Novel Materials for Advanced Optical Fibers

John Ballato, Clemson University

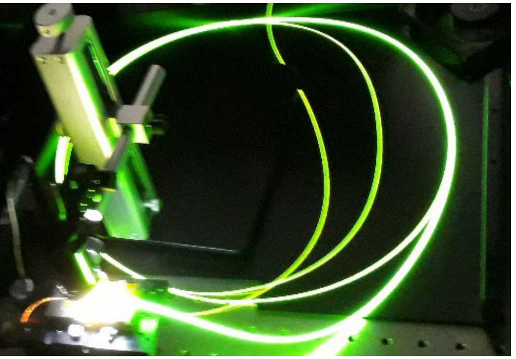
Fiber Modeling
and Fabrication
Technical Group

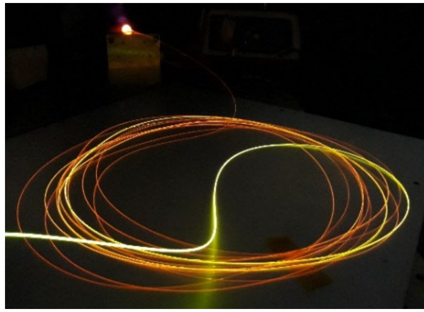
Fiber Modeling and Fabrication Technical Group

Welcomes You for the webinar on

“Novel Materials for Advanced Optical Fibers”

April *24 2020, 11 am EDT*





OSA Fiber Modeling and Fabrication Technical Group

About us: A unique group of more than 900 researchers from 70+ countries from North America, South America, Europe, Asia, Africa, and Oceania.

Goals:
To benefit **OSA members** having interest in Fiber Design, Modeling, Fabrication, and Applications of fibers.
To Provide a platform to Fiber Community for connecting, Engaging and Exciting with others.
To Organize Webinars, Technical and Networking Events, and Special Journal Issues.

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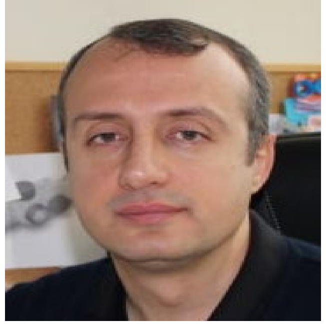
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Manish Sharma,
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Past Events:

1. Networking Event: Date: Tuesday, 16 Jul 2019 17:00-18:00
Location: Naupaka III, Waikoloa Beach Marriott Resort & Spa, Waikoloa Beach, Hawaii

2. Webinar 1: Everything you always wanted to know about supercontinuum modelling in optical fibers (but were afraid to ask) Date: 26th August 2019, at Swiss time 2pm/ EDT 8am
A/Prof. Alexander Heidt, University of Bern, Switzerland.

3. Webinar 2: The development of thulium and holmium fiber sources
Date: 30th September, 2019 at 1pm (UK time)/ EDT 7am
Dr. Nikita Simakov, DSTO, Australia.

4. Webinar 3: Recent development in hollow-core optical fiber
Date: 14 November, 2019, 8 am Beijing Time
A/Prof. Y Wang, Beijing University of Technology, China.

Many More to come shortly !!!!

OSA Fiber Modeling and Fabrication Technical Group

Events at CLEO San Jose, CLEO Pacific-Rim, and FIO USA !!!!

Current/Future Webinars:

Webinar 1: Integration of 2-dimensional materials in fiber optics for ultra-short pulse lasers
Date: 13th March 2020, 8 pm EDT.
Prof. Kyunghwan Oh, Yonsei University, South Korea.

Webinar 2: Novel Optical Materials for optical Fibers
Date: 24th April 2020, 11 am EDT.
Prof. John Ballato, Clemson University, USA.

Webinar 3: Mid-Infrared Supercontinuum Generation in Optical Fibers
Date: 20 May 2020, 10 am EDT.
Dr. Christian Petersen, Technical University of Denmark, Fotonik.

Webinar 4: Hybrid (M-type) fibers for dispersion management
Date: 18 September, 3 pm EDT.
Dr. Svetlana Aleshkina, Fiber Optics Research Center, Russian Academy of Sciences, Russia.

Fiber Modeling
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Technical Group

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You can contact me if you are interested in giving a Webinar/Talk/Panel Discussion, on **deepakjain9060@gmail.com**

Today’s Webinar

Fiber Modeling
and Fabrication
Technical Group

Novel Materials for Advanced Optical Fibers

Prof. John Ballato, Clemson University

Speaker’s Short Bio: John Ballato is a professor of materials science and engineering at Clemson University (Clemson, SC USA) where he holds the Sirrine Endowed Chair of Optical Fiber. A Fellow of the OSA, IEEE, AAAS, SPIE, and ACerS, Ballato has over 425 publications, 35 US and foreign patents, and is an elected member of the World Academy of Ceramics (limited to < 300 members world-wide) and the US National Academy of Inventors (NAI). His collaborative work on Anderson localizing optical fiber was selected as one of the Top Ten Breakthroughs of 2014 by Physics World (Institute of Physics, IoP).

CLEMSON UNIVERSITY
COMSET
CENTER FOR OPTICAL MATERIALS SCIENCE + ENGINEERING TECHNOLOGIES

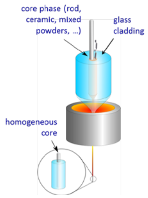
Novel Materials for Advanced Optical Fibers

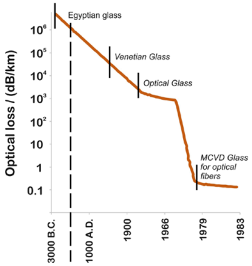
John Ballato

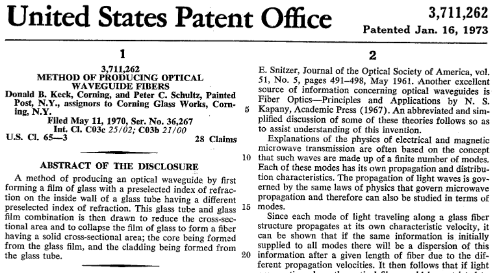
Sirrine Endowed Chair of Optical Fiber and Professor
Department of Materials Science and Engineering
Clemson University, Clemson, SC

Outline

- Background
  - Trends
  - Optical fiber material options
- Exemplars
  - Advanced SiO_2 fibers
  - Semiconductor core fibers
- A fun future…
- Conclusions
- Extra / background slides
  - Material family basics
  - Fiber fabrication approaches
  - Suggested reading







United States Patent Office 3,711,262
Patented Jan. 16, 1973

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METHOD OF PRODUCING OPTICAL WAVEGUIDE FIBERS
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Filed May 11, 1970, Ser. No. 36,267
Int. Cl. C03c *25/02*; C03b *21/00*
U.S. Cl. 65—3 28 Claims

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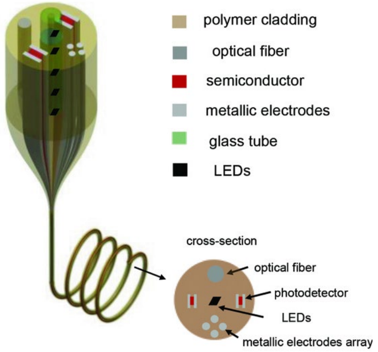

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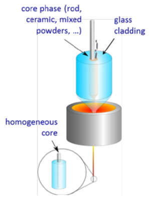

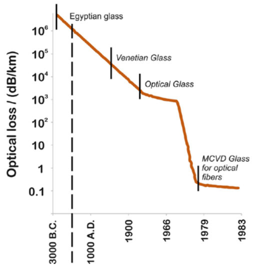

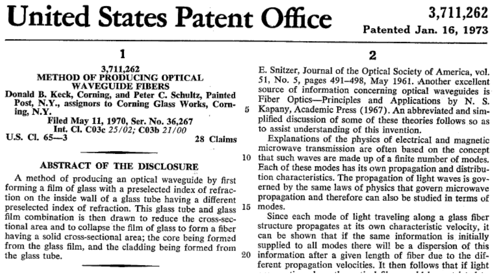

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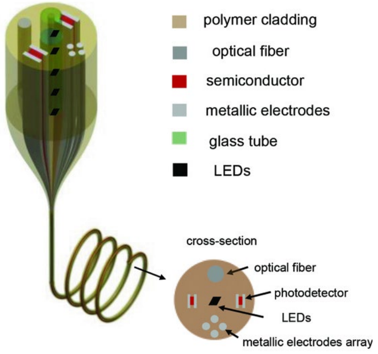
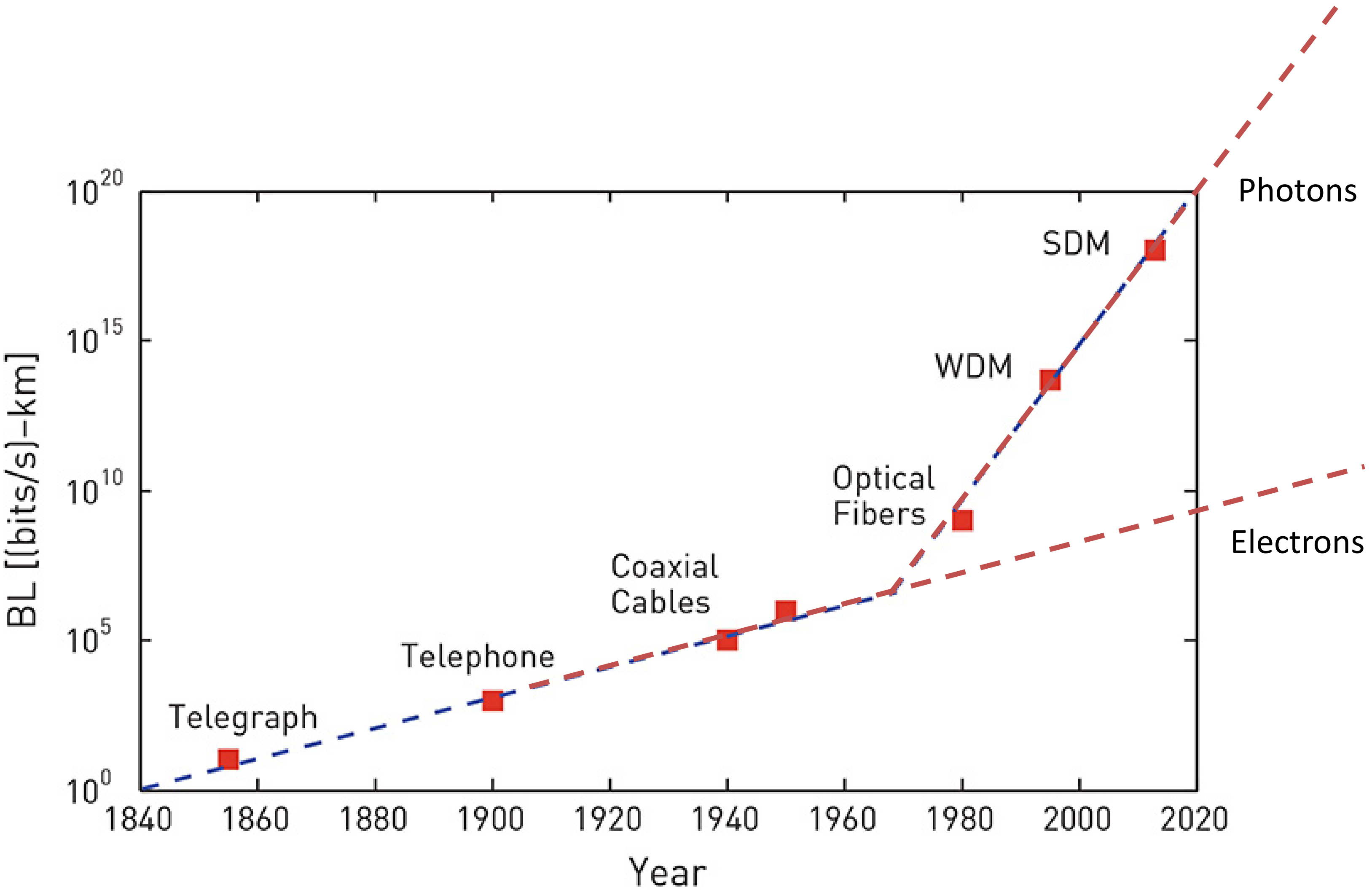
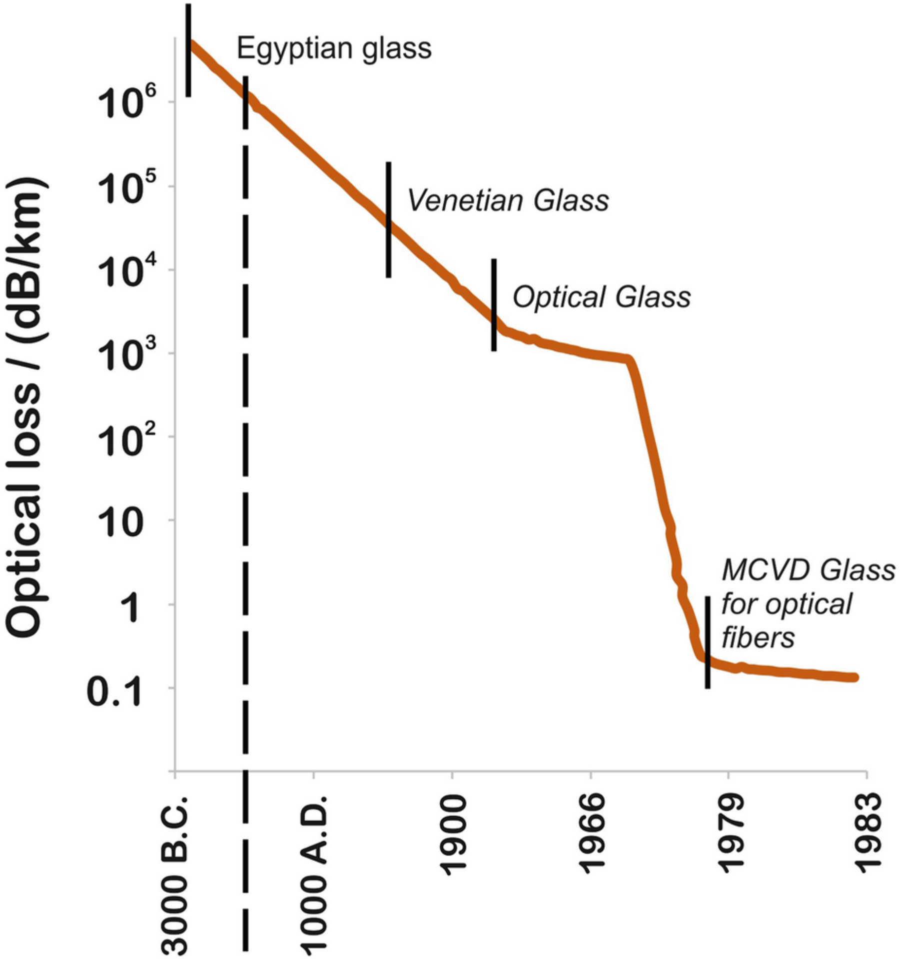


Trends… performance



After G. Agrawal, “Optical communication: Its history and recent progress,” in *Optics in Our Time*, M.D. Al-Amri et al., eds. (Springer, 2016).

