Perspective: Molten core optical fiber fabrication—A route to new materials and applications

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Perspective: Molten core optical fiber fabrication—A route to new materials and applications

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The molten core method, whereby a precursor core phase melts at the draw temperature of the cladding glass that encapsulates it, has proven to be a remarkably versatile approach to realize novel optical fibers. Employed globally for both scientific inquiry and practical applications, it is arguably the only approach that leads to long lengths of novel material fiber with both crystalline and glassy cores. This article reviews the history of the process, the ever-broadening range of compositions, the unique applications that have been enabled, and provides a perspective on current challenges and future opportunities. https://doi.org/10.1063/1.5067337

I. INTRODUCTION

Optical fibers have transformed our lives. Not only do they act as the pipeline through which information is transmitted around the globe, but they are also critical components in a diverse array of areas spanning environmental sensing, medical surgery, and innovative manufacturing, to name but a few. Presently, most commercial fibers are produced entirely from silica glass, principally because of the decades of investment that have gone into perfecting the fabrication techniques to reduce the losses in the telecommunications spectral band. However, silica is somewhat limited in terms of its transmission window, which is largely confined to the near-infrared wavelength region, its nonlinear coefficients, which can be too high or too low depending on the application, and its lack of electronic functionality.

In order to circumvent the aforementioned limitations with silica, new materials are required that can be fabricated into a fiber waveguide geometry. Unfortunately, the chemical vapor deposition (CVD) techniques used to fabricate the preforms from which silica-based fibers are drawn are known to be fairly restrictive in terms of the glass compositions they permit (Ballato and Dragic, 2013). Thus, the production of advanced optical fibers based on novel core materials that meet present and future demands will require new approaches, not only in terms of the preform fabrication but also in the drawing procedures. Accordingly, the focus of this article is the molten core method of fiber fabrication, which has, over the past 25 years, proven to be remarkably versatile for the production of a wide variety of novel multicomponent all-glass optical fibers as well as practical crystalline core semiconductor optical fibers. These novel core fibers are expected to find application in a wide range of areas, such as high power fiber laser development, surgical probes, and terahertz waveguides for security measures.

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II. THE STORY SO FAR

A. History of the MCM

The history of what today is called the molten core method (MCM) is somewhat difficult to piece together given the wide variety of innovative approaches to making fibers, be them optical or non-optical. This section is a brief perspective based on both the literature and the authors' recollection (mainly JB), highlighting the seminal innovations and advancements.

Although important differences exist, the earliest relative to the MCM is the Taylor wire method, which was developed to fabricate very thin metal (micro)wires encased in a glass sheath, primarily for the development of "resistance thermometers, thermocouples, galvanometer suspensions, and hair lines for the eye pieces of telescopes" (Taylor, 1924). Taylor's original paper included glass-clad metal cores of lead, antimony, bismuth, tin, cadmium, gallium, thallium, copper, silver, gold, iron, indium, and aluminum, as well as a variety of related alloys. These metals filled the interior of a glass tube, which was heated above the melting point of the core metal and drawn. More specifically, as Taylor states "[t]he glass selected must soften at a temperature between the melting and the boiling point of the metal used and must not react chemically with the metal at high temperatures."

A closer chronological and technical relative to the MCM is the soft glass volatile core method (VCM) of Snitzer and Tumminelli, which was conceived principally for the development of lasers (Snitzer and Tumminelli, 1989). In that work, a soft glass rod was first formed and then clad in a thick-walled pure SiO_2 tube. At the draw temperature, certain components, specifically alkali- and alkaline-earth oxides, volatilized away leaving a high-silica content glass as the resultant fiber core composition. The important differentiating features of Snitzer versus Taylor are (1) a glass precursor core phase, (2) reactivity (volatility) of the melt during the draw, and (3) interactions between the molten core and glass cladding. This latter point is especially germane. Referring to the refractive index and compositional profiles of the non-volatile species (e.g., Al_2O_3 and SiO_2) in the as-drawn fiber, Snitzer states that these "suggest significant mixing of the core glass with the SiO_2 cladding."

The conclusions of Snitzer stated that the soft glass VCM "may be best suited for high concentrations in the core, which are difficult to get by modified chemical-vapor deposition (MCVD), such as for Faraday rotators based on high Tb content [6]." Reference 6 noted in that quote is to Robinson and Graf (1964), which relates to bulk aluminosilicate glasses containing 58 weight percent of selected rare earth oxides (specifically praseodymium, terbium, or dysprosium) [note, the page number for Robinson and Graf (1964) cited in Snitzer and Tumminelli (1989) is incorrect; the interested reader should follow the citation herein]. Of these, terbium received greater attention due to its larger Verdet constant and lower absorption value relative to the phosphate and lead silicate glasses treated therein. The bulk glass composition deduced from Robinson and Graf (1964), in mole percent, for their terbium aluminosilicate was 67 SiO_2–19 Al_2O_3–14 Tb_2O_3. This is, in fact, not only a higher concentration than possible using optical fiber vapor deposition methods as Snitzer remarked, but it is also quite close to the glass-forming limit of lanthanide oxide aluminosilicate glasses (Makishima *et al.*, 1982). This is important since the VCM relies on a pre-fabricated core glass rod that is drawn via the rod-in-tube method. If said composition is not permissible due to a lack of glass formation, then this defines an upper composition limit to the resultant core material.

