside a box vacuum furnace either just for air evacuation or both for heating and evacuation.

Figure A- 7: Manual vacuum-press systems

Figure A- 8 shows two variations of the final system that was extensively used for extrusion of doped cores and un-doped cladding with two different stainless sleeves and their corresponding vacuum components.

Figure A- 8: Vacuum extrusion sleeves and components

Un-doped Cladding Fabrication

In addition to the vacuum extrusion method that was described in detail in Chapter 6, the method of rolling polymer films followed by thermal consolidation under vacuum was also used in early stages of the projects before the vacuum extrusion method was optimized and practical.

APPENDIX B:

SIDE PROJECTS

This Appendix briefly describes the side projects that I have worked on beside the “Fiber Luminescent Solar Concentrator” which is the major theme of this dissertation. These projects are left incomplete and will be continued in the future.

B.1. Theoretical Study of Acoustic Band-gaps in 1D periodic structures

It is known that one dimensional periodic optical structure (periodic variation in refractive index) cannot have complete bandgaps. Some combinations of light frequency (ω) and wave vector (k) are not allowed to propagate in the periodic system. Complete band gap is referred to a range of frequencies of light that cannot propagate in the periodic system regardless of their wave vector orientation. Although such complete band gaps do not exist in 1-D photonic crystal systems, in 1998, Winn *et. al.* pointed out a practical limit that had not drawn people’s attention to that point [125]. They showed that although no complete band gap exists for infinite 1-D periodic structures, in reality where light strikes such a periodic stack from an ambient, under certain circumstances omni-directional reflection can happen. This is due to the fact that propagation light cone for the light incident on the periodic system from the ambient intersects with the band structure of the period system in a way that any light in a certain range of frequency (regardless of wave vector orientation) that is allowed to propagate in the ambient cannot propagate in the periodic structure and therefore gets reflected. Figure B- 1 from reference [126] shows schematically a 1-D periodic structure with alternating layers of different refractive indices, the band structures for two cases with small and large index contrast between the layers and a two-

dimensional map of range-to-midrange ratio for the forbidden gaps as a function of refractive index contrast and the smaller of the two indices in the structure.

Figure B- 1: a 1-D periodic structure with its photonic band structure

It is seen in this figure that a high index contrast between layers compared to the index of refraction of the ambient allows for omnidirectional reflection in certain frequency ranges (shaded black in figure).

In recent years researchers have questioned the possibility of generating phononic crystals as opposed to photonic crystals. Several reports have been published on phononic band gap structure of 1-D, 2-D and 3-D periodic structures with high contrast in sound velocity and material density which are the acoustic counterparts of optical refractive index.

In this research the question of existence of omnidirectional reflection bands in 1-D phononic crystal structure is addressed. The approach taken here is based on application of sound wave propagation equations and boundary conditions at the interface of two media with various sound properties. Transfer matrix is then constructed to predict the wave state in a second medium with its state in the first medium and the sound properties of both media known. This can be similarly repeated for other interfaces. Finally a transfer matrix can be constructed for a unit cell of the infinite bilayer structure.

Figure B- 2 below shows the interface between two media with the rays representing sound waves incident on the interface from the first medium, reflected waves back into the first medium and those transmitted into the second medium.

Figure B- 2: Acoustic wave reflection and transmission at a solid-solid interface

It is noticeable that sound waves have three polarizations: Shear Vertical (SV), Shear Horizontal (SH) and Longitudinal (L). Another major difference between optical and acoustic waves is that

the SH polarization is decoupled from the other two polarizations, while SV and L polarizations are coupled. Below relations between acoustic parameters of materials at the interface are listed without detailed description which is beyond the scope of this Appendix.

Equations for the sound wave velocity that is similar to electric field of optical waves:

$$v_x^{(1)} = \{-v_{S1+} \sin \theta_{S1} e^{+ik_{S1x}x} + v_{S1-} \sin \theta_{S1} e^{-ik_{S1x}x} + v_{L1+} \cos \theta_{L1} e^{+ik_{L1x}x} - v_{L1-} \cos \theta_{L1} e^{-ik_{L1x}x}\} e^{ik_z z} \quad (8)$$

$$v_x^{(2)} = \{-v_{S2+} \sin \theta_{S2} e^{+ik_{S2x}x} + v_{S2-} \sin \theta_{S2} e^{-ik_{S2x}x} + v_{L2+} \cos \theta_{L2} e^{+ik_{L2x}x} - v_{L2-} \cos \theta_{L2} e^{-ik_{L2x}x}\} e^{ik_z z} \quad (9)$$