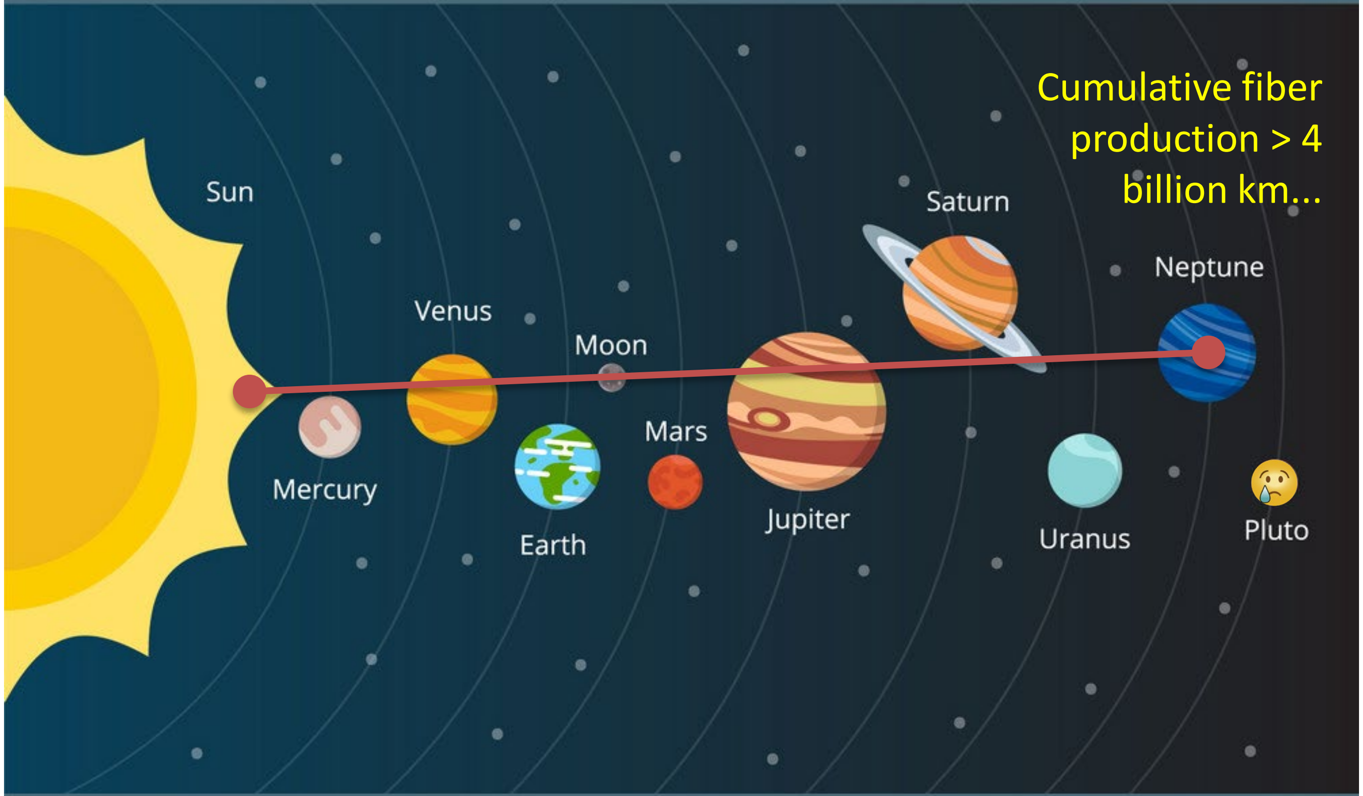
Trends… purity



V. Romano, S. Pilz, and H. Najafi, “Powder Process for Fabrication of Rare Earth-Doped Fibers for Lasers and Amplifiers,” in *Handbook of Optical Fibers*, G. D. Peng, ed. (Springer, Singapore, 2018).

Trends… production

~ 500 M·km fiber demand in 2017; 17% CAGR from 2005 – 2017.

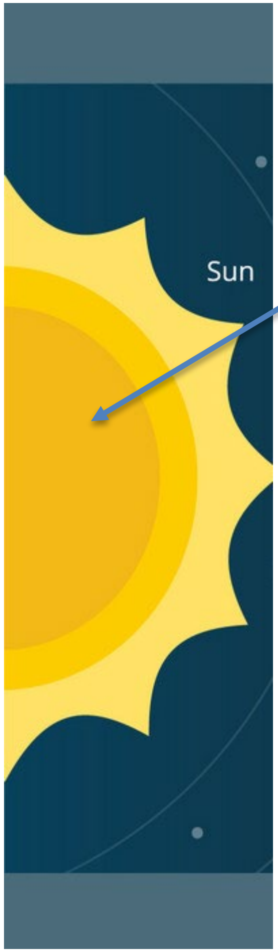


Cumulative fiber production > 4 billion km…

Background graphic from vectorstock.com/18926506; distance data c/o Corning Incorporated (2018).

Trends… power

$$\text{Power Density} = \frac{\text{Power}}{\text{Area}}$$



Sun's surface area: 6.1 × 10^{12} km^2 = 6.1 × 10^{18} m^2
Sun's radiant power ~ 385 yotta W (3.85 × 10^{26} W)

Sun's (surface) power density: 6.3 × 10^7 W/m^2

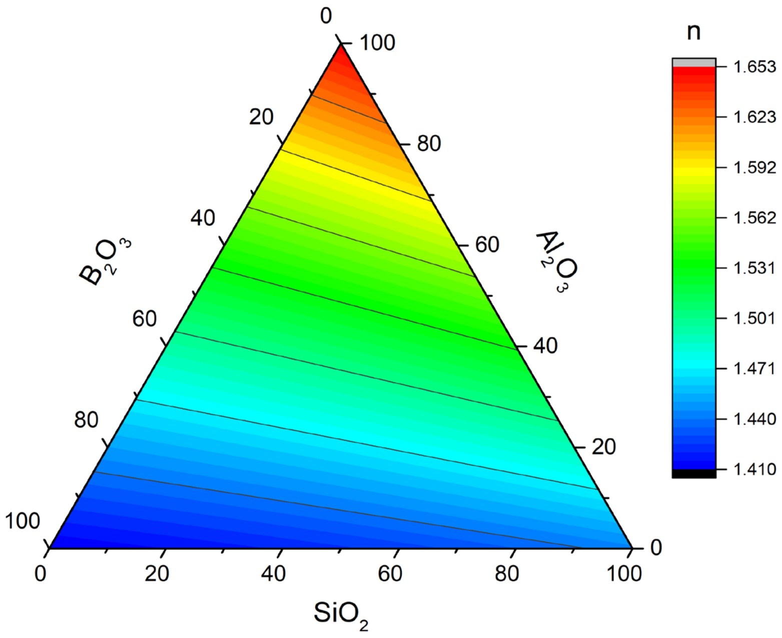
Core area (25 μm): 490 μm^2 = 4.9 × 10^{-10} m^2
Laser output power: 10 kW = 10^4 W

Commercial fiber laser power density: 2 × 10^{13} W/m^2

> 3 × 10^5 times brighter!

Commercial 10 kW fiber laser

Background graphic from vectorstock.com/18926506.



Ballato's musings…

- Staggering growth in use of optical fiber, driven by wide range of commodity (e.g., telecom) and specialty (e.g., HEL) applications.

- Continued progress in all applications requires continued advancements in the properties and performance of optical fiber.

- How materials uniquely influence fiber properties and performance is the focus of this webinar!

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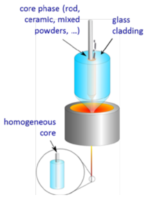

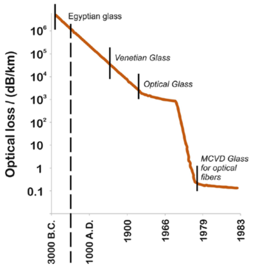

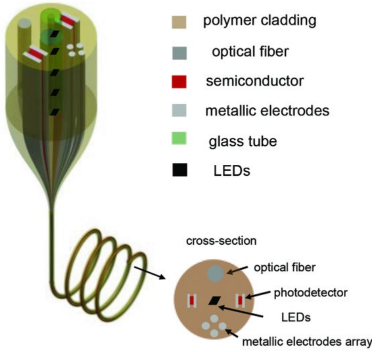

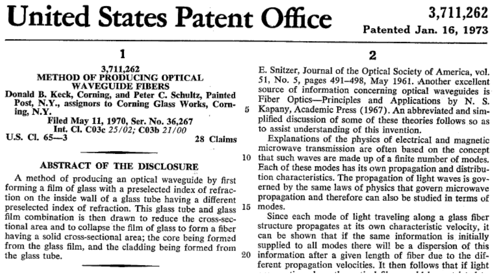

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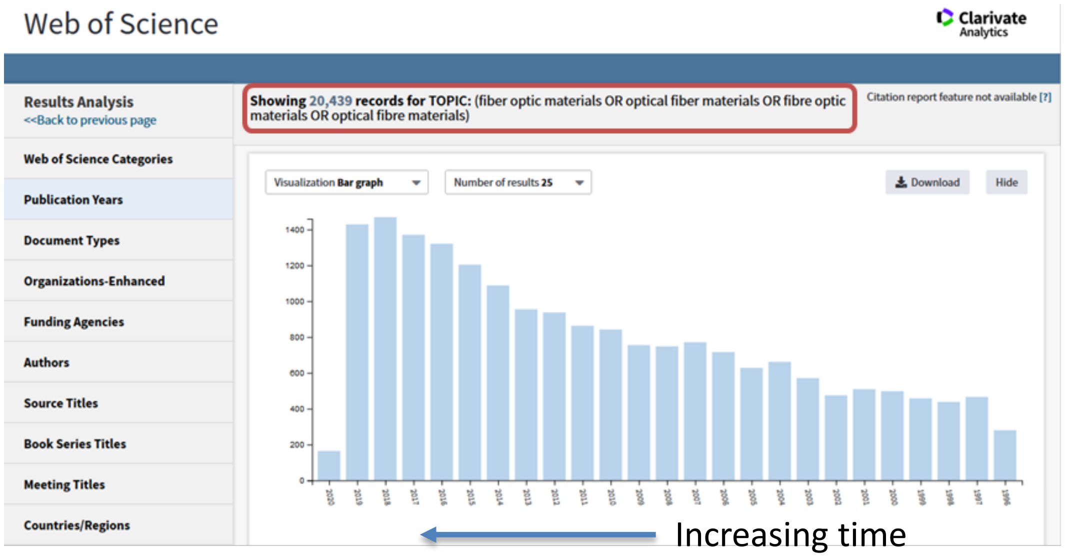
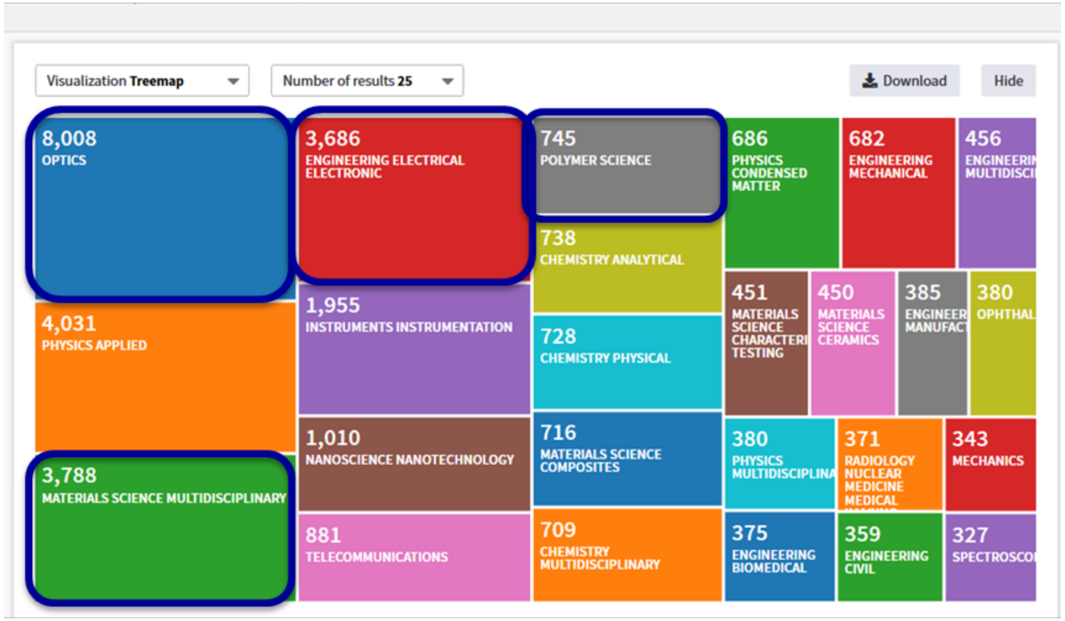
Optical fiber materials



Showing 20,439 **records for TOPIC:** (fiber optic materials OR optical fiber materials OR fibre optic materials OR optical fibre materials)



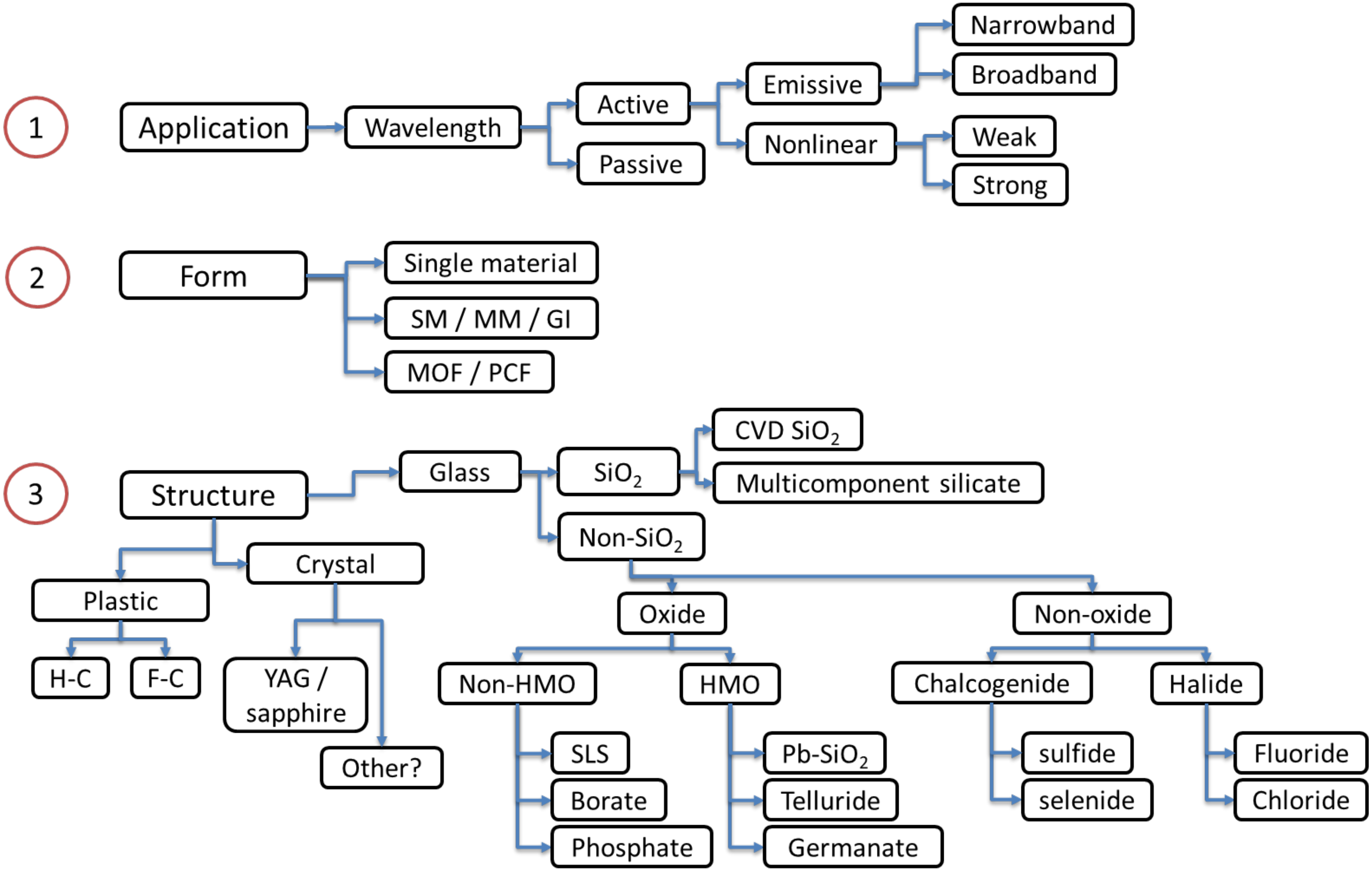
Ballato observations / musings…

- 20,500 publications since 1996… and growing steadily.
- Virtually all nations around the globe (not shown).
- Nearly 12,000 out of 20,500 (**57%**) are in “optics” or “electrical engineering”… no offense, but, IMHO, they know very little materials science.
- The more sophisticated the fiber / application, the more critical it is to understand the underlying / enabling materials science and fiber fabrication.

Web of Science; accessed 12 March 2020.

Optical fiber material options

Not meant to be complete… but is meant to be confusing, which is the point…



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- Application
  - Wavelength
    - Active
      - Emissive
        - Narrowband
        - Broadband
      - Nonlinear
        - Weak
        - Strong
    - Passive

2
- Form
  - Single material
  - SM / MM / GI
  - MOF / PCF

3
- Structure
  - Glass
    - SiO_2
      - CVD SiO_2
      - Multicomponent silicate
    - Non-SiO_2
      - Oxide
        - Non-HMO
          - SLS
          - Borate
          - Phosphate
        - HMO
          - Pb-SiO_2
          - Telluride
          - Germanate
      - Non-oxide
        - Chalcogenide
          - sulfide
          - selenide
        - Halide
          - Fluoride
          - Chloride
  - Plastic
    - H-C
    - F-C
  - Crystal
    - YAG / sapphire
    - Other?