To circumvent this issue, Ballato and Snitzer employed a powder-in-tube approach whereby constituent powders that were mixed, but not otherwise reacted, were loaded inside a SiO_2 cladding tube (Ballato and Snitzer, 1995). Upon heating, the precursor powders undergo solid- and liquid-state reactions and ultimately melt by the time the draw temperature is reached and the fiber is formed and hence the name MCM. The defining attributes of the MCM approach are thus (1) a core phase, placed inside a cladding glass tube, which melts as the draw temperature of the cladding tube is reached; (2) said core composition is not one that could be formed into a bulk glass and drawn by itself (i.e., the composition is insufficiently stable to be formed into a bulk glass sample and drawn); and (3) interactions between the molten core and softened cladding glass can occur.

Although today's MCM shares similarities with the Taylor method, the latter relies on no chemical interaction between the molten (metal) core and the glass cladding, whereas the former, in most cases, benefits from such a reaction product. The MCM, in its present form, was borne out of the work on

the VCM and was begun in 1992, first presented publically in 1993 (Ballato and Snitzer, 1993), and published in 1995 (Ballato and Snitzer, 1995). Furthermore, and in order to make clear the historical record, though Taylor was discussed, it was deemed sufficiently different from the volatile or molten core approach for the reasons noted above that it was not cited in either Snitzer and Tumminelli or Ballato and Snitzer.

Within a year, the first report of photonic crystal fibers (PCFs) was published (Knight *et al.*, 1996), which set the optical fiber community in a remarkable new direction. In simplest terms, the properties of light in a fiber are controlled/tailored by both the material through which it propagates and the nature of the waveguide that is confining it. The majority of PCFs are silica-based, given its near-theoretical low-loss and high strength, properties that are courtesy of decades of material and process optimization associated with telecommunications. Put another way, the optical fiber community focused extraordinary efforts into the geometric control of light while relying on, for all intents and purposes, a singular material. One can argue that there are benefits and detriments of either approach. PCFs have opened doors to a cornucopia of novel and useful effects that would be very difficult to realize based on a materials approach alone. This includes fibers with endlessly single mode operation (Birks *et al.*, 1997), highly engineered dispersion profiles (Poletti *et al.*, 2005), and ultra-small cores (Birks *et al.*, 2000), properties that have led to the development of the highly efficient supercontinuum sources used in spectroscopy, imaging, and frequency metrology (Ranka *et al.*, 2000).

The mid-2000s witnessed something of a renaissance in the study and development of optical fiber materials and material combinations. Although this has been termed a return to simplicity (Ballato and Dragic, 2013), it was in fact driven by a realization that novel materials, in fiber form, could enable a wide variety of optoelectronic functions that fiber design alone could not (Abouraddy *et al.*, 2007), i.e., the resulting fibers would be anything but simple. The field of "multi-material" [sometimes also referred to as "hybrid" (Schmidt *et al.*, 2016)] optical fibers has played a central role in this rebirth of fiber materials. However, much of the early work in this area made use of materials that had sufficiently similar thermal properties that they could be co-drawn together, such as low melting temperature soft glasses, metals, and polymers (Bayindir *et al.*, 2004). Since this article focuses on the MCM, the reader is referred to the following reviews for more information on such fibers (Tao *et al.*, 2012; 2015).

A critical advancement related to the MCM was the innovative use of a (single) crystalline rod as the core precursor. In this case, the pioneering work is that of Huang *et al.* (2006) in which a YAG (yttrium aluminum garnet, $Y_3Al_5O_{12}$) single crystal was sleeved inside a silica tube to create a preform. The 1950 °C melting point for the YAG crystal (which obviously cannot be drawn on its own) is below the ~2000 °C draw temperature for SiO_2 and so the crystal melts and draws along with the silica cladding. The result was a fiber with a glassy core material consisting of an yttrium aluminosilicate composition, owing to oxygen incorporation from the oxide glass (silica) cladding.

A second critical advancement with respect to the MCM was its use to realize long lengths of glass-clad crystalline core optical fibers, specifically using semiconducting silicon (Ballato *et al.*, 2008). As with YAG, silicon is crystalline and, therefore, does not possess a glass transition and so does not soften prior to the melting point such that it could be drawn into a fiber. Two particularly unexpected outcomes of this work are (a) that the core was highly crystalline despite the quench rate of the molten core into solidified fiber and (b) that the silicon did not fully oxidize despite being clad in glass and drawn at approximately 600K above its melting point. [A brief historical note: Dr. Robert (Bob) Rice, a co-author on the original "Silicon optical fiber" publication (Ballato *et al.*, 2008), had suggested in November 2004 to the author (JB) to try to make a silicon optical fiber. Ballato had proposed to use the MCM but was convinced that it would not work due to the extreme temperature differences in the case of silicon in silica and the oxidizing environment and so put off the effort for several years. After sufficient badgering, the silicon-in-silica fiber was drawn on December 13, 2007, and Ballato watched in stunned amazement as the black core of the fiber traversed down the draw tower.] While glass-clad crystalline silicon and germanium optical fibers had been previously realized (Sazio *et al.*, 2006), the method employed was not commercially realistic in terms of fiber lengths or production times.