$$v_z^{(1)} = \{v_{S1+} \cos \theta_{S1} e^{+ik_{S1x}x} + v_{S1-} \cos \theta_{S1} e^{-ik_{S1x}x} + v_{L1+} \sin \theta_{L1} e^{+ik_{L1x}x} + v_{L1-} \sin \theta_{L1} e^{-ik_{L1x}x}\} e^{ik_z z} \quad (10)$$

$$v_z^{(2)} = \{v_{S2+} \cos \theta_{S2} e^{+ik_{S2x}x} + v_{S2-} \cos \theta_{S2} e^{-ik_{S2x}x} + v_{L2+} \sin \theta_{L2} e^{+ik_{L2x}x} + v_{L2-} \sin \theta_{L2} e^{-ik_{L2x}x}\} e^{ik_z z} \quad (11)$$

These equations write the two components of velocity vector for material at the interface in the two media on two sides of the interface as a function of left-propagating and right-propagating waves with shear and longitudinal polarizations. Acoustic Snell's law is also applied and a sinusoidal wave form is considered for all velocity waves. The following relations hold between velocity components (v), oscillation amplitude (u), strain tensor elements (S_{ij}), stress tensor elements (T_{ij}), Young's modulus (λ) and Shear modulus (μ). Subscripts i and j refer to x and z directions, while subscripts 1 and 2 refer to first and second medium.

Extensional stress:

$$T_{ii} = \lambda(S_{xx} + S_{yy} + S_{zz}) + 2\mu S_{ii} \quad (12)$$

Tangential stress:

$$T_{ij} = 2\mu S_{ij}, \quad i \neq j \quad (13)$$

Strain tensor:

$$S_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (14)$$

Velocity wave:

$$v = v(x, z) e^{-i\omega t} \quad (15)$$

$$v = \frac{\partial u}{\partial t} = -i\omega u \quad (16)$$

Boundary conditions for the sound waves at the boundary between two solid media are continuity of the normal component of stress and continuity of the total velocity.

$$\begin{aligned} \vec{T}_1 \cdot \hat{n} &= \vec{T}_2 \cdot \hat{n} \\ \vec{v}_1 &= \vec{v}_2 \end{aligned} \quad (17)$$

Applying these relations and the boundary conditions to the wave equations 8-11 above and rearranging the equations in the form of a matrix equation gives the following for the coupled

and decoupled wave polarizations. This equation relates the right-propagating and left-propagating velocity components in the two media via a transfer matrix, M .

Decoupled SH polarization:

$$\begin{aligned} & \begin{bmatrix} e^{ik_{S1x}x} & e^{-ik_{S1x}x} \\ -Z_{S1} \cos \theta_{S1} e^{ik_{S1x}x} & Z_{S1} \cos \theta_{S1} e^{-ik_{S1x}x} \end{bmatrix} \begin{bmatrix} A_{y1} \\ B_{y1} \end{bmatrix} \\ &= \begin{bmatrix} e^{ik_{S2x}x} & e^{-ik_{S2x}x} \\ -Z_{S2} \cos \theta_{S2} e^{ik_{S2x}x} & Z_{S2} \cos \theta_{S2} e^{-ik_{S2x}x} \end{bmatrix} \begin{bmatrix} A_{y2} \\ B_{y2} \end{bmatrix} \end{aligned} \quad (18)$$

Coupled SV and L polarizations:

$$\begin{aligned} & \begin{bmatrix} -\sin \theta_{S1} e^{+ik_{S1x}x} & \sin \theta_{S1} e^{-ik_{S1x}x} & \cos \theta_{L1} e^{+ik_{L1x}x} & -\cos \theta_{L1} e^{-ik_{L1x}x} \\ \cos \theta_{S1} e^{+ik_{S1x}x} & \cos \theta_{S1} e^{-ik_{S1x}x} & \sin \theta_{L1} e^{+ik_{L1x}x} & \sin \theta_{L1} e^{-ik_{L1x}x} \\ [Z_{S1}][\sin 2\theta_{S1} e^{+ik_{S1x}x}] & [Z_{S1}][\sin 2\theta_{S1} e^{-ik_{S1x}x}] & [-Z_{L1}][\cos 2\theta_{S1} e^{+ik_{L1x}x}] & [-Z_{L1}][\cos 2\theta_{S1} e^{-ik_{L1x}x}] \\ [-Z_{S1}][\cos 2\theta_{S1} e^{+ik_{S1x}x}] & [Z_{S1}][\cos 2\theta_{S1} e^{-ik_{S1x}x}] & [-Z_{S1}][\frac{V_{S1}}{V_{L1}}][\sin 2\theta_{L1} e^{+ik_{L1x}x}] & [Z_{S1}][\frac{V_{S1}}{V_{L1}}][\sin 2\theta_{L1} e^{-ik_{L1x}x}] \end{bmatrix} \begin{bmatrix} v_{S1+} \\ v_{S1-} \\ v_{L1+} \\ v_{L1-} \end{bmatrix} \\ &= \begin{bmatrix} -\sin \theta_{S2} e^{+ik_{S2x}x} & \sin \theta_{S2} e^{-ik_{S2x}x} & \cos \theta_{L2} e^{+ik_{L2x}x} & -\cos \theta_{L2} e^{-ik_{L2x}x} \\ \cos \theta_{S2} e^{+ik_{S2x}x} & \cos \theta_{S2} e^{-ik_{S2x}x} & \sin \theta_{L2} e^{+ik_{L2x}x} & \sin \theta_{L2} e^{-ik_{L2x}x} \\ [Z_{S2}][\sin 2\theta_{S2} e^{+ik_{S2x}x}] & [Z_{S2}][\sin 2\theta_{S2} e^{-ik_{S2x}x}] & [-Z_{L2}][\cos 2\theta_{S2} e^{+ik_{L2x}x}] & [-Z_{L2}][\cos 2\theta_{S2} e^{-ik_{L2x}x}] \\ [-Z_{S2}][\cos 2\theta_{S2} e^{+ik_{S2x}x}] & [Z_{S2}][\cos 2\theta_{S2} e^{-ik_{S2x}x}] & [-Z_{S2}][\frac{V_{S2}}{V_{L2}}][\sin 2\theta_{L2} e^{+ik_{L2x}x}] & [Z_{S2}][\frac{V_{S2}}{V_{L2}}][\sin 2\theta_{L2} e^{-ik_{L2x}x}] \end{bmatrix} \begin{bmatrix} v_{S2+} \\ v_{S2-} \\ v_{L2+} \\ v_{L2-} \end{bmatrix} \end{aligned} \quad (19)$$

In order for a sound (velocity) wave to be allowed to propagate in an infinite periodic structure, the wave should be an eigenmode of the structure. This means that the transfer matrix in equations 18 and 19 should be unitary so that wave entering a bilayer cell is identical to that exiting the same cell. Therefore, the transfer matrix is constructed for a bilayer and the condition for unitary matrix is applied to the matrices for the decoupled SH components and the coupled SV and L components separately. Trace of the transfer matrix for SH component should be less

than 2 and trace for the transfer matrix for the coupled SV and L components should be less than 4 in order for the matrices to be unitary. All possible values of sound wave normalized frequency (ω) and normalized parallel wave vector component (k) are scanned and the condition on the trace of the two transfer matrices are checked. Figure B- 3 shows the bilayer infinite structure and Figure B- 4 shows acoustic and optical band structures for such a periodic configuration assuming two materials PolyCarbonate and As_2Se_3 . Layer thicknesses are adjusted for an optical quarter wave stack.

Figure B- 3: An infinite bilayer stack of two solids

Figure B- 4: Acoustic and optical band structures

Figure B- 6: Acoustic band structure evolution with layer thickness change

It is expected that the acoustic band structure be sensitive to layer thicknesses just in the case of optical bilayer stacks. Figure B- 5 above shows how the band structure evolves with change in layer thicknesses. Panel 1 is the case with uniform polymer (PolyCarbonate) with zero glass (As₂Se₃), panel 2 is the case with uniform glass with zero thickness for polymer layers, and panels 2-7 are the intermediate states with non-zero thickness for both materials with gradually changing thickness ratio. This is now extended to scan all thickness ratios in search for widest band gap for given incident angles (Figure B- 6). Horizontal axes are thickness ratios (d_1/d_2) and vertical axes are normalized frequency. Left column is for the decoupled SH polarization, middle column is for the coupled SV and L polarizations, and the right column is the superposition of the two. Black areas correspond to forbidden gaps (reflection gaps) for a certain thickness ratio.

Figure B- 7: Reflection bands for certain incident angles

This can be further generalized to include all incident angles from 0 to 90°. Figure B- 7 below shows the superposition of the reflection band maps (Figure B- 6) for all angles.

Figure B- 8: Superposition of all reflection bands for all angles

Black regions in these maps correspond to thickness ratios and frequency ranges that allow omni-directional reflection of sound waves.

Future works on this project can include extension of this theory to finite periodic systems with defect layers to represent realistic situations. The same problem can be solved in cylindrical geometry to represent a sound wave Bragg fiber that transmits sound via Bragg reflections.