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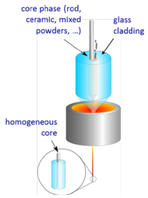

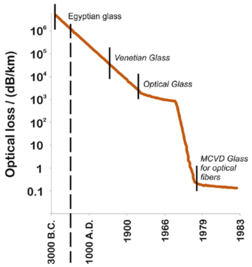

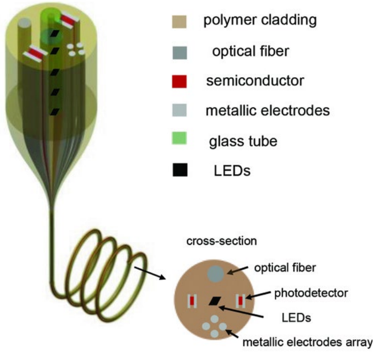

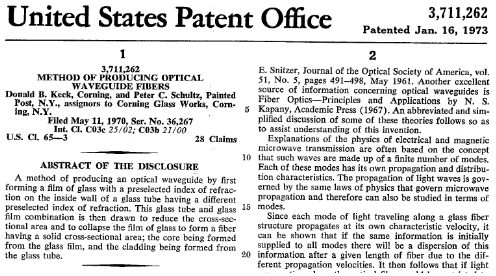

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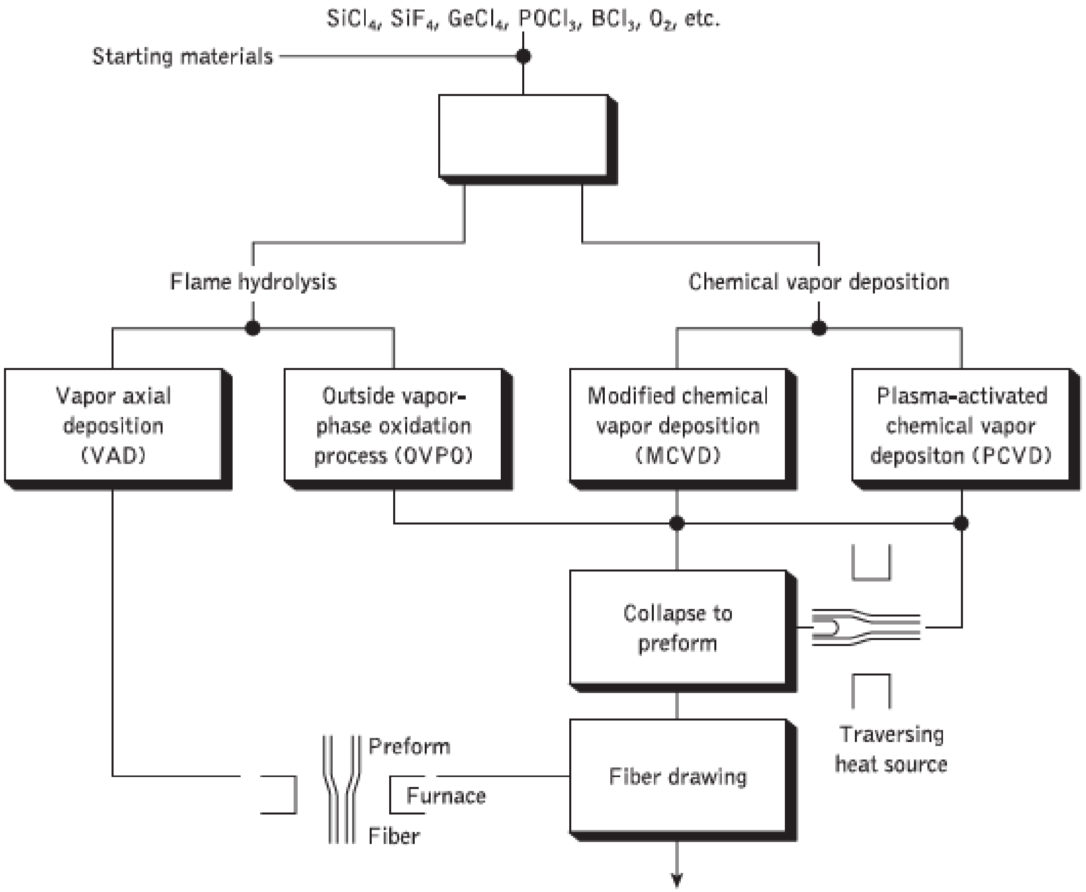
Vapor deposition techniques



- Silica-based fibers are enabled by one of 4 main vapor deposition processes.
- They employ the same base chemistry, though the deposition approach and process conditions are different.

$$SiCl_4 + O_2 \rightarrow SiO_2 + 2Cl_2$$

$$GeCl_4 + O_2 \rightarrow GeO_2 + 2Cl_2$$

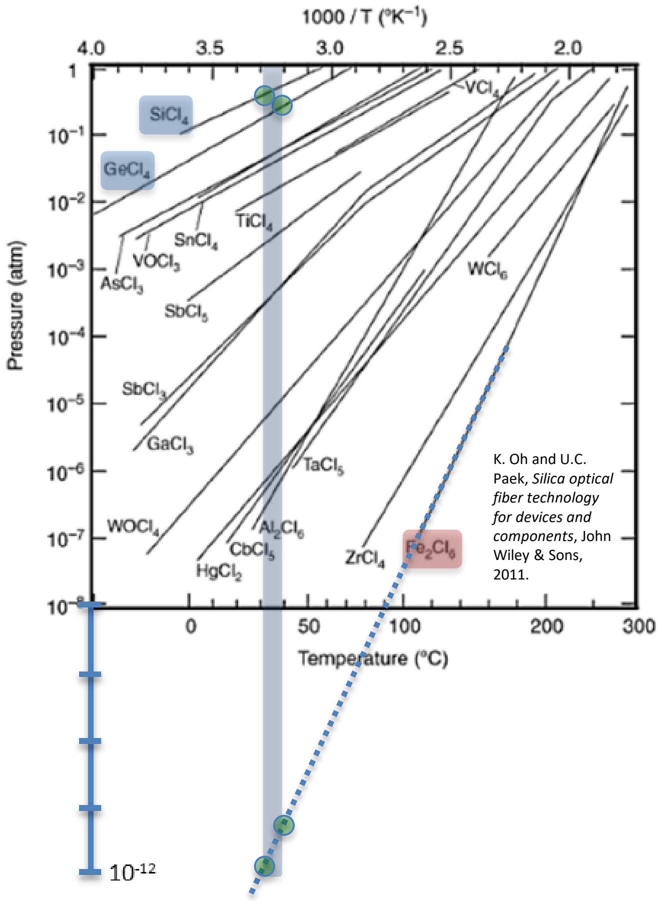
$$4POCl_3 + \ 3O_2 \rightarrow 2P_2O_5 + 6Cl_2$$

$$4BCl_3 + \ 3O_2 \rightarrow 2B_2O_3 + 6Cl_2$$

J. Senior, *Optical Fiber Communications: Principles and Practice*, 3rd ed., pp. 177 (2009).

Vapor deposition techniques

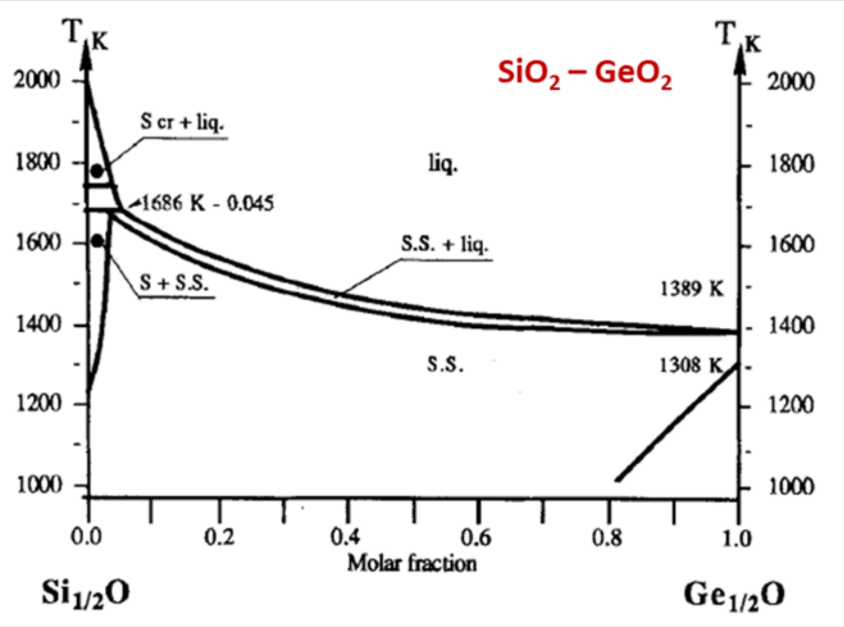
- Development of long-haul telecommunication networks drove need for glass processing approach with potential for very low (intrinsic) loss.
- Central to CVD processes is the difference in vapor pressures between species we want (precursors to SiO_2, GeO_2, etc) and those we don't (Fe, Cu, etc.).
- Differential VP is ~ 11 orders of magnitude (!!), which leads to a "self-purification" of the precursor vapor from the (already purified) liquid source.
- This is the fundamental origin of the low loss potential of CVD silica and what led to the realization of Kao's < 20 dB/km prediction and the development of long haul global communication networks.
- Record loss ~ 0.14 dB/km today: Tamura, et al., "The first 0.14-dB/km loss optical fiber and its impact on submarine transmission," *Journal of Lightwave Technology* **36**, 44 – 49 (2018).

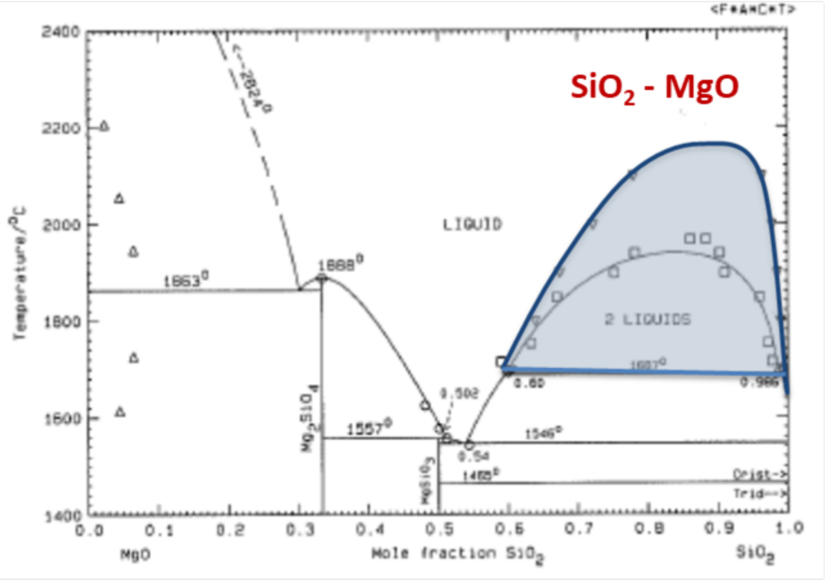


K. Oh and U.C. Paek, *Silica optical fiber technology for devices and components*, John Wiley & Sons, 2011.

Optical Fiber (as you know it)

- Necessarily restricted to compounds that can be added to silica and form a **“good” glass**… stable upon thermal cycling 800 °C > T > 2200 °C and time …

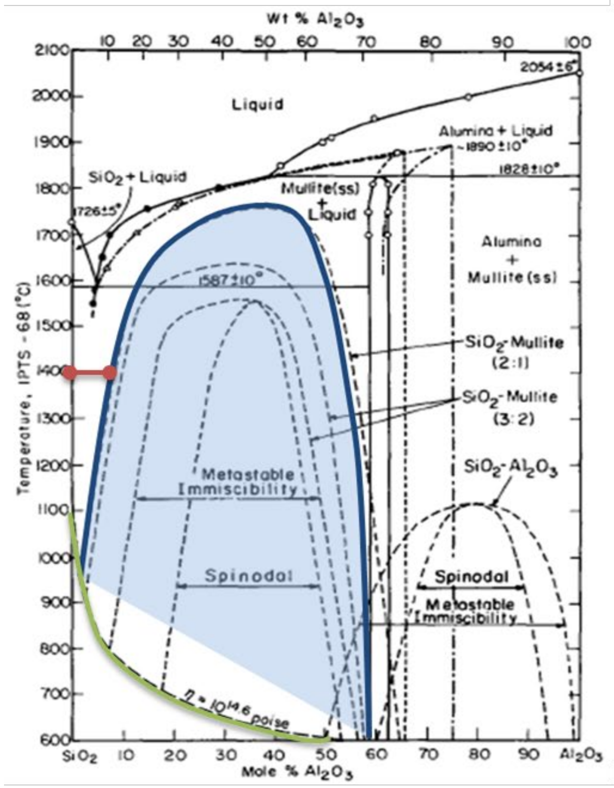


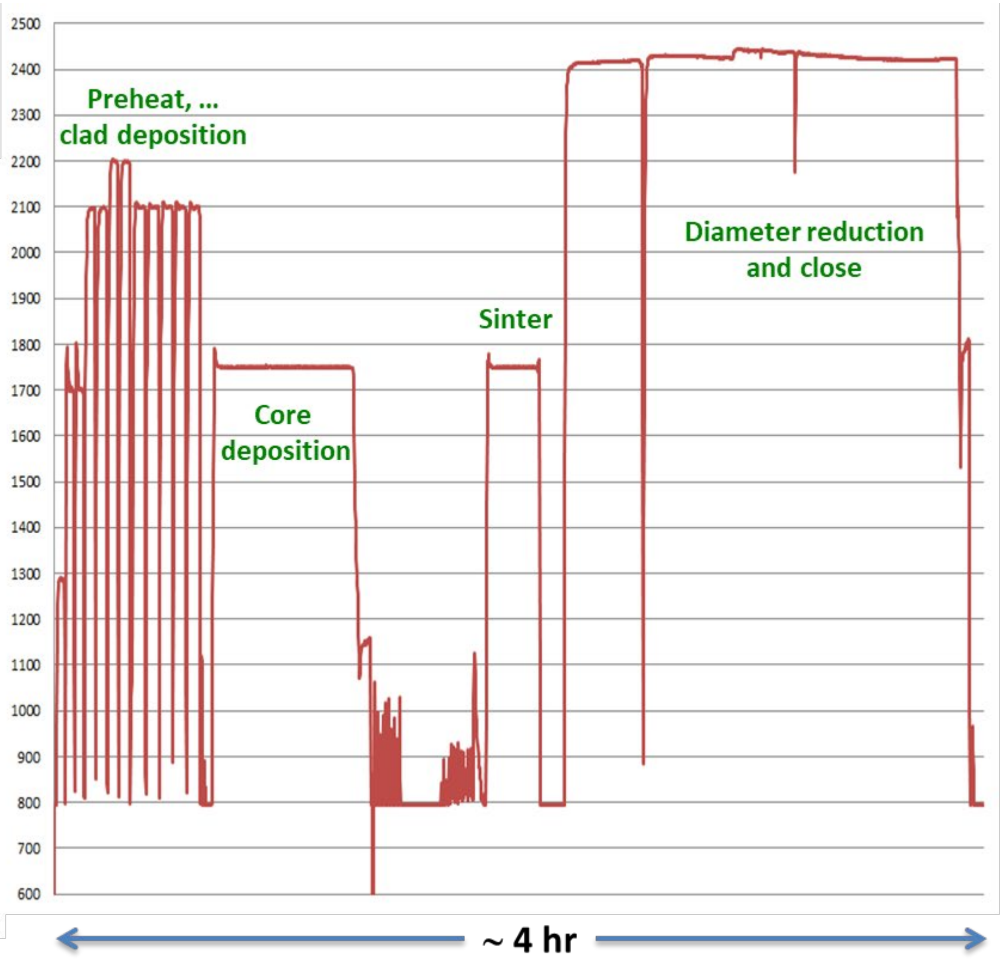


pre-Google

F. Kracek, “The cristobalite liquids in the alkali oxide-silica systems …,” Am. J. Sci. 52, 1436 – 1442 (**1930**).

Optical Fiber (as you know it)