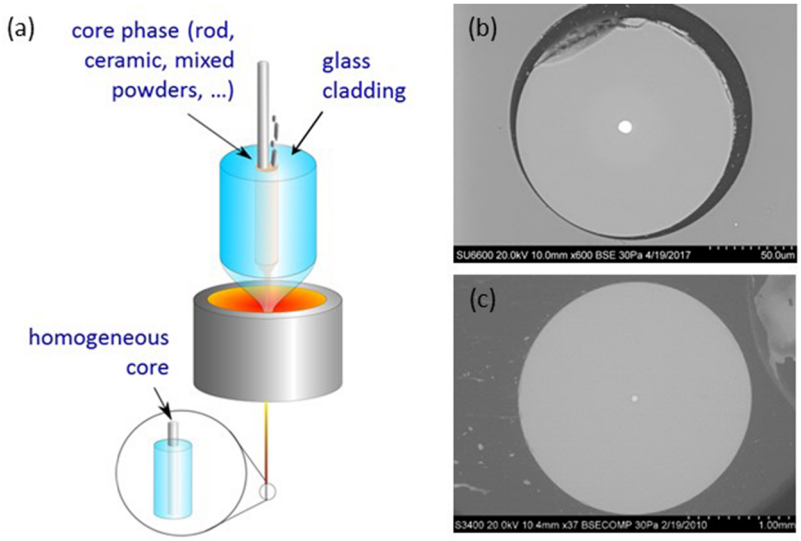

FIG. 1. (a) Schematic representation of the molten core method (MCM) for the direct fabrication of optical fibers; image modified from Coucheron *et al.* (2016). Cross-sectional images of representative optical fibers fabricated using the molten core method: (b) bismuth oxide-derived bismuth silicate glassy core and (c) crystalline silicon core.

Figure 1 provides a generalized schematic of the MCM along with representative cross sections of both an all-glass core and a crystalline core fiber. It is clear from the high index contrast that in both cases the material properties of the core and cladding are quite different, yet the circular cores are well formed without any defects. More in-depth discussions of the core phases realized using the MCM, as well as their novel properties and potential applications, are provided below. For completeness, four variations on the molten core theme that warrant specific mention are the "core suction technique" (Goel *et al.*, 2006; 2014), the "granulated silica method" (Renner-Erny *et al.*, 2007; Di Labio *et al.*, 2008; and Pilz *et al.*, 2017), the (modified) "Powder-in-Tube Technique" (Scott *et al.*, 2009a; Auguste *et al.*, 2014; and Kudinova *et al.*, 2017), and the "Melt-in-Tube" method (Fang *et al.*, 2015a and Zhang *et al.*, published online).

B. Survey of materials, compositions, and properties

As noted above, the MCM is arguably the only practical method to fabricate long lengths of both glassy and crystalline core optical fibers with unusual compositions. The purpose of this section is to inventory the materials made to date into optical fibers, as shown in Table I, and highlight any especially unique or useful properties. The future opportunities and present challenges are treated in Sec. III.

1. All-glass optical fibers

As noted above, the original MCM fiber was based on the powder-in-tube approach (Ballato and Snitzer, 1995). In that work, a high terbia (Tb_2O_3) content core was desired for use in an all-fiber Faraday isolator. Specifically, Tb_2O_3 was employed as the paramagnetic species and an aluminosilicate host glass was selected for its thermophysical robustness and compatibility with conventional silica optical fibers. In keeping with the previously defined attributes of the MCM, though a small (approximately 4 mm × 1 mm × 1 mm) bulk sample of the precursor core glass was fabricated and characterized, the composition exceeded the stability of the Tb_2O_3-Al_2O_3-SiO_2 system and it could not be formed into a sufficiently sized rod for conventional thermal drawing. Furthermore, even if it was formed into a larger rod, the glass would have crystallized upon heating to the fiber drop and draw temperatures. Incorporation of SiO_2 from the cladding glass into the molten core occurred, as it did in Snitzer and Tumminelli (1989), which reduced the effective terbium concentration. Losses in that fiber were not directly measured, only inferred from modal patterns, though they would have been quite high given the low purity levels employed.

TABLE I. Precursor core phases fabricated into optical fiber to date using the molten core method.