B.2. Thermal Embossing for Fiber-tip Device Fabrication

This project suggests thermal embossing as an easy way of creating a certain class of devices on the tip of optical and multi-functional fibers. As an example, prisms are embossed on fiber tips with single and dual cores for the final goal of making fiber-tip sensors for remote sensing in a novel mode with light interacting with the surrounding only at the tip of the same fiber that carries light.

Embossing

For a simple proof-of-concept demonstration a 60° V-groove with a depth of approximately 200 μm is cut very carefully from the circular facet of a small brass rod on a regular milling machine. This mold is then pressed upon the facet of a circular fiber with a PolyCarbonate core and COP cladding while it is heated from the top using a soldering iron. The brass mold and the heater are mounted on an XYZ translation stage. X and Y translation is used for alignment of the mold with fiber which is held firm on a holder fixed on the table, while Z translation is used for application of a controllable pressure on the fiber tip during hot embossing. Figure B- 8 shows the embossing setup. Figure B- 9 also shows the target shape, microscopic images and a SEM image of the first successful fiber-tip prism sample that was made with this method.

Eventually the goal of such a device is to use the micro-prism to deflect the light that is propagating along the fiber core. Two identical fibers with the prisms on their tips can then be mounted next to each other so that light deflected normal to the first fiber gets coupled into the second one after travelling a brief length in the environment between the two fibers. This can be used for sensing applications with the sensing probe being the bundle of these two fibers and all

light sources and detectors being on one end of the sensing device. In order to test this and verify that the prism on the fiber tip is acting as expected a test setup is arranged to capture the angular intensity variation around the fiber exit tip when a green (532 nm) laser light is coupled into the other end of the fiber which is intact and flat. Figure B- 10 shows the deflected spot which is at approximately 90° angle from the fiber axis.

Figure B- 9: Embossing setup for fiber-tip device fabrication

Figure B- 10: First successful fiber-tip embossed device

Figure B- 11: Light deflection from the first prism-tip fiber

In order to more quantitatively test the performance of this prism-tip fiber, a single-mode silica fiber is used to sample local intensity distribution around the fiber tip. This probe fiber is rotated around the test fiber tip in a way that the distance between the two fibers remains unchanged within the accuracy of the test setup. Power picked up with the probe fiber is coupled into a power meter and recorded as a function of angle with respect to normal to the fiber axis. Figure B- 11 shows this measurement setup and the measurement result that shows partial deflection of light along the expected direction.

Figure B- 12: Quantitative measurement on prism-tip fiber

Figure B- 12 below also shows qualitatively how light normal to the fiber is coupled into the fiber core using the prism on its tip.

Figure B- 13: Normal light coupling into prism-tip fiber

To prove the feasibility of embossing more than one object on the fiber tip with higher quality than the first demonstration a dual-core fiber is fabricated with two PC cores and COP cladding Figure B- 13. A dual-prism mold is machined in a similar way as described above with accurate alignment, spacing and depth adjustment on a milling machine. As depicted in the first panel, it can be envisioned that multiple devices including prisms and other optical components may have strong interactions and sensing capabilities all on the small tip of a single fiber.

Figure B- 14: Dual-core dual-prism fiber-tip device

B.3. Thermal Drawing of Structured Sheets

Optical fibers have been traditionally drawn from cylindrically symmetric preforms in cylindrically symmetric furnaces. This is necessary to achieve long lengths of uniform circular fibers that are best choices for low-loss communication fibers thousands of miles long. This traditional approach was applied to a new class of optical fibers, Photonic Crystal Fibers (PCF) in 2003 with a modification to allow gas flow into the preform during the drawing process to maintain air capillaries from collapsing [127, 128]. This same fiber drawing geometry was applied to multi-material fibers [40] and even non-circular fibers [129].

In the process of drawing FLSC fibers (main subject of this thesis) and arranging them in the form of flexible sheets, the idea of pulling sheets directly was conceived. This could potentially make the fabrication process much faster and therefore economically more viable. The basic idea of changing the drawing geometry from circular to flat with all symmetries changed from circular to linear is shown in the Figure B- 14 below.

Figure B- 15: Circular vs. linear draw geometry

It is straightforward to extend this idea to applications other than faster drawing of FLSC's. This new drawing geometry can potentially allow for fabrication of micro- and nano-structured sheets for applications spanning from optics to electronics, magnetic films, etc.

Based on the basic principle of translating all symmetries from circular to linear, a new furnace was designed and constructed to test the idea (Figure B- 15).

Figure B- 16: Flat furnace constructed in house

Figure B- 16 in the next page shows several flat preforms and successfully drawn sheets with simple embedded structures along the different axes. Successful samples were made with a slightly modified furnace after months of failures and systematic investigation and correction of possible reasons.

Figure B- 17: Flat preforms and drawn sheets

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