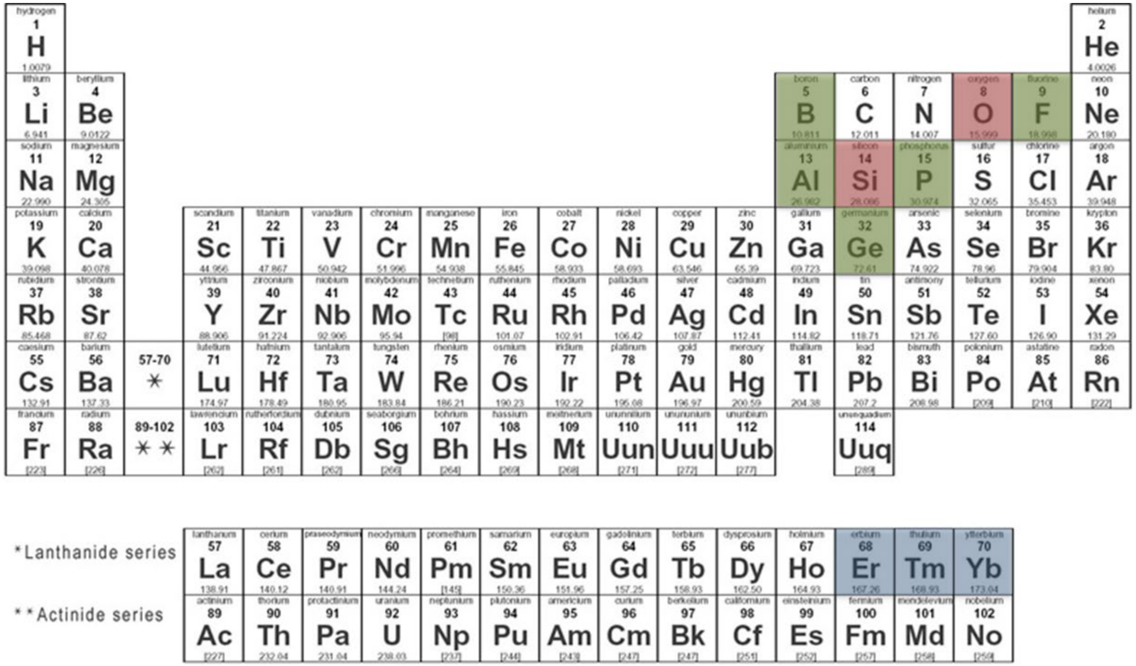




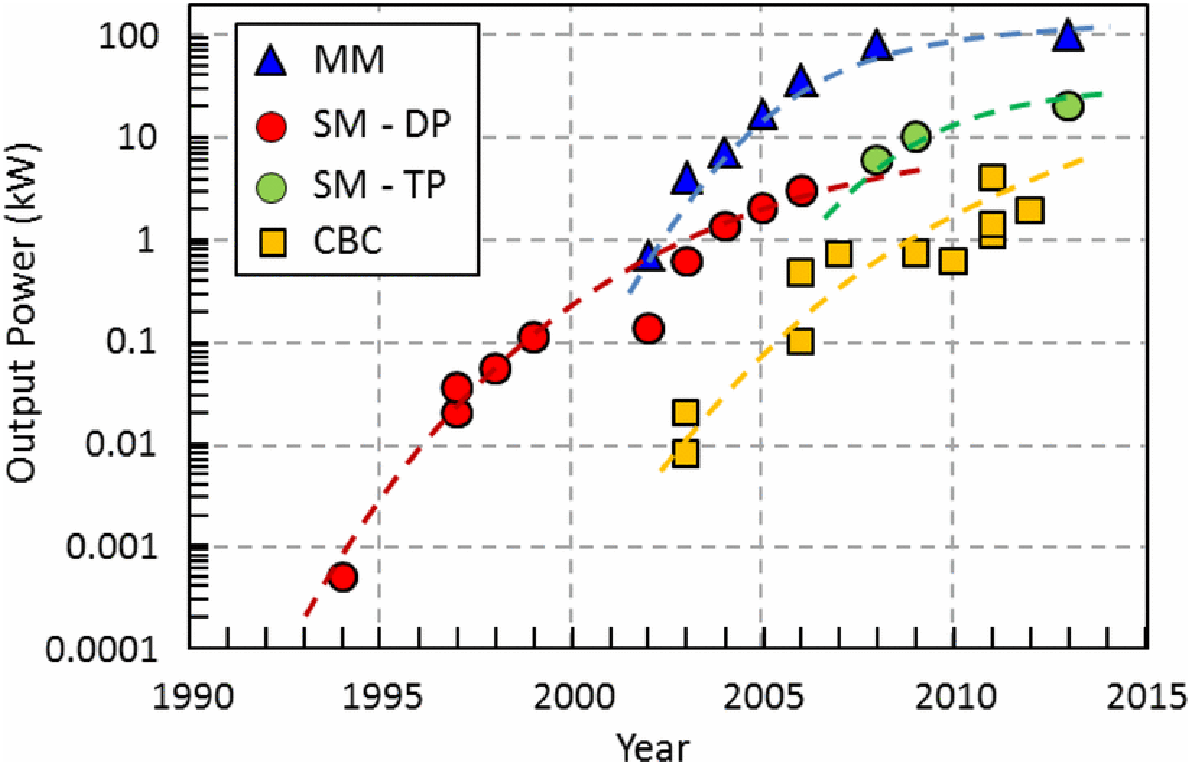
- One really needs to understand the underlying materials science to unleash the full potential of the periodic table on fiber properties and performance.

But… (and there's always a but…)…

1. Silica is amazing… but is limited in what can be doped into it.
2. MCVD / OVD / VAD further limit range of silicate compositions; greatly restricts material, hence property richness.



Another but… trend… power



M. Zervas and C. Codemard, *IEEE J. Sel. Topics Quant. Electron.* **20**, 219 – 241 (2014); Legend: MM: multimode; SM-DP: single-mode, diode pumped; SM-TP: single-mode, tandem pumped; and CBC: coherent beam combination.

Nonlinearities in optical fiber…

SBS

- **The Effect**: interaction between acoustic phonons and the optical signal through Brillouin scattering. Interference between the forward-propagating signal and back-scattered light creates a highly-efficient reflector to the optical signal.
- **The Problem**: limits the power per unit bandwidth and is a major limitation in the scaling to higher powers.

SRS

- **The Effect**: interaction between optical signal and optical phonons through Raman scattering causing a shift in signal wavelength.
- **The Problem**: parasitic effect in high-peak-power fiber lasers where wavelength control is mandatory.

HOMI (TMI)

- **The Effect**: Modal interaction driven by the thermo-optic coefficient, dn/dT.
- **The Problem**: At some threshold power, beam modal distribution randomizes and becomes dynamic.

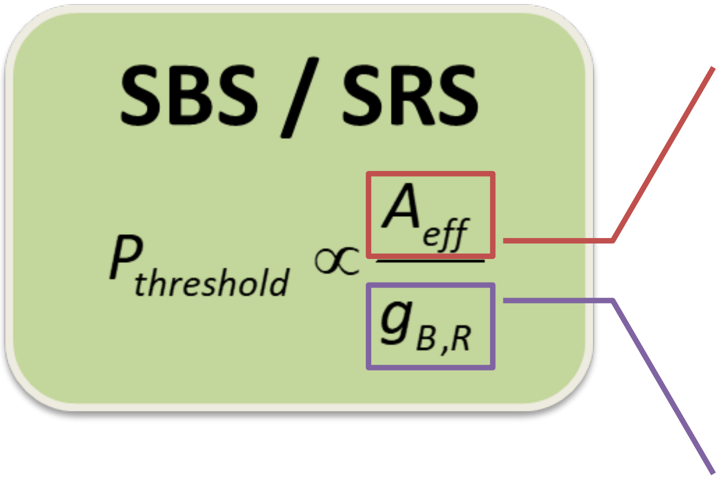
n_2-Related Effects

- **The Effect**: Nonlinear processes, such as SPM and FWM, arise from $n(I) = n_o + n_2 I$.
- **The Problem**: broadens and modifies optical spectrum; undesirable in high peak power laser systems.

Thermal Limitations

- **The Effect**: Thermal fracture and melting of core.
- **The Problem**: Thermal fracture and melting of core…

Nonlinearities in optical fiber…



SBS / SRS

$$P_{threshold} \propto \frac{\boxed{A_{eff}}}{\boxed{g_{B,R}}}$$

Conventional Approach

- Make A_{eff} bigger (LMA…) and control modes through fiber design / structure… i.e., MOFs and / or PCFs…
- But… more complex, low yield, and <u>unintended consequences</u>; e.g., TMI.

Materials Approach

- Let the material do the work for you… the most fundamental of approaches.
- Affords simplicity… conventional core / clad fiber design.

The materials science of optical nonlinearities

Brillouin scattering

$$P_S^{SpBS} \propto n^8 p_{12}^2 K_S$$

Rayleigh scattering

$$P_{S,density}^{Rayleig\ h} \propto n^8 p^2 T_f K_S(T)$$

Rayleigh scattering

$$P_{S,composition}^{Rayleig\ h} \propto \left(\frac{\partial \epsilon}{\partial C}\right)_{P,T}^2 \frac{C(1-C)T}{(T-T_s)}$$

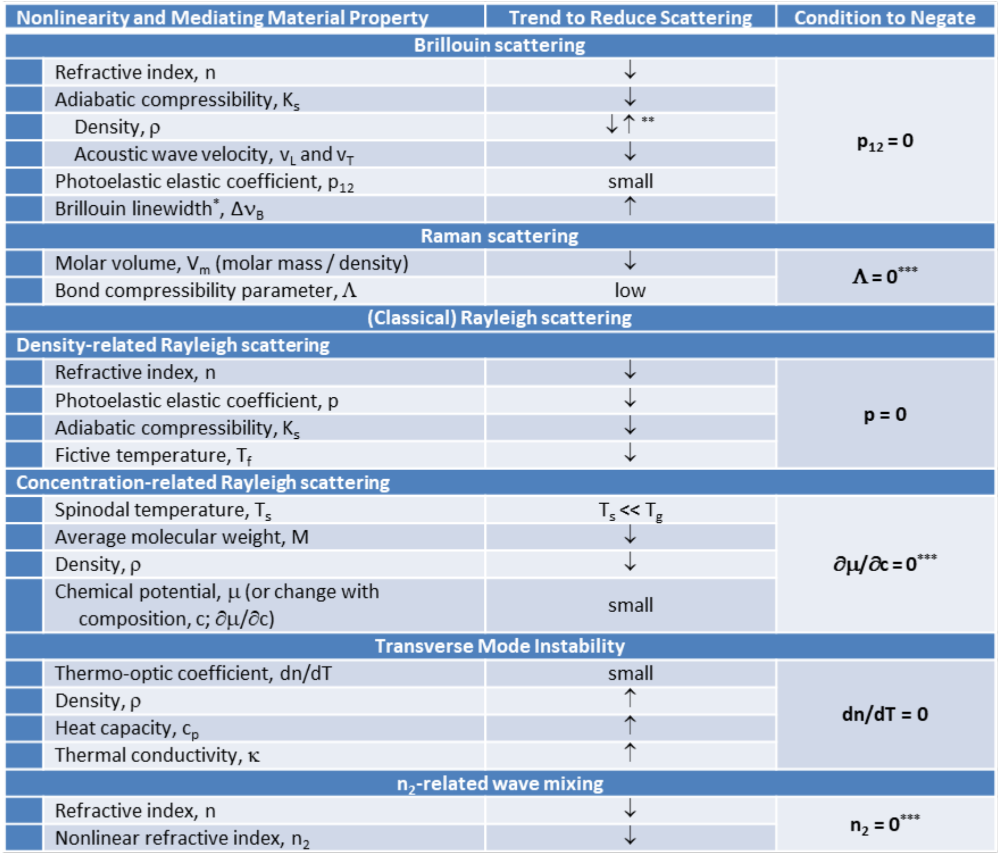
Raman scattering

$$P_S^{Raman} \propto V_m \cdot \Lambda^2$$

Transverse Mode Instability

$$P_{TMI} \propto \frac{dn/dT}{\rho \cdot c_p}$$

Material origins of optical nonlinearities and property trends to reduce their impact



Nonlinearity and Mediating Material Property	Trend to Reduce Scattering	Condition to Negate
Brillouin scattering		
Refractive index, n	↓	**$p_{12} = 0$**
Adiabatic compressibility, K_s	↓	
Density, ρ	↓↑ **	
Acoustic wave velocity, v_L and v_T	↓	
Photoelastic elastic coefficient, p_{12}	small	
Brillouin linewidth*, $\Delta\nu_B$	↑	
Raman scattering		
Molar volume, V_m (molar mass / density)	↓	**$\Lambda = 0^{***}$**
Bond compressibility parameter, Λ	low	
(Classical) Rayleigh scattering		
Density-related Rayleigh scattering		
Refractive index, n	↓	**p = 0**
Photoelastic elastic coefficient, p	↓	
Adiabatic compressibility, K_s	↓	
Fictive temperature, T_f	↓	
Concentration-related Rayleigh scattering		
Spinodal temperature, T_s	$T_s << T_g$	**$\partial\mu/\partial c = 0^{***}$**
Average molecular weight, M	↓	
Density, ρ	↓	
Chemical potential, μ (or change with composition, c; ∂μ/∂c)	small	
Transverse Mode Instability		
Thermo-optic coefficient, dn/dT	small	**dn/dT = 0**
Density, ρ	↑	
Heat capacity, c_p	↑	
Thermal conductivity, κ	↑	
n_2-related wave mixing		
Refractive index, n	↓	**$n_2 = 0^{***}$**
Nonlinear refractive index, n_2	↓	

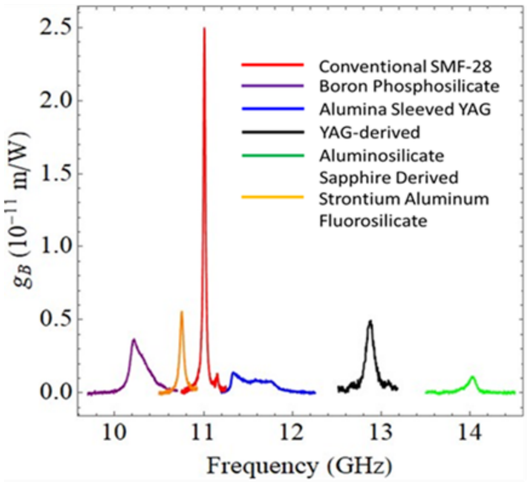
This is the power of a materials approach to reducing parasitic nonlinearities.

The materials science of optical nonlinearities

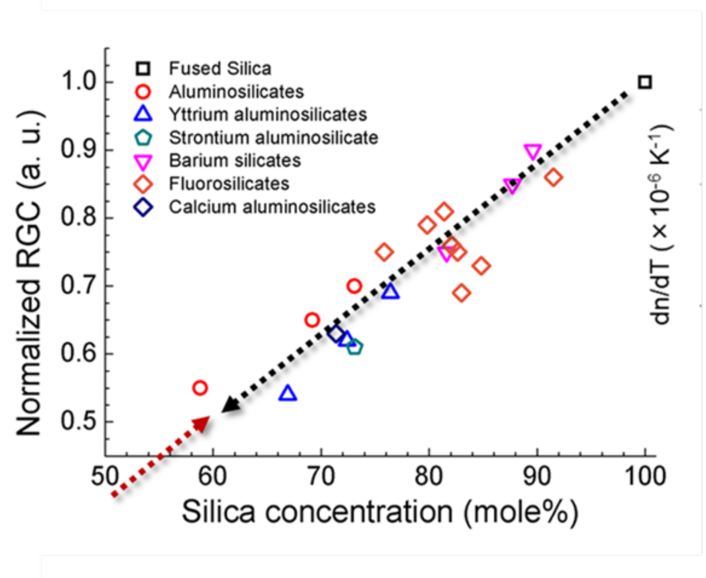
Compound	Physical**				Brillouin**		STRS**	Raman**	Wave-Mixing**
	n	ρ	CTE	V_a	$\Delta\nu_B$	p_{12}	dn/dT	V_m	n_2
SiO_2***	1.444	2200	0.55×10^{-6}	5970	17	0.226	10.4×10^{-6}	27.31	2.5×10^{-20}
GeO_2	↑	↑	↑	↓	↑	↑	↑	↑	↑
F	↓	↓	↑	↓			↓		↓
P_2O_5	↑	↑	↑	↓	↑	↑	↓	↑	
B_2O_3	↓	↓	↑	↓	↑	↑	↓	↑	
Al_2O_3	↑	↑	↑	↑	↑	↓	≈	↑	↑
Yb_2O_3	↑	↑		↓		↓		↑	
La_2O_3	↑	↑		↓		↓		↑	
Lu_2O_3	↑	↑		↓		↓		↑	
MgO	↑	↑	↑	↑				↓	
CaO	↑	↑	↑						
SrO	↑	↑	↑	↓	↑	↓	↓	↓	
BaO	↑	↑	↑	↓	↑	↓	↑	↑	
Li_2O	↑	↑	↑	↑		↓	↓	↓	
Na_2O	↑	↑	↑				↓		
K_2O	↑	↑	↑				↓		
$Y_3Al_5O_{12}$	↑	↑		↑	↑	↓		↑	

The materials science of optical nonlinearities

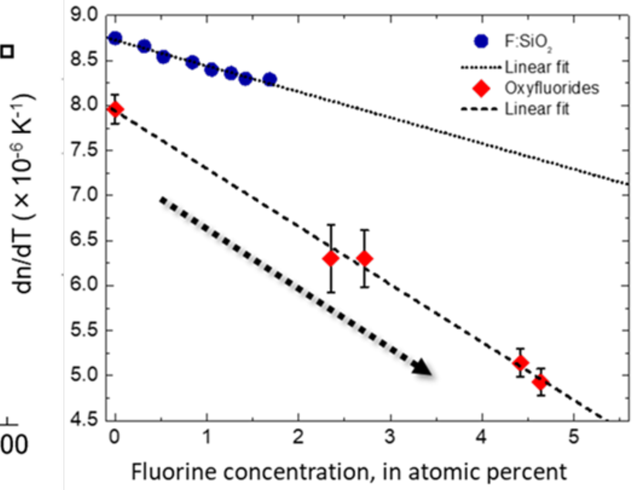
SBS



SRS



TMI



Measured reductions in relevant materials coefficients:

- Brillouin gain coefficient: - 5 – 15 dB; as low as > - 20 dB
- Raman gain coefficient: - 3 dB
- Thermo-optic coefficient: - 3 dB