Precursor phase	Reference
All-glass core fibers	
Terbium aluminosilicate (Tb_2O_3-Al_2O_3-SiO_2)	(Ballato and Snitzer, 1995)
Yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$)	(Huang *et al.*, 2006) and (Ballato *et al.*, 2009a)
Sapphire (Al_2O_3)	(Dragic *et al.*, 2012b)
Spinel ($MgAl_2O_4$)	(Mangognia *et al.*, 2013)
Barium oxide (BaO)	(Dragic *et al.*, 2013)
Strontium aluminate (SrO-Al_2O_3) oxide and oxyfluoride	(Cavillon *et al.*, 2018b) and (Cavillon *et al.*, 2016)
Lithium aluminate (Li_2O-Al_2O_3)	(Dragic *et al.*, 2015a)
Bismuth germanate (Bi_2O_3-GeO_2)	(Faugas *et al.*, 2018)
Lutetium aluminum garnet (LuAg, $Lu_3Al_5O_{12}$)	(Dragic *et al.*, 2015b)
Crystalline semiconductor core fibers	
Silicon (Si)	(Ballato *et al.*, 2008)
Doped silicon	(Scott *et al.*, 2009b) and (Homa *et al.*, 2014)
Germanium (Ge)	(Ballato *et al.*, 2009b)
Indium antimonide (InSb)	(Ballato *et al.*, 2010)
Gallium antimonide (GaSb)	(Scott and Pickrell, 2013a) and (Song *et al.*, 2018)
Selenium (Se)	(Tang *et al.*, 2015a)
Tellurium (Te)	(Tang *et al.*, 2015b)
Selenium-tellurium (SeTe)	(Tang *et al.*, 2015c)
Silicon-germanium (SiGe)	(Coucheron *et al.*, 2016)
Antimony selenide (SbSe)	(Tang *et al.*, 2017a)
Bismuth (Bi)	(Tang *et al.*, 2017b)
Crystalline oxide core fibers	
Bismuth silicate/germanate ($Bi_4(Ge_{1-x}Si_x)_3O_{12}$, $BiGeO_5$)	(Ballato *et al.*, 2012) and (Faugas *et al.*, 2018)

The transition from using the MCM as a means to fiberize unstable glasses from individual powder precursors to the one that employed a homogeneous crystalline precursor phase was both non-obvious (even counter-intuitive) and, in time, remarkably useful as it opened up a new sub-field: intrinsically low nonlinearity optical fibers. Again, this advancement is credited to Huang *et al.* (2006) who sleeved a single crystalline (chromium doped) YAG rod inside of a silica tube. At the draw temperature of the silica, the YAG melted and the resultant fiber core glass was an yttrium aluminosilicate composition (Y_2O_3-Al_2O_3-SiO_2). The focus of Huang *et al.* was to investigate the spectroscopy of chromium (Cr) in these YAG-derived glasses for use as a potential optical amplifier over the entire 1.3-1.6 μm spectral range of interest to telecommunications. Following this proof of concept work, Ballato *et al.* conducted an in-depth investigation of molten core/clad interactions in both undoped and erbium-doped YAG-derived fibers (Ballato *et al.*, 2009a). More important, from an application perspective, was the subsequent investigation of the optical nonlinearities of these fibers. Initially, Dragic *et al.* determined that these YAG-derived yttrium aluminosilicate glasses possessed reduced Brillouin scattering in comparison to conventional, silica-based telecommunication glasses (Dragic *et al.*, 2010). A reduction of almost 8 dB (83%) was deduced, relative to conventional single mode optical fiber (SMF), principally due to the reduced transverse Pockels coefficient and enhanced Brillouin linewidth of the sesquioxide constituents. From there, further investigations verified reduced Raman scattering as well (Dragic and Ballato, 2013). Since Brillouin and Raman scattering, in their stimulated forms, are detrimental to fiber laser performance, it was not long after these initial studies when attention turned to the feasibility of these intrinsically low nonlinearity, molten-core derived multicomponent glasses as novel gain media, using both Yb (Dragic *et al.*, 2012a) and Nd (Yoo *et al.*, 2012) as the active dopants.

Subsequent to this foundational work on YAG-derived all-glass optical fibers, research soon switched to examining other crystalline phases as the precursor to novel core compositions, generally not permissible using either chemical vapor deposition methods [MCVD, outside vapor deposition (OVD), vapor axial deposition (VAD)] or conventional melt/quench techniques for optical fibers. As noted in Table I, a wide variety of crystalline precursors have now been studied, including sapphire

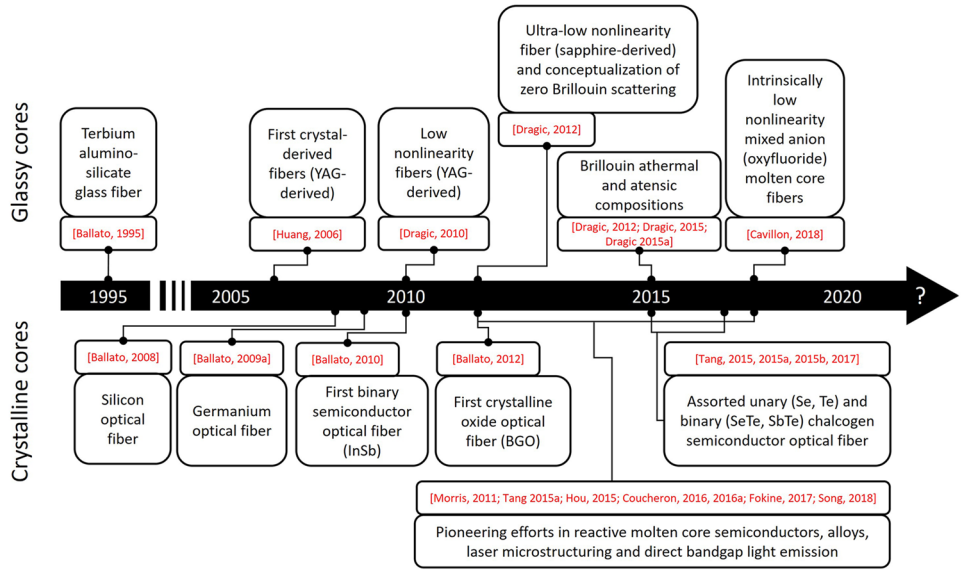

FIG. 2. A historical representation of seminal advances in optical fibers made using the molten core method (MCM).