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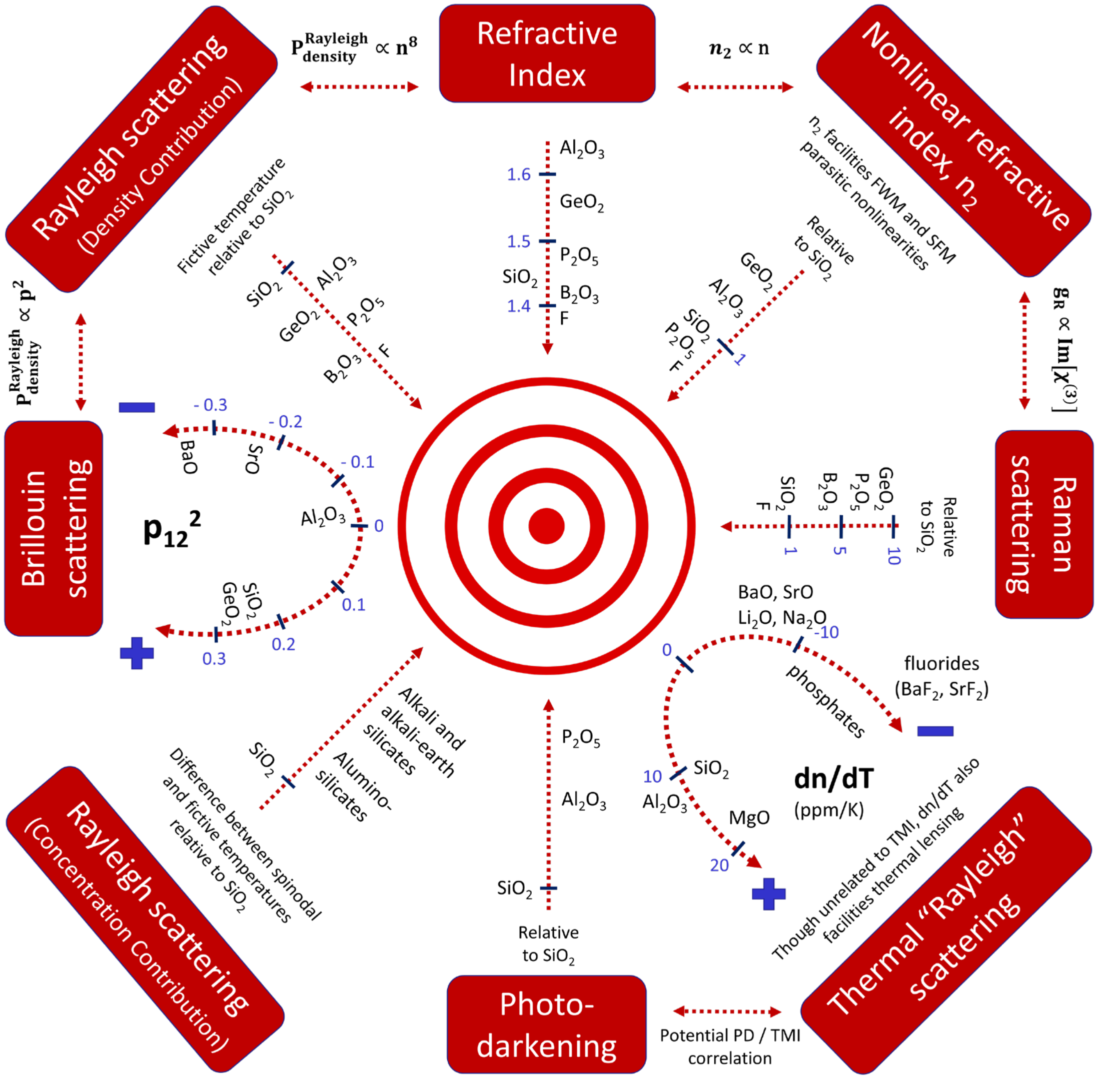
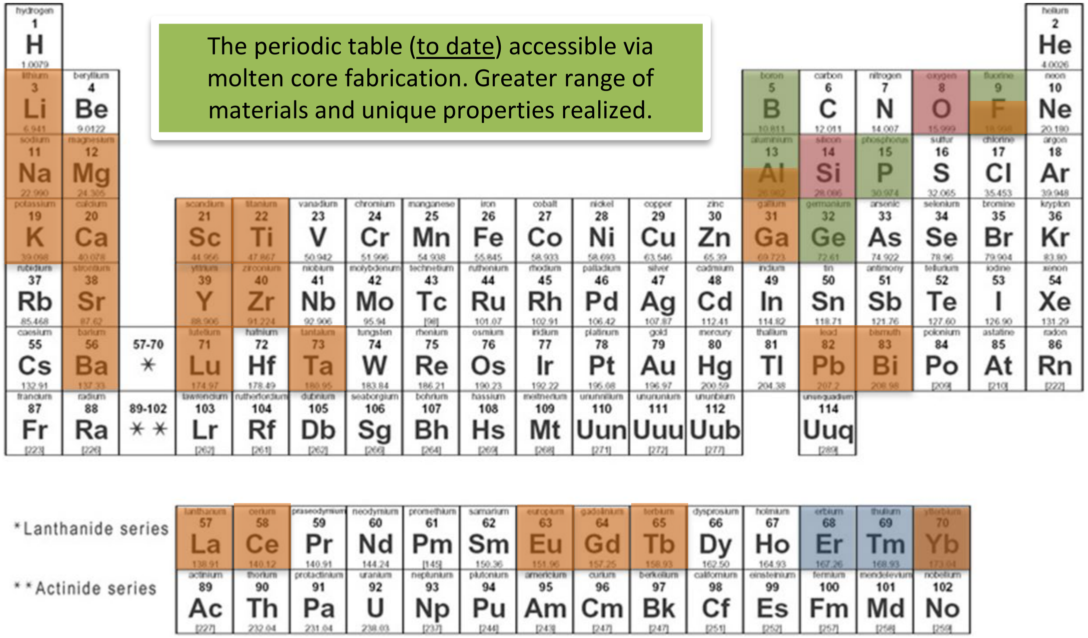
The materials science of optical nonlinearities



The materials science of optical nonlinearities

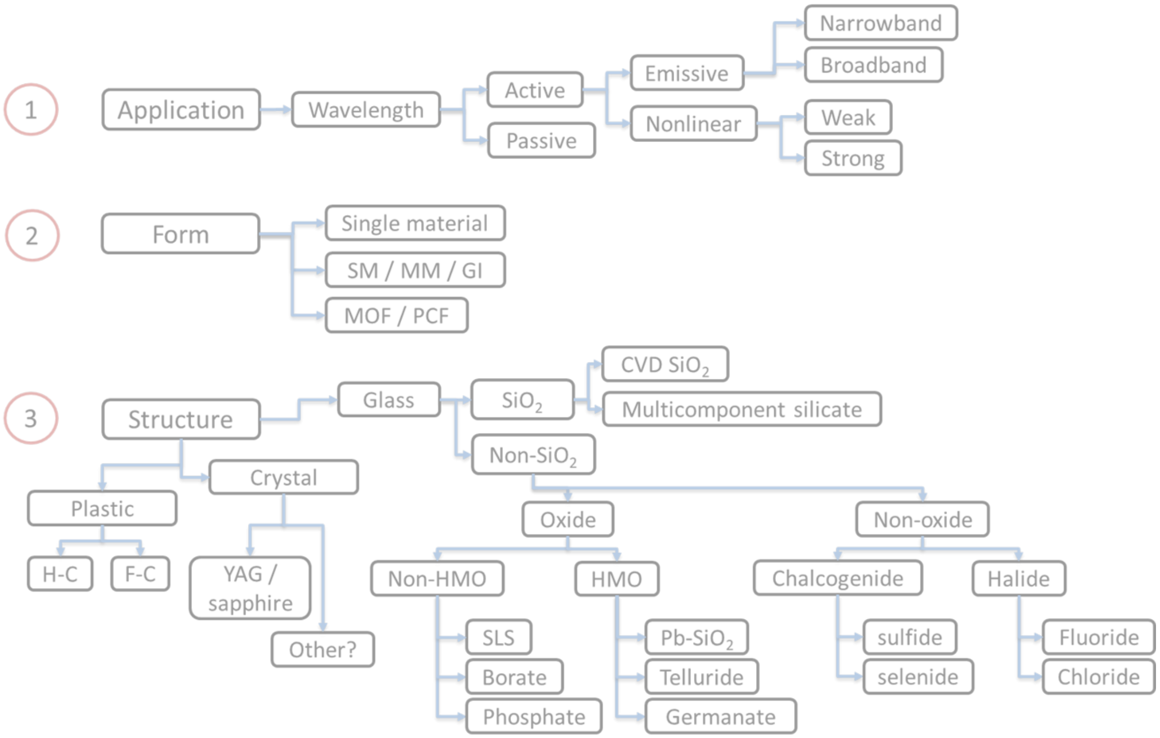


The periodic table (<u>to date</u>) accessible via molten core fabrication. Greater range of materials and unique properties realized.

- Opening up the periodic table…
- Deeper understanding of the enabling optical materials science has permitted novel glass science AND enables new optical physics and applications.

- Record low Brillouin scattering and reduced Raman scattering; working towards dn/dT and n_2-related effects for HEL applications.
- Athermal and atensic compositions, previously unknown, open new doors for sensing.
- *Materials offer simpler solutions than complex geometries!*

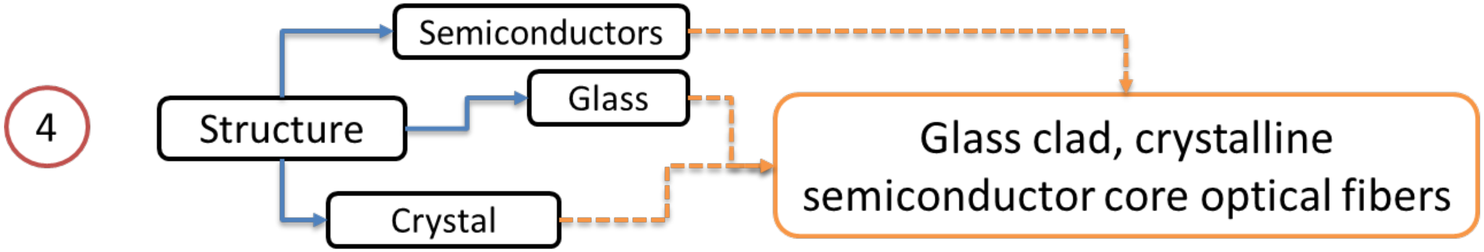
Optical fiber material options



① Application
- Wavelength
  - Active
    - Emissive
      - Narrowband
      - Broadband
    - Nonlinear
      - Weak
      - Strong
  - Passive

② Form
- Single material
- SM / MM / GI
- MOF / PCF

③ Structure
- Glass
  - SiO_2
    - CVD SiO_2
    - Multicomponent silicate
  - Non-SiO_2
    - Oxide
      - Non-HMO
        - SLS
        - Borate
        - Phosphate
      - HMO
        - Pb-SiO_2
        - Telluride
        - Germanate
    - Non-oxide
      - Chalcogenide
        - sulfide
        - selenide
      - Halide
        - Fluoride
        - Chloride
- Crystal
  - YAG / sapphire
  - Other?
- Plastic
  - H-C
  - F-C

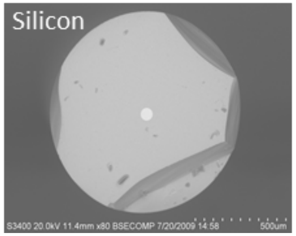


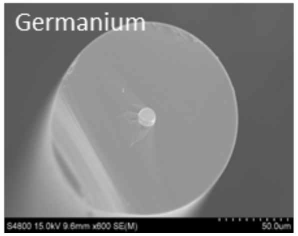
④ Structure
- Semiconductors
- Glass
- Crystal

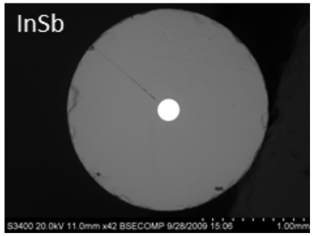
→ Glass clad, crystalline semiconductor core optical fibers

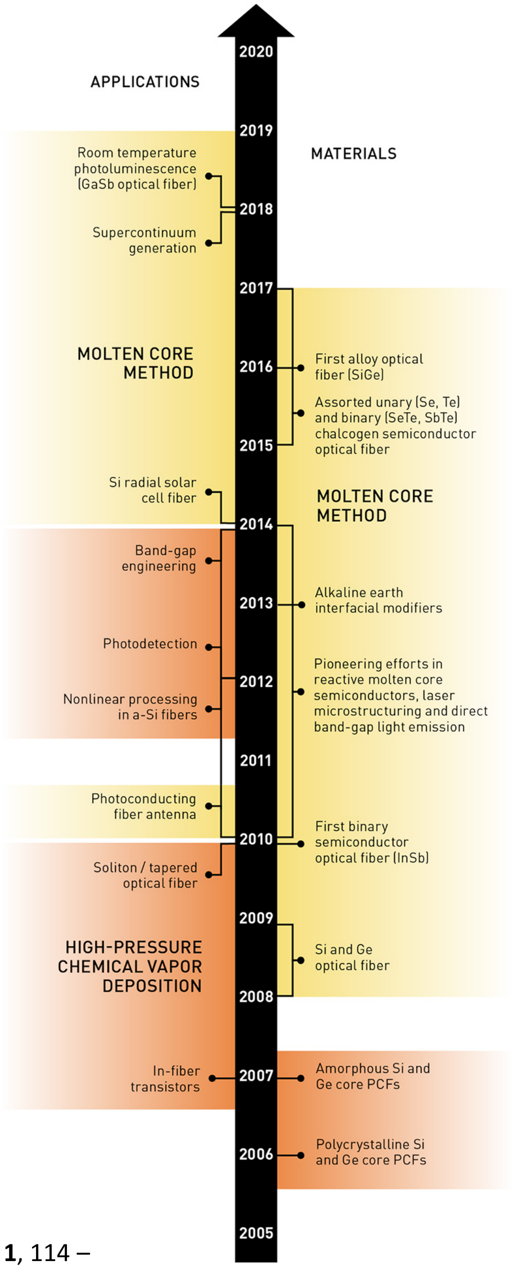
Semiconductor optical fiber

- Glass clad, crystalline semiconductor core optical fibers is a great example of materials science and engineering at play since they really shouldn't exist.
    - *Si melted inside SiO_2 at 600K above its melting point and quenched quickly yet still highly crystalline*.
- Unary, binary, and ternary systems permit significant practical value (mid-IR transmission and very strong nonlinearities). Plus the whole field is only about 15 years old so still nascent and opportunities to learn.









APPLICATIONS

Room temperature photoluminescence (GaSb optical fiber)

Supercontinuum generation

MOLTEN CORE METHOD

Si radial solar cell fiber

Band-gap engineering

Photodetection

Nonlinear processing in a-Si fibers

Photoconducting fiber antenna

Soliton / tapered optical fiber

HIGH-PRESSURE CHEMICAL VAPOR DEPOSITION

In-fiber transistors

MATERIALS

First alloy optical fiber (SiGe)

Assorted unary (Se, Te) and binary (SeTe, SbTe) chalcogen semiconductor optical fiber

MOLTEN CORE METHOD

Alkaline earth interfacial modifiers

Pioneering efforts in reactive molten core semiconductors, laser microstructuring and direct band-gap light emission

First binary semiconductor optical fiber (InSb)

Si and Ge optical fiber

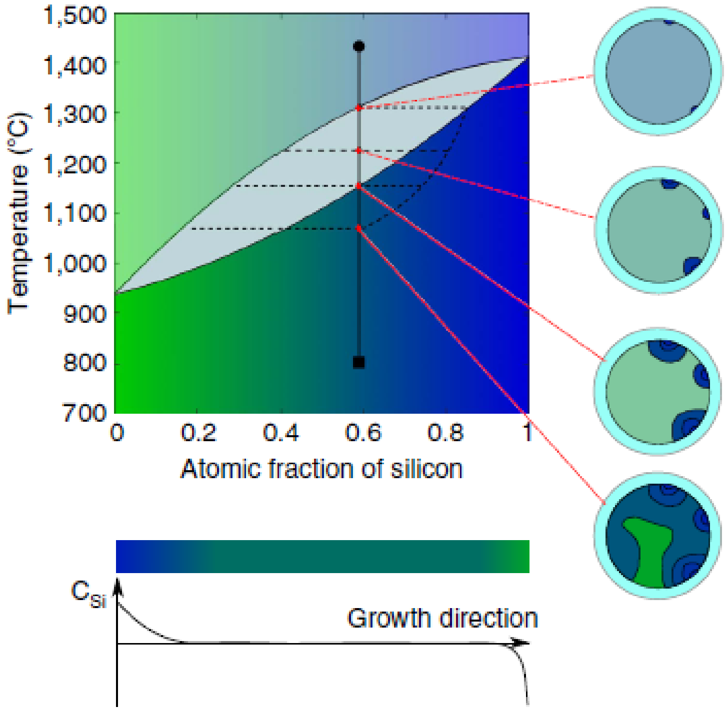
Amorphous Si and Ge core PCFs

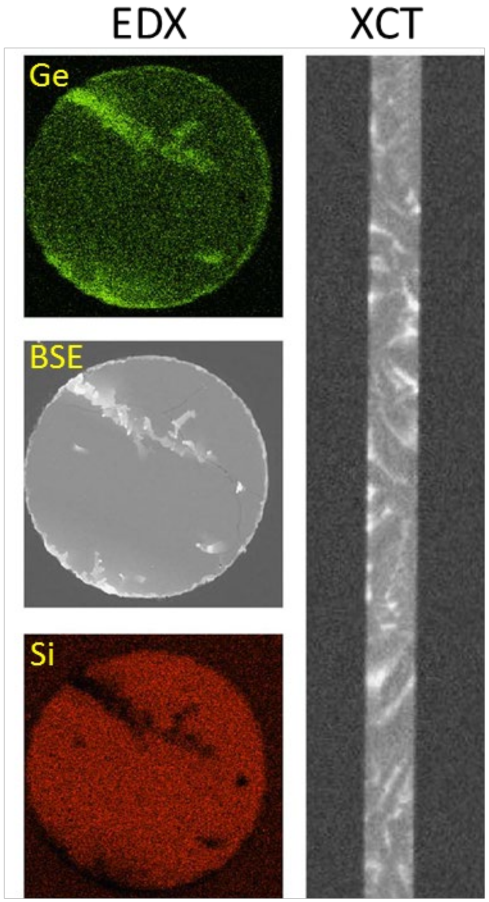
Polycrystalline Si and Ge core PCFs

A. C. Peacock, U. J. Gibson, and J. Ballato, "Silicon Optical Fiber – Past, Present, and Future," *Advances in Physics: X* (APX) **1**, 114 – 127 (2016); A. C. Peacock and J. Ballato, "In-fiber silicon photonics," *Optics and Photonics News*, pages 32 - 39, March 2019.

SiGe optical fiber – tailorable bandgap

- As-drawn fibers have compositional variations due to non-equilibrium cooling.



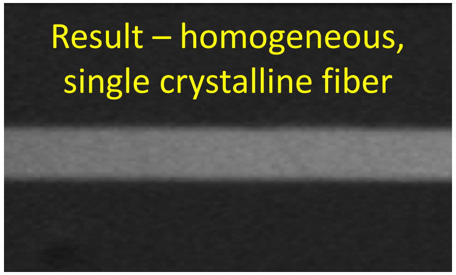


6 atom % Ge in Si (average)

D. Coucheron, M. Fokine, N. Patel, D. Breiby, O. Tore Buset, T. Hawkins, M. Jones, J. Ballato and U. Gibson, "Laser inscription of compositional microstructures in crystalline SiGe-core fibres," *Nature Communications* **7**, Article 13265 (2016).

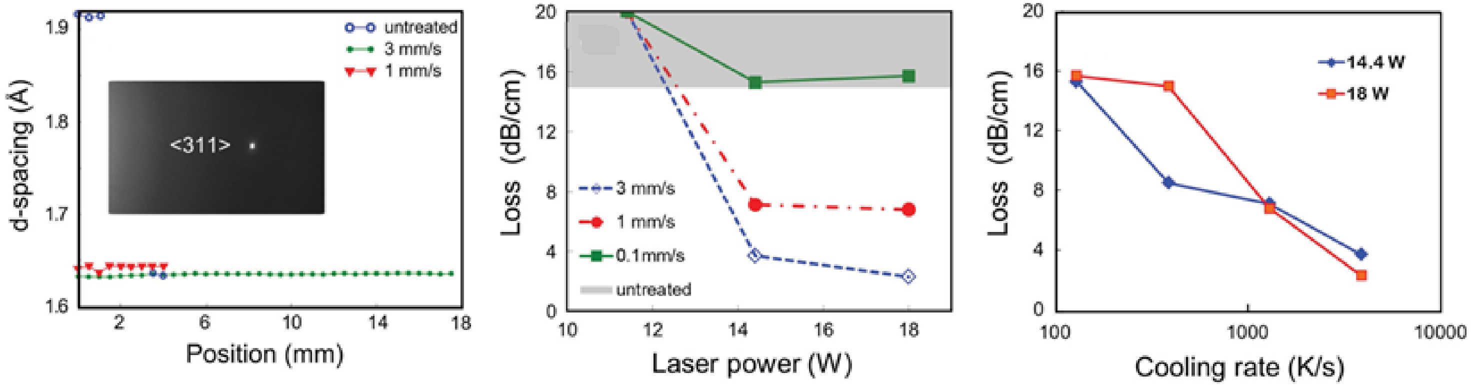
SiGe optical fiber – laser recrystallization

- CO_2 laser heating:
  - Ge-rich material accumulates in high temperature region.
  - Establish melt zone… translate through fiber; competition between nucleation suppression and unstable growth front.



Result – homogeneous, single crystalline fiber

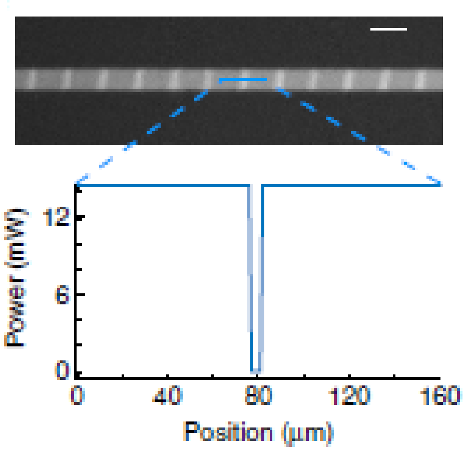
- Nucleation suppressed (*this example if for Si fiber; but same CO_2 laser*…)
  - Single crystal over entire scan; preferential segregation of impurities
  - **Loss reduction from 16 → 2 dB/cm (!)**

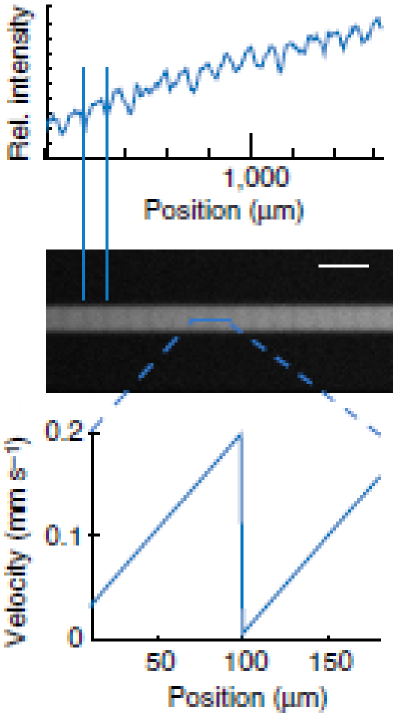


D. Coucheron, M. Fokine, N. Patil, D. Breiby, O. Buset, N. Healy, A. Peacock, T. Hawkins, M. Jones, J. Ballato, and U. Gibson, “CO_2 Laser-Induced Directional Recrystallization to Produce Single Crystal Silicon-Core Optical Fibers with Low Loss,” *Advanced Optical Materials* **4**, 1004 – 1008 (2016).

SiGe optical fiber – laser recrystallization

- Velocity-induced gratings in SiGe fibers
  - Composition of crystal behind melt zone is velocity dependent.
  - X-ray CT of 200 µm period grating with Δn ~ 0.018.
  - Created by periodic interruption of the beam.
    - Suitable for THz Bragg grating?

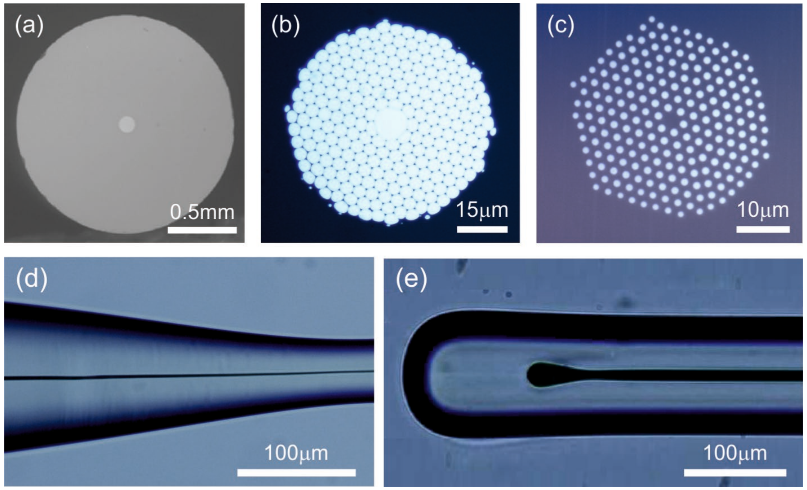




D. Coucheron, M. Fokine, N. Patel, D. Breiby, O. Tore Buset, T. Hawkins, M. Jones, J. Ballato and U. Gibson, "Laser inscription of compositional microstructures in crystalline SiGe-core fibres," *Nature Communications* **7**, Article 13265 (2016).

Semiconductor optical fiber

- **Semiconductor core fibers: Si, Ge, SiGe, InSb, ZnSe, a-Si, H:Si, …**
  - Intriguing and improving properties…
  - Easier to fabricate and couple into than planar devices… economical production using draw tower (molten core).
  - CO_2 laser processing improves quality (crystallinity, loss) and can alter form and composition
  - Losses comparable with on-chip technologies; enabled first nonlinear characterization of Si fibers (telecom into MIR).
  - Access novel device geometries… solar cells, Bragg gratings, NLO fibers, in-fiber OE devices, …



(a) molten core Si fiber, two HP-CVD PCFs: (b) index guiding Si and (c) bandgap guiding Si fibers. Post-processed Si fibers: (d) longitudinally tapered core and (e) microspherical resonator.*

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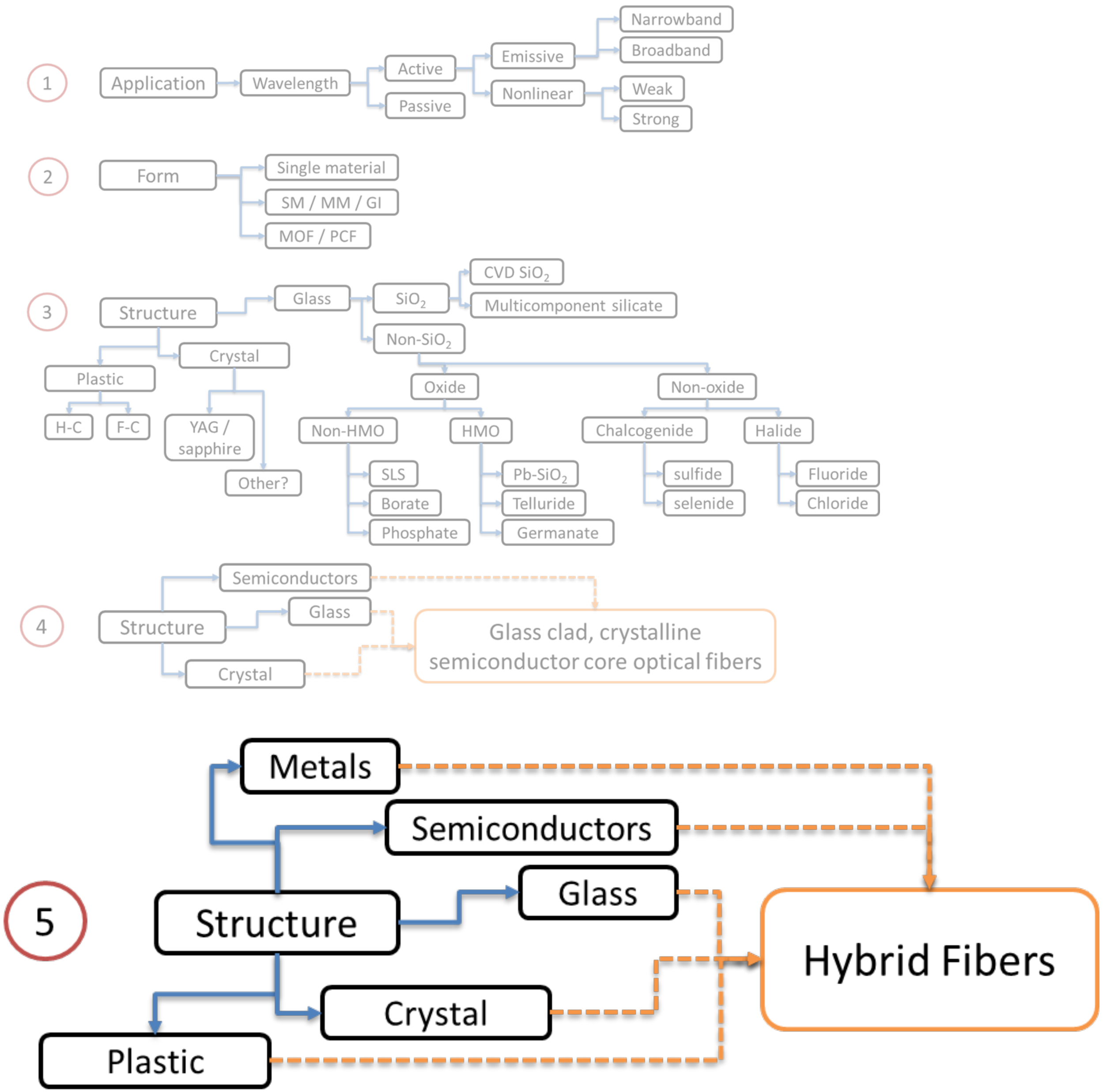
* A. Peacock, U. Gibson, and J. Ballato, *Advances in Physics: X* (APX) **1**, 114 – 127 (2016).

Optical fiber material options



1
- Application
  - Wavelength
    - Active
      - Emissive
        - Narrowband
        - Broadband
      - Nonlinear
        - Weak
        - Strong
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2
- Form
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- Structure
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          - SLS
          - Borate
          - Phosphate
        - HMO
          - Pb-SiO_2
          - Telluride
          - Germanate
      - Non-oxide
        - Chalcogenide
          - sulfide
          - selenide
        - Halide
          - Fluoride
          - Chloride
  - Crystal
    - YAG / sapphire
    - Other?
  - Plastic
    - H-C
    - F-C

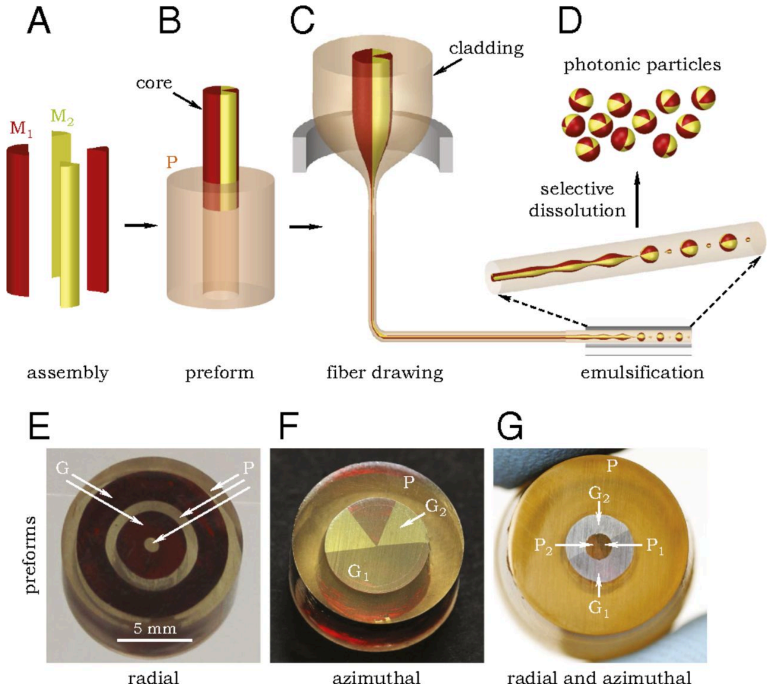
4
- Structure
  - Semiconductors
  - Glass
  - Crystal

Glass clad, crystalline semiconductor core optical fibers

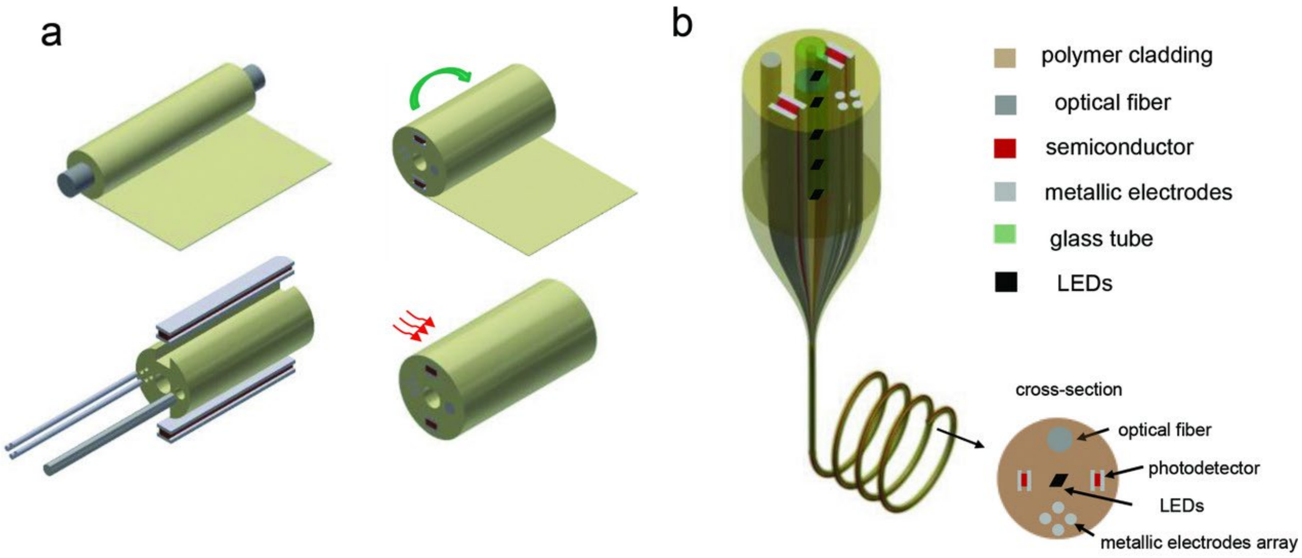
5
- Structure
  - Metals
  - Semiconductors
  - Glass
  - Crystal
  - Plastic

Hybrid Fibers

Hybrid optical fibers…



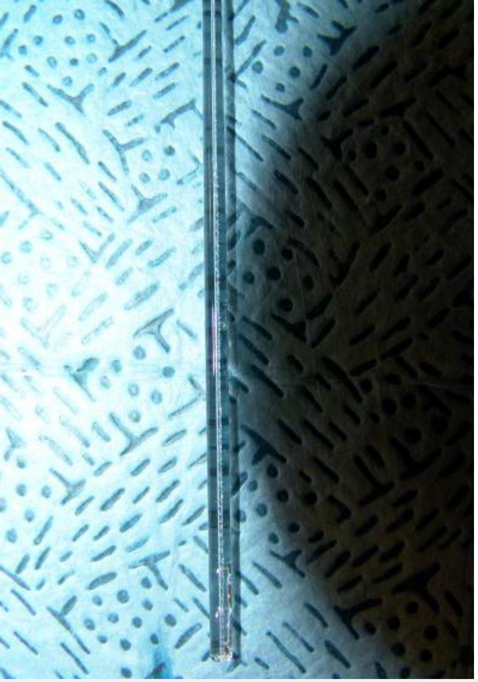
Whole new world of "multimaterial" fibers consisting of plastics, metals, semiconductors all processed into a single fiber. New properties never thought possible until recently.