(Dragic *et al.*, 2012b), spinel (Mangognia *et al.*, 2013), and alkaline earth oxides (Dragic *et al.*, 2013 and Cavillon *et al.*, 2018b). In general, the benefit of employing a crystalline precursor in the MCM is that it typically contains the highest percentage of a given compound, which usually translates into much higher concentrations of said compound in the resultant core glass. In other words, for example, forming an aluminosilicate glass using conventional methods is limited to about 8 mol. % Al_2O_3 (Nassau *et al.*, 1975 and Simpson and MacChesney, 1983). Contrast this by starting with pure (100%) Al_2O_3 in the form of sapphire, which results in a molten core-derived aluminosilicate with Al_2O_3 concentrations as high as 54 mol. % (Dragic *et al.*, 2012b). The top part of Fig. 2 provides a historical representation of the critical advancements in MCM fibers with glassy cores.

2. Crystalline core optical fibers

While not especially surprising that the rapid quench rates associated with the MCM, coupled with dissolution of glass-forming SiO_2 from the cladding into the (molten) core, would yield amorphous cores, the realization of (poly)crystalline cores was indeed unexpected. [For completeness, it is worth noting that glass formation in the case of the YAG-derived, yttrium aluminosilicate optical fibers benefits from the additional factor that the YAG crystal is quite complex, with 160 atoms per unit cell; this facilitates vitrification upon rapid cooling (Cockayne, 1985).] As noted above, this important advancement was originally based on semiconducting silicon (Ballato *et al.*, 2008) and subsequently extended to other Group IV and II-V unary and binary semiconductors including germanium (Ballato *et al.*, 2009b), silicon-germanium (Coucheron *et al.*, 2016), indium antimonide (Ballato *et al.*, 2010), gallium antimonide (Scott and Pickrell, 2013a and Song *et al.*, 2018), and, more recently, a variety of selenides and tellurides (Tang *et al.*, 2015a; 2015b; 2015c; and 2017a).

Initial efforts largely concentrated on understanding the sources of attenuation and the crystallographic orientation of the core's crystalline axes relative to those of the fiber. With regard to the former, early efforts focused on cracks and stress-optic influences arising from the significant mismatch in (semiconductor) core/(glass) cladding coefficients of thermal expansion (CTE), longitudinal variations associated with non-uniformities in melt solidification, oxide impurities/precipitates (Morris *et al.*, 2012a), and optical scattering from grain boundaries [grain size, hence number of grain boundaries, has been shown to be fiber diameter dependent (Scott and Pickrell, 2013b)]. Relative to the issue of optical scattering, early efforts to reduce this focused on thermal annealing (Gupta *et al.*, 2011), the influences of core geometry (Morris *et al.*, 2012c), and tapering (McMillen *et al.*, 2012) in order to control the grain size and orientation with the view to obtaining single crystal-like properties over a given distance (McMillen *et al.*, 2010).

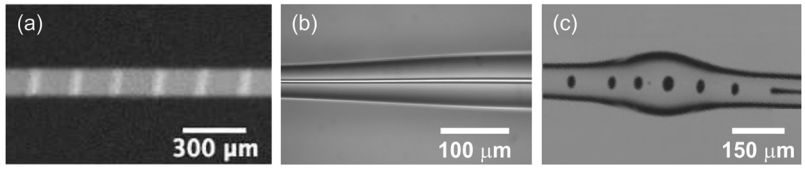

FIG. 3. Representative images of laser-processed semiconductor core fibers showing the unique variety of microstructures that can be obtained. (a) Compositional microstructuring in a SiGe fiber, (b) tapering of a silicon fiber to reduce the core size, and (c) localized heating to form spherical micro-resonators in a silicon fiber.

Other important developments involved the identification of designer cladding glasses with CTE values and draw temperatures matched to those of the semiconductor cores (Morris *et al.*, 2012b), as well as a reactive version of the molten core method. Such tailoring of the cladding glass remains an opportunity and active area of study (Dmitrieva *et al.*, published online). On the other hand, reactive molten core fabrication takes advantage of liquid phase chemistry that can occur in the melt during the draw and has been used to react away contaminating oxide species (Morris *et al.*, 2011), to form a compound semiconductor from two unary species (Tang *et al.*, 2015b), or even to completely replace the initial core phase with a different one, e.g., start with Al to end with Si (Hou *et al.*, 2015). This latter case is not unlike the *in situ* reactive processing, though not MCM, which has been employed to produce ZnSe fibers (Orf *et al.*, 2011 and Hou *et al.*, 2013).