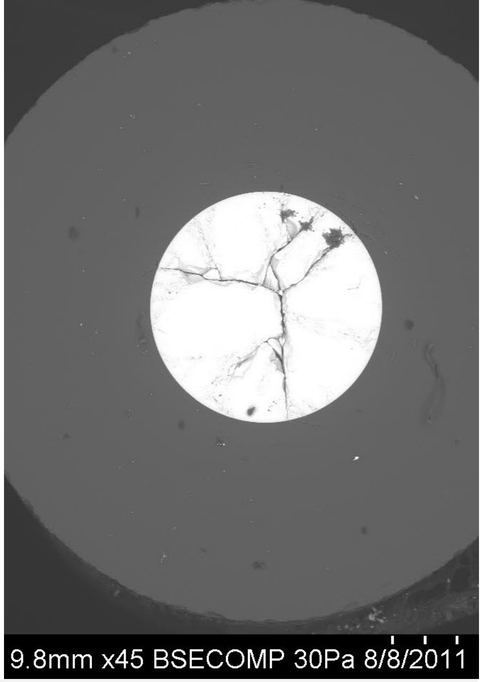


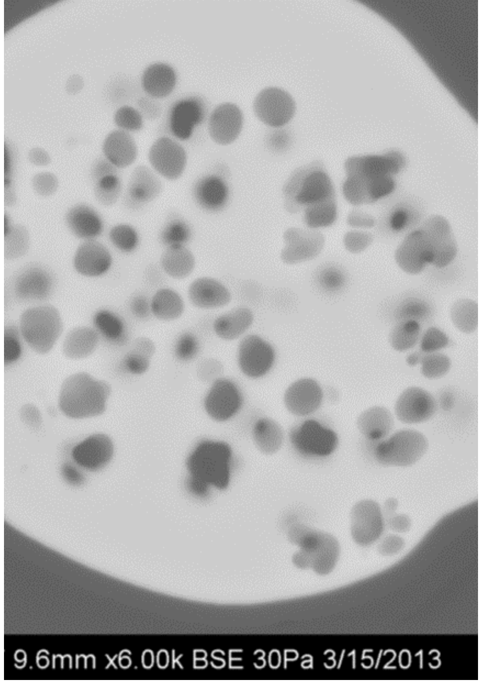
W. Yan, et al., "Advanced multimaterial electronic and optoelectronic fibers and textiles," *Advanced Materials* **31**, 1802348 (2019);
G. Tao, et al., "Digital design of multimaterial photonic particles," *Proceedings of the National Academy of Sciences* **113**, 6839 – 6844 (2016).

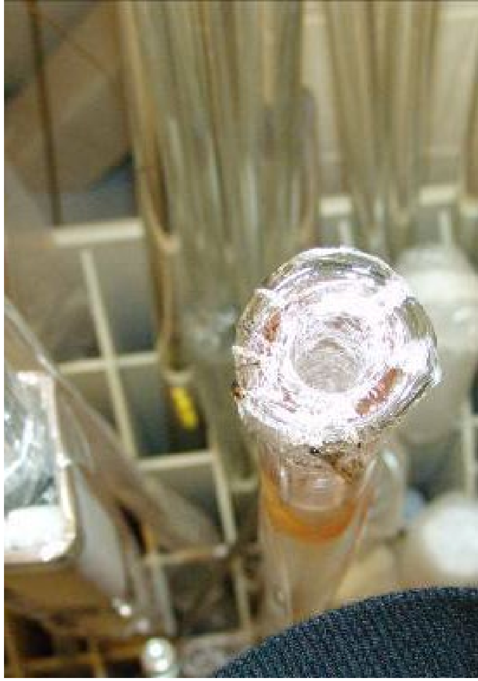
What you should know…

- For every material from which a fiber can be made, there is a process by which to make it. Industrially, CVD dominates because of scalability (volume) and low loss (SiO_2). For fiber, thermal draw dominates, again for scale and speed.
- CVD low loss from “self-purification” where VP of desired precursors is many orders higher than those of impurities.
- Extrusion and molten core are important “specialty” methods both scalable and enabling of wider (than CVD) compositional ranges.
- Glasses are kinetic so each preform (composition, size, etc) might process differently. Understanding the materials science and engineering is critical.
- Anyone can make fiber. Very few can make good fiber.









What (else) you should know…

The more complex, materially or geometrically, the more likely unexpected effects come into play; e.g., volatility, phase separation, cracking, diffusion, viscoelasticity, etc.

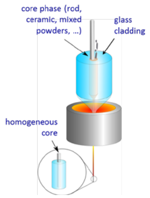
Market Street, San Francisco (Photonics West, 2013)

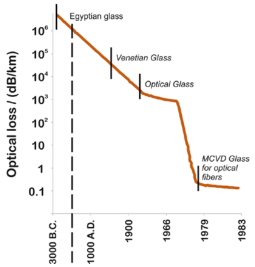
Thank You !!

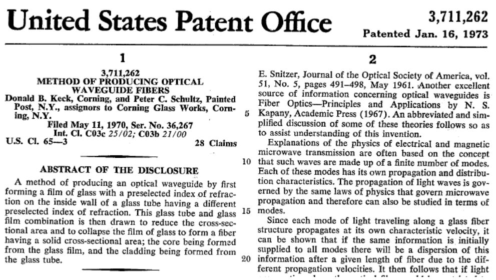
John Ballato
jballat@clemson.edu

Outline

- Background
  - Trends
  - Optical fiber material options
- Exemplars
  - Advanced SiO_2 fibers
  - Semiconductor core fibers
- A fun future…
- Conclusions
- Extra / background slides
  - *Material family basics*
  - Fiber fabrication approaches
  - Suggested reading






United States Patent Office

3,711,262
Patented Jan. 16, 1973

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3,711,262
METHOD OF PRODUCING OPTICAL WAVEGUIDE FIBERS
Donald B. Keck, Corning, and Peter C. Schultz, Painted Post, N.Y., assignors to Corning Glass Works, Corning, N.Y.
Filed May 11, 1970, Ser. No. 36,267
Int. Cl. C03c *25/02*; C03b *21/00*
U.S. Cl. 65—3 28 Claims

ABSTRACT OF THE DISCLOSURE

A method of producing an optical waveguide by first forming a film of glass with a preselected index of refraction on the inside wall of a glass tube having a different preselected index of refraction. This glass tube and glass film combination is then drawn to reduce the cross-sectional area and to collapse the film of glass to form a fiber having a solid cross-sectional area; the core being formed from the glass film, and the cladding being formed from the glass tube.

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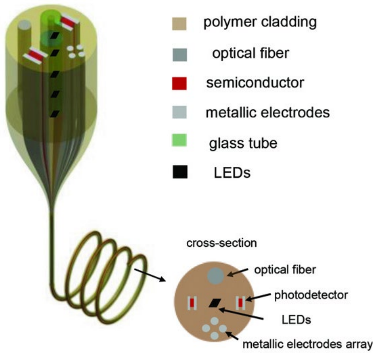
E. Snitzer, Journal of the Optical Society of America, vol. 51, No. 5, pages 491–498, May 1961. Another excellent source of information concerning optical waveguides is Fiber Optics—Principles and Applications by N. S. Kapany, Academic Press (1967). An abbreviated and simplified discussion of some of these theories follows so as to assist understanding of this invention.

Explanations of the physics of electrical and magnetic microwave transmission are often based on the concept that such waves are made up of a finite number of modes. Each of these modes has its own propagation and distribution characteristics. The propagation of light waves is governed by the same laws of physics that govern microwave propagation and therefore can also be studied in terms of modes.

Since each mode of light traveling along a glass fiber structure propagates at its own characteristic velocity, it can be shown that if the same information is initially supplied to all modes there will be a dispersion of this information after a given length of fiber due to the different propagation velocities. It then follows that if light



Primer on fiber material families

- Generalized Glass Families
  - Silica and Silicates: Based on SiO_2
  - Phosphates: Based on P_2O_5
  - Borates: Based on B_2O_3
  - Common binaries: phosphosilicates ($P_2O_5 – SiO_2$), borosilicates ($B_2O_3 – SiO_2$), aluminosilicates ($Al_2O_3 – SiO_2$), etc.

  - Heavy Metal Oxides
    - Based on GeO_2 or TeO_2 (or others heavier metals like Pb)

  - IR Glasses (Halides and Chalcogenides)
    - Halides based on ZrF_4
    - Chalcogenides based on As, S, Se, Te, Ge, Ga, etc.

Primer on fiber material families

- Silica and Silicate Glasses
  - Thermally stable (> 1000˚C)
  - Mechanically robust (> 4 GPa strength)
  - Mass production, high yields, broad US infrastructure
  - Can be low optical attenuation (< 0.2 dB/km)
    - Transparent to about 2 μm
  - Chemically inert, environmentally “green”
  - Relatively low nonlinearity
  - Fairly low (active) dopant level
  - Fairly high vibrational environment; lower QE

Primer on fiber material families

- Phosphate Glasses
  - Lower thermal stable (> 500 ˚C)
  - Mechanically less robust
  - Can be reasonable optical attenuation (100 dB/km)
    - Requires purification and dry processing
    - Transparent to about 2 μm
  - Can be hygroscopic
  - Low nonlinearity
  - High compositional tolerance for (active) dopants
  - High vibrational environment; lower QE
  - Limited commercialization

Primer on fiber material families

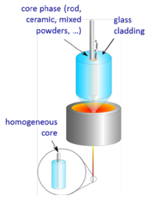
- Heavy Metal Oxide Glasses
  - Lower thermal stable (> 800 ˚C)
  - Reasonable mechanical robustness
  - Reasonable optical attenuation (> 100 dB/km)
    - Requires purification and dry processing
    - Transparent to 3 – 5 μm
  - Reasonable chemical durability
  - Acceptable nonlinearity
  - Good compositional tolerance for (active) dopants
  - Lower vibrational environment; good QE
  - Not generally that “green”
  - Limited commercialization

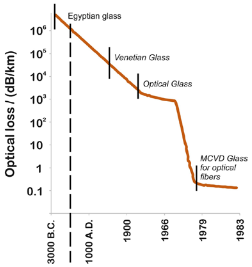
Primer on fiber material families

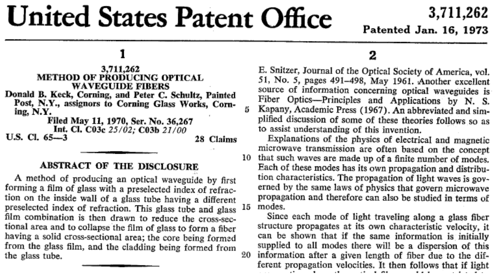
- IR Glasses (Halides and Chalcogenides)
  - Halides:
    - Brittle and low temperature
    - Potentially very low attenuation and nonlinearity
    - Difficult to manufacture **(well)**
    - Good compositional tolerance for (active) dopants
    - Low vibrational environment for (active) dopants; high QE
    - Limited commercialization
  - Chalcogenides:
    - Same as halides but less brittle
    - Difficult to manufacture **(well)**
    - Higher intrinsic attenuation and higher nonlinearity
    - Limited commercialization

Outline

- Background
    - Trends
    - Optical fiber material options
- Exemplars
    - Advanced SiO_2 fibers
    - Semiconductor core fibers
- A fun future…
- Conclusions
- Extra / background slides
    - Material family basics
    - *Fiber fabrication approaches*
    - Suggested reading







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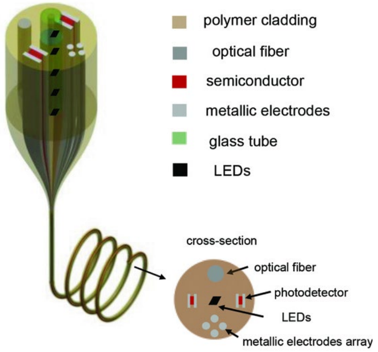
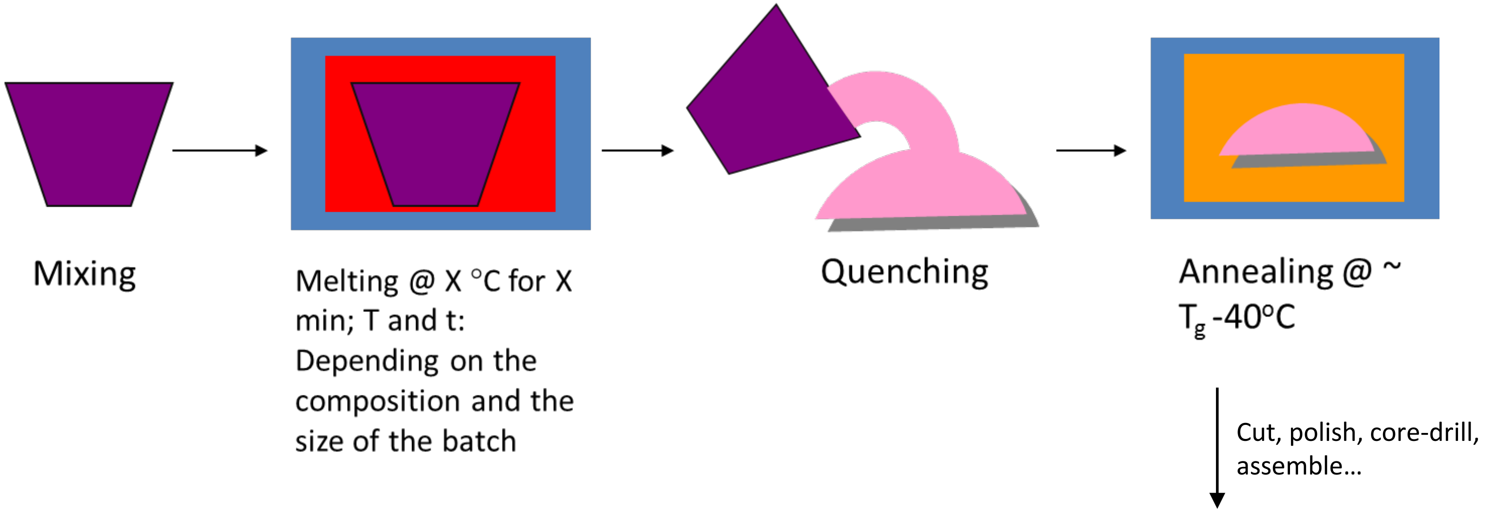


Bulk oxide glass synthesis



Mixing

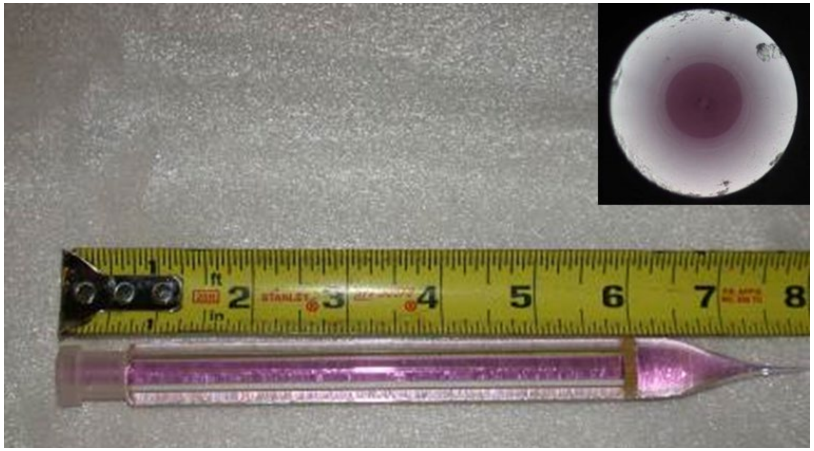
Melting @ X °C for X min; T and t: Depending on the composition and the size of the batch

Quenching

Annealing @ ~ T_g -40°C

Cut, polish, core-drill, assemble…

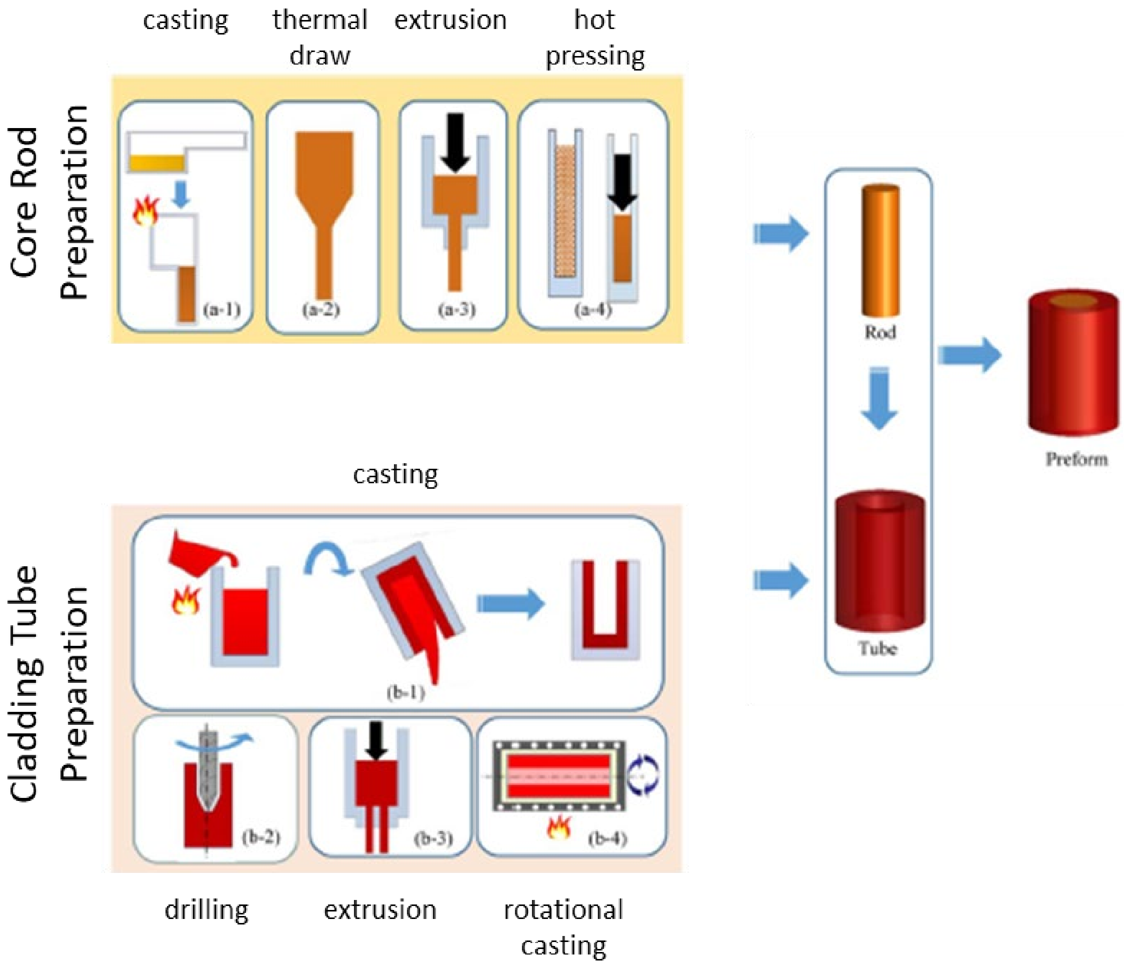
- For phosphate, germanates, and most other (heavy metal) oxides, synthesis done by batching, melting, casting, annealing, and substantial post-processing; i.e., grinding and polishing into rods and tubes.
- Labor-intensive process limits the use of these glasses because of achievable size, purity, quality, and cost.



Nd:phosphate core sleeved inside passive phosphate glass cladding tube

Top graphic c/o Prof. Laeticia Petit, Tampere University, Finland.

Bulk IR glass synthesis

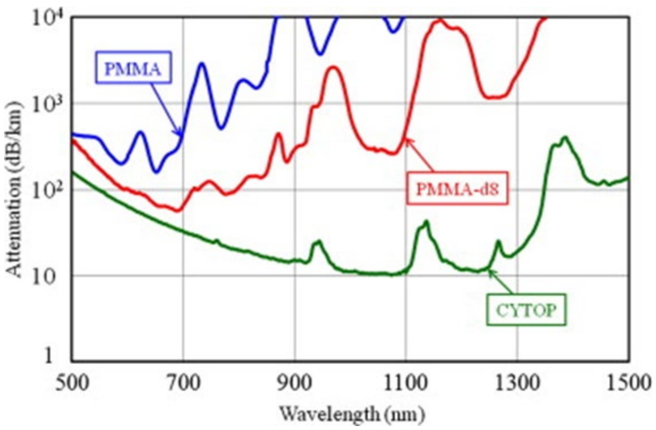


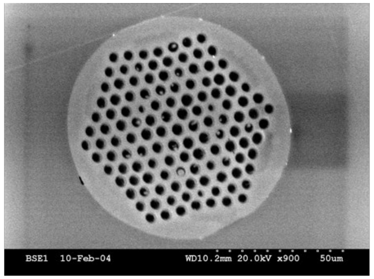
- Fluorides (halides) and chalcogenides are similarly prepared using batching, melting, casting, annealing, and substantial post-processing.
- Must be done in controlled atmospheres for either safety reasons or to minimize oxygen contamination.
- Also very labor-intensive process that limits the use of these glasses because of achievable size, purity, quality, and cost.

After: G. Tao, et al., “Infrared fibers,” *Advances in Optics & Photonics* **7**, 379 – 458 (2015).

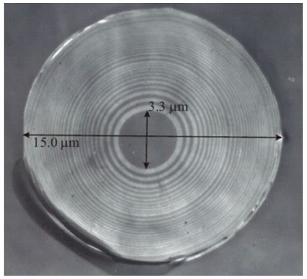
Polymer extrusion

- Polymer optical fibers (POFs) are useful for short distance communication environments.
- If made properly, they can have surprisingly low losses (< 10 – 100 dB/km) away from organic vibrational harmonic absorptions.
- Can be made in step index and graded index forms either by rod-in-tube / copolymerization routes or continuously via extrusion.

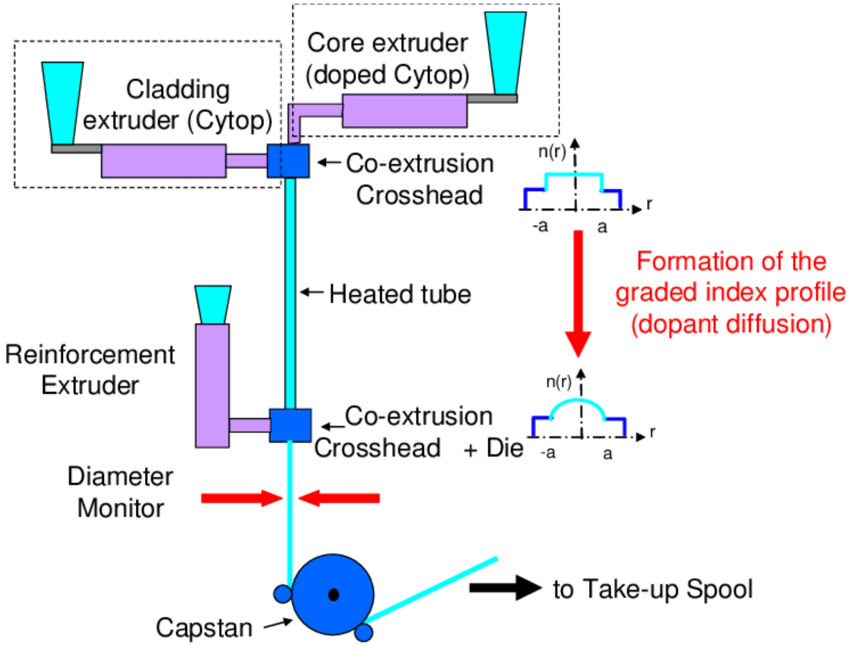




PET/EvOH extruded fiber with 127 islands and the islands dissolved out.



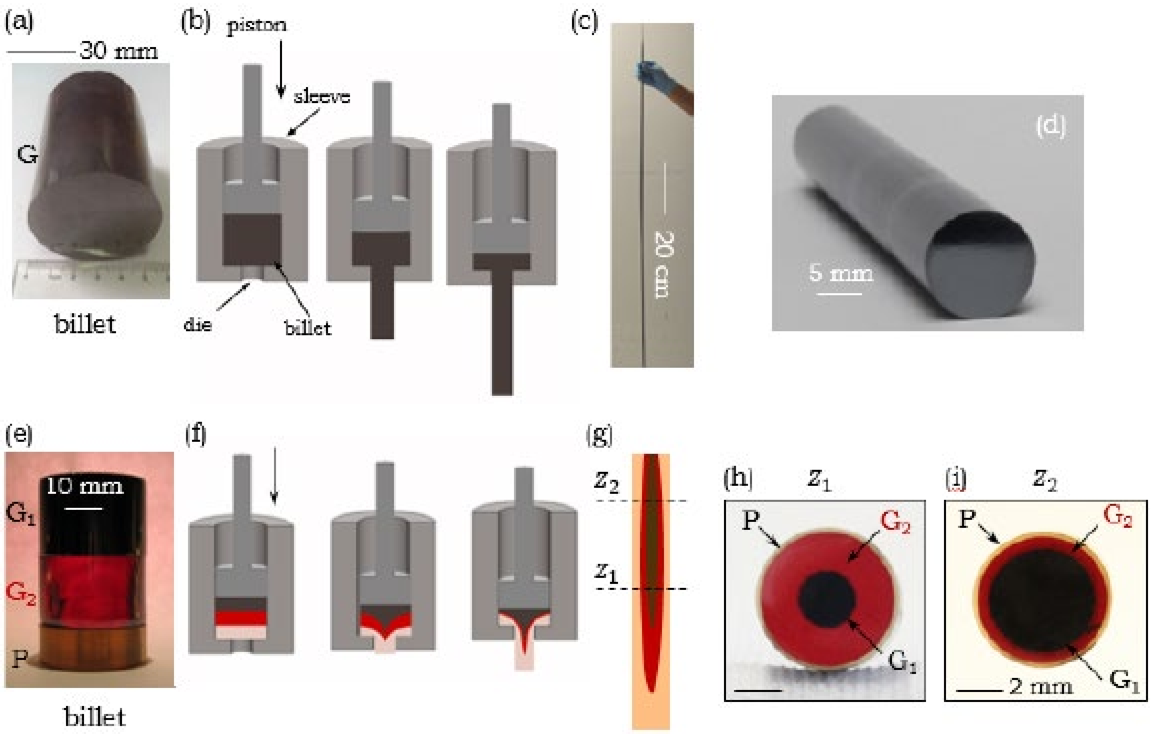
Coaxially symmetric fiber with approximately 60 alternating layers.



Y. Koike and R. Gaudino in Optical Fiber Telecommunications, 6th Edition, Academic Press, 2013; C. Lethien, J. Loyez, J. Vilcot, N. Rolland and P. Rolland, Polymers 3, 1006 – 1028 (2011); M. Mignanelli, K. Wani, J. Ballato, S. Foulger, and P. Brown, *Optics Express* **15**, 6183 – 6189 (2007).

Soft glass extrusion

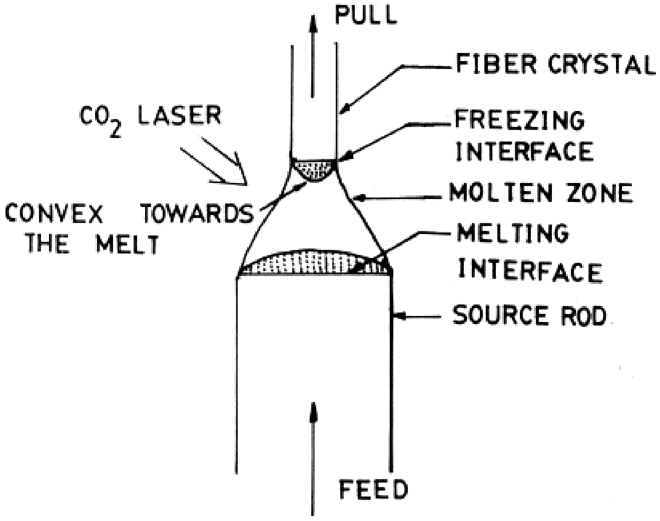
- Extrusion has also been used to make preforms from soft glasses that subsequently are drawn using a conventional fiber draw tower.
- This is becoming a useful tool for multimaterial fibers.
- Clever use of different materials can lead to the extrusion of a core / clad preform.



Tao, G., Shabahang, S., Wang, X. and Abouraddy, A.F., 2013, October. Efficient disc-to-fiber multimaterial stacked coextrusion for robust infrared optical fibers. In Frontiers in Optics (pp. FTu4B-3). Optical Society of America.

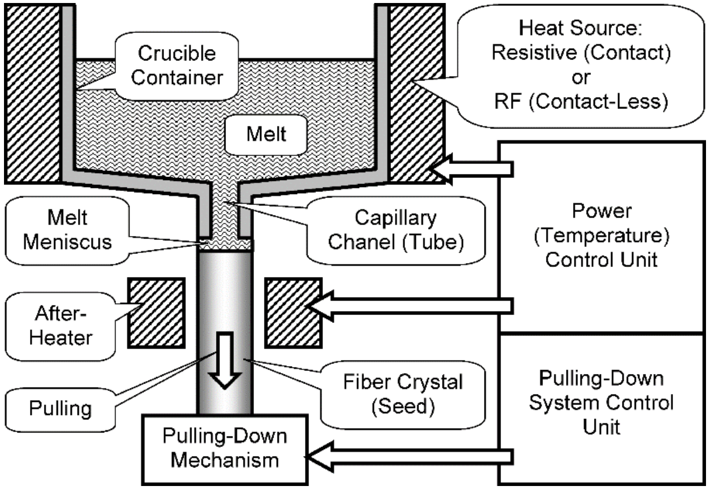
Crystalline fiber growth

Laser Heated Pedestal Growth (LHPG)



- + Growth rate ~ mm / min
- + CO_2 laser heated, no contact with crucible; decreases internal stress and prevents parasitic nucleation
- + Smaller diameter fibers
- – Melt zone stability
- – Difficulty cladding

Micro-Pulldown (μ-PD)

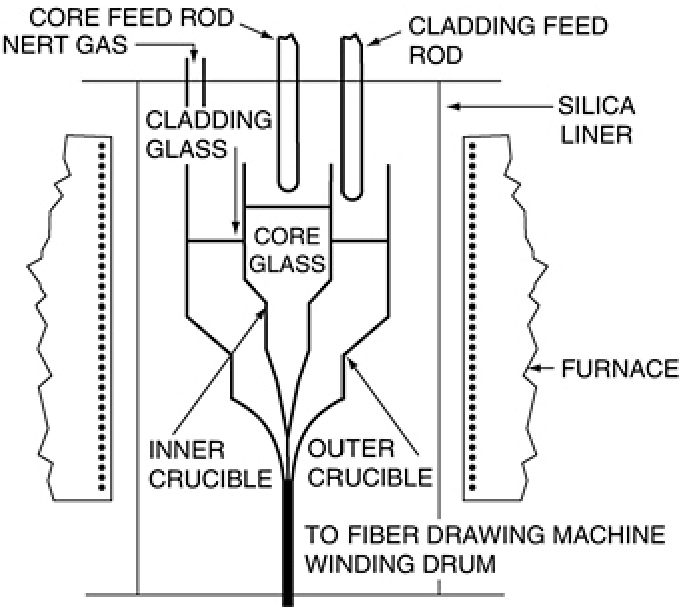