Reactive MCM enjoyed a critical advancement with the work of Nordstrand *et al.*, who developed an interfacial (core/clad) modifier method to getter oxide contaminations from the glass cladding from incorporation into the semiconductor core (Nordstrand *et al.*, 2013). In hindsight, this work arguably is amongst the most important for the practical subsequent development of semiconductor optical fibers as it wholly mitigated issues associated with oxide contamination, which led to smaller core sizes being possible, as well as reducing the effective expansion mismatch that often led to cracking. A second critical advancement was the development of directional laser recrystallization to produce single crystalline regions within the fiber (Healy *et al.*, 2016) as well as to compositionally tailor the core phase in a binary or alloy system, as illustrated in Fig. 3(a) (Coucheron *et al.*, 2016 and Fokine *et al.*, 2017). Moreover, such laser processing also allows for controllable heating of both the core and cladding structure, which can be exploited for the formation of longitudinal tapers or optical microresonators, as demonstrated in Figs. 3(b) and 3(c). Taken together, these developments have led to oxygen free, small core, single crystalline semiconductor fibers from which a wide variety of devices are now being made (as discussed below). A historical graphic of the critical advancements in semiconductor-derived optical fibers fabricated using the MCM is provided in the bottom part of Fig. 2.

III. FUTURE PROSPECTS

With the current state-of-the-art of the MCM in mind, the remainder of this article will provide perspectives on the future opportunities and present challenges for these fibers.

Unquestionably, the MCM has opened up a remarkably broad range of compositions, both amorphous and crystalline, as enabling core phases for novel optical fibers. The underlying materials science and engineering of MCM-derived optical fibers is by no means simple (further differentiating it from the Taylor method) with chemical interactions between core melt and cladding glass inevitably playing a role, whether advantageous or detrimental.

That said, in only about a decade, both amorphous and crystalline (semiconductor) MCM fibers have been transitioned into quite a few devices and prototypes which are summarized in Table II.

A. Opportunities

Crystal-ball notwithstanding, this section provides perspectives on those opportunities that are realistic and potentially transformative over the next 5–10 years.

TABLE II. Prototypes and devices fabricated from molten core derived optical fibers.

Prototype/device	Reference
All-glass core fibers	
Faraday isolator	(Ballato and Snitzer, 1995)
Fiber laser/amplifier	(Dragic and Ballato, 2013 and Yoo *et al.*, 2012)
Low nonlinearity optical fibers	[Dragic *et al.*, 2010 and Cavillon *et al.*, 2018b)
High nonlinearity optical fibers	(Tuggle *et al.*, 2017)
Brillouin athermal fiber sensor	(Dragic *et al.*, 2015a; 2015b)
Low quantum defect fiber laser	(Yu *et al.*, 2018)
Crystalline semiconductor core fibers	
Photoconducting fiber antenna	(Davis *et al.*, 2010)
High-Q fiber resonator	(Wang *et al.*, 2012)
Raman-based fiber infrared light source	(Wang *et al.*, 2013)
Si/SiGe particle in-fiber formation	[Gumennik *et al.*, 2013; 2017]
In-fiber p-n junctions	(Homa *et al.*, 2014)
Fiber-based solar cells	(Martinsen *et al.*, 2014b; 2014a; and 2015]
Fiber Bragg gratings	(Coucheron *et al.*, 2016)
Nonlinear fiber optics	(Suhailin *et al.*, 2016 and Peacock *et al.*, 2018)
In-fiber couplers to conventional fibers	(Ren *et al.*, 2017)

1. Crystal-derived glass fibers

With respect to the crystal-derived all-glass fibers, arguably the most intriguing opportunities revolve around the possibility to greatly reduce, if not entirely negate, optical nonlinearities (Cavillon *et al.*, 2018a). This potential arises directly from the material property dependences of Brillouin, Raman, Rayleigh, and thermal Rayleigh scattering, which can be made very low, or possibly zero, through judicious compositional selection (Ballato *et al.*, 2018). As shown by Cavillon *et al.*, the power-scaling from a single-aperture fiber laser fabricated using one of the identified (MCM-derived) multicomponent glass compositions could be orders of magnitude larger than what is possible using conventional fibers (Cavillon *et al.*, 2018a). The related possibilities of a "zero nonlinearity" high power laser fiber are stunning, both scientifically and practically.

A second area of noted opportunity for these fibers revolves around their use as distributed fiber sensors. In an analogous approach to that above with respect to nonlinearities, the thermal and strain dependence of a (fiber) sensor can be controlled separately through glass composition and hence material properties. In general, balancing positive and negative contributions to the thermo- and strain- optic and acoustic coefficients of the glass components permits athermal or atensic behavior. This is opportunistic since present sensors usually convolve temperature and strain responses, which necessitates the use of multiple fibers or sophisticated electronics, adding to system complexity and cost. Such athermal and atensic performance has been identified in MCM all-glass fibers derived from sapphire (Dragic *et al.*, 2012b), baria [Dragic *et al.*, 2013], lithium aluminate (Dragic *et al.*, 2015a), and LuAG (Dragic *et al.*, 2015b). Presently, however, these (Brillouin) athermal compositions also tend to possess reduced Brillouin gain coefficients making them less than ideal sensors even though the temperature and pressure dependences have been decoupled.

2. Glass-clad semiconductor core fibers

As already noted, two critical advancements beyond the initial MCM fabrication of long lengths of crystalline core fiber was the development of an oxide-gettering interfacial layer (Nordstrand *et al.*, 2013) and the laser refinement/recrystallization process (Coucheron *et al.*, 2016). These efforts have opened the door to reduced losses, smaller cores, and tailored compositional microstructures, helping to expand the application potential. In particular, as these fibers offer an intriguing combination of high nonlinear coefficients and useful optoelectronic properties, they are well suited to a wide array of signal processing type applications. A detailed history and compilation of progress that has been made in this area has been captured in a series of recent reviews, to which the reader is referred (Peacock *et al.*, 2014; 2016; and Healy *et al.*, 2018).

The applications highlighted in Table II give a sense of what has been achieved over a fairly short time scale. This includes devices that draw on the unique optical properties of the core materials, such as the nonlinear demonstrators (Suhailin *et al.*, 2016 and Peacock *et al.*, 2018) and infrared light sources [Raman (Wang *et al.*, 2013) and photoluminescent (Song *et al.*, 2018)], as well as those that utilize the optoelectronic properties, such as photoconductive antennas (Davis *et al.*, 2010) and fiber-based solar cells (Martinsen *et al.*, 2014b; 2014a; and 2015).

Although, as of to date, all of the demonstrators have utilized Group IV core materials, clear opportunities exist to further expand the range of applications simply by exploiting the full library in Table I. In the more immediate term, the optimization of binary, and even ternary, systems seems a reasonably straight-forward yet important advancement. Compared to unary materials, compound semiconductors can possess useful optoelectronic properties such as a second order $\chi^{(2)}$ nonlinearity and direct bandgaps, thus opening the door to a wider range of nonlinear applications (Vukovic *et al.*, 2015) as well as the development of in-fiber semiconductor light sources (Song *et al.*, 2018). Opportunities also clearly exist for developing fibers with amorphous semiconductor cores, which presently are only enabled through the high pressure CVD process (Shen *et al.*, 2013). Amorphous semiconductors can potentially offer enhanced nonlinearities and lower losses than their crystalline counterparts, which have obvious device and application benefits, though at the expense of reduced electronic functionality. Employing the MCM to fabricate long lengths of low cost crystalline semiconductor fibers that are subsequently processed using the aforementioned laser heating/cooling methodologies as a route to amorphous cores is worth investigation. Laser heating, refining, and recrystallization remain a very powerful approach to tailoring the semiconductor core post-fabrication. Using it to further define in-fiber compositional microstructures (Coucheron *et al.*, 2016), regions of differing orientation and/or bandgap effects (Healy *et al.*, 2014) are also well worthy of study.

Another clear opportunity for the crystalline core semiconductor fibers is to capitalize off their extended transparency range, which covers everything from the visible spectrum up to the far-infrared. In particular, one area yet to be investigated is their use for terahertz waveguiding, where applications include homeland security, imaging, spectroscopy, and medical diagnostics, to name but a few. The large core MCM fibers would be well suited for this work as the light can be confined entirely within the semiconductor material, minimizing interaction with the lossy cladding glass. At the opposite end of the wavelength scale is their potential application in quantum optical systems, where most efforts to date have focused on the visible to near-infrared wavelength region (Rarity *et al.*, 2005). By reducing the losses in the small core fibers to the dB/m level, or lower, it should be possible to make use of the high nonlinear coefficients in the semiconductor materials to generate, transmit, and manipulate correlated photons within quantum information and/or imaging systems (Vukovic *et al.*, 2015).

3. Crystalline oxide core fibers

The use of the MCM to realize crystalline oxide core optical fibers is perhaps the most exciting opportunity, though it also is the least mature of the families of fibers enabled to date (hence its lack of inclusion in Table II). Indeed, initial efforts in YAG-derived fibers were driven by a (unsuccessful) desire for crystalline YAG-core fibers. [Ballato *et al.* (2009a) states that "Although our initial hope was that the fibers would possess some degree of YAG crystallinity." This was because the initial work on Cr:YAG-derived optical fibers (Huang *et al.*, 2006; 2007) suggested the formation of YAG crystallites in the fiber; though this was never observed in the subsequent work of the Ballato *et al.*] That said, the subsequent discovery of intrinsically low nonlinearities in the multicomponent crystal-derived optical fibers has opened an entirely new field relevant to high energy fiber lasers (Dragic *et al.*, 2018).

The initial realization of MCM-derived crystalline oxide core fibers [and subsequently both crystalline and amorphous heavy-metal oxide core fibers (Faugas *et al.*, 2018)] was admittedly surprising (Ballato *et al.*, 2012). Those first fibers were biphasic and so scattering from the different compositions as well as the random grain orientation precluded light transport. However, it served as a valuable proof-of-concept that the MCM could permit crystalline oxide formation and clearly warrants further study and development, particularly using laser recrystallization/processing. In the specific case of bismuth germinate [BGO, (Ballato *et al.*, 2012)] and bismuth silicate [BSO, (Faugas *et al.*, 2018)],

depending on the stoichiometry and orientation, fiber-based scintillators, current/voltage sensors, pyroelectric, piezoelectric, ferroelectric, and $\chi^{(2)}$ nonlinear optical devices would be possible.

For completeness, it is worth noting that the MCM, followed by annealing to facilitate crystallite formation (i.e., glass ceramic) within the core of an optical fiber, has been studied somewhat recently (Fang *et al.*, 2015b). This represents a "hybrid" approach whereby the MCM permits the formation of glass cores that could not be fabricated using convention methods and thermal post-processing yields an optically desirous nanophase, such as a low phonon energy environment for efficient mid-infrared emissions (Kang *et al.*, 2018).

B. Challenges

In all cases, several on-going challenges remain. In the perspective of the authors, the two most paramount challenges are (1) loss reduction and (2) interconnection/compatibility with conventional fibers and optoelectronic circuits.

1. Loss reduction

With regard to loss in the crystal-derived all-glass optical fibers, the lowest attenuation values achieved are on the order of 150 dB/km (Ballato *et al.*, 2009a), which, although sufficient for testing purposes, is about approximately an order of magnitude higher than practical for fiber-laser applications (Cavillon *et al.*, 2018a). Present loss values are believed to arise from both impurities in the precursor sources and scattering from nano-scale phase separation in the multicomponent glasses (Cavillon *et al.*, published online). Acceptably low losses (<20 dB/km) have been achieved in powder-derived core-glass optical fibers (Shibata *et al.*, 1980), so enhanced purification is certainly a route forward. Scattering from inhomogeneities in the glass is a trickier issue and depends, to first order, on composition. There is, therefore, a balance to be struck between composition, hence scattering and losses, and the reduction of parasitic nonlinearities when employing a materials-approach to their diminution as in Cavillon *et al.* (2018a).

Although comparable to their planar counterparts, the transmission losses in the crystalline semiconductor core fibers are also situated above practical values for a fiber platform, at around 1 dB/cm (Franz *et al.*, 2017). As most of this loss has been attributed to the polycrystalline nature of the core materials (scattering and absorption at the grain boundaries), recent advances in the post-processing of these fibers using both tapering and laser treatment methods offer a clear route for future loss reduction (Healy *et al.*, 2018). Further work will also need to consider the role of impurities in the starting core materials as well as optimizing the interfacial modifier layer to minimize oxygen contamination and cracking during the heating/cooling stages.

2. Interconnection

Despite their physical similarity to traditional all-silica-based fibers, coupling light efficiently into and out of the high refractive index cores of the MCM-derived fibers remains a difficult task. For the all-glass fibers, it may be possible to consider solutions such as integration with PCFs for mode area matching and the use of antireflection coatings to reduce interface losses. However, for the crystalline core structures, more innovative solutions will be needed, such as the tapered nano-spikes previously used for improving coupling to chalcogenide core/silica clad fibers (Granzow *et al.*, 2013). Indeed, integration between a crystalline silicon core MCM fiber and SMF has recently been demonstrated using this latter approach, as illustrated schematically in Fig. 4(a). Although the current coupling losses recorded via this integration method are around 4 dB, simulations indicate that this should be reduced to ~0.5 dB by further optimizing the core/clad ratio. Interestingly, the silicon core fibers could also act as an intermediary link to improve coupling between SMF, used for the mass transport of optical signals, and silicon waveguides on-chip, used in the construction of integrated optoelectronic circuits, as indicated in Fig. 4(b). Clearly, the ability to fully integrate the MCM fibers with a variety of infrastructures already in day-to-day use will greatly enhance the adoption of this technology.

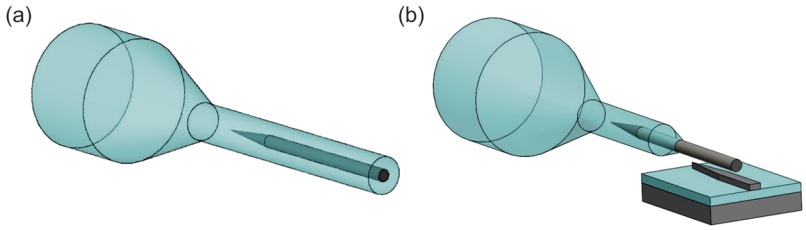

FIG. 4. Schematic images illustrating coupling schemes for semiconductor core fibers. (a) Coupling from SMF to a crystalline semiconductor core fiber via a tapered transition. (b) Coupling from SMF through a crystalline core fiber to an integrated waveguide on chip.

IV. CONCLUSIONS

This paper has reviewed the first 25 years of the molten core method (MCM) for fabricating optical fibers, with a goal to providing a general perspective as to their future prospects. The MCM is arguably the most versatile single approach to fabricating optical fibers from an extremely wide range of materials, i.e., both glassy and crystalline precursors that can result in either glass or crystalline core fibers. Such diversity enables an equally wide range of potential applications, some of which have already been realized while others are still to be. In addition to setting straight the historical record, inventorying key innovations, and defining a series of future challenges, this review took aim at generating excitement for the next quarter century of developments that will continue to advance the breadth of optical fiber material contributions to the field.

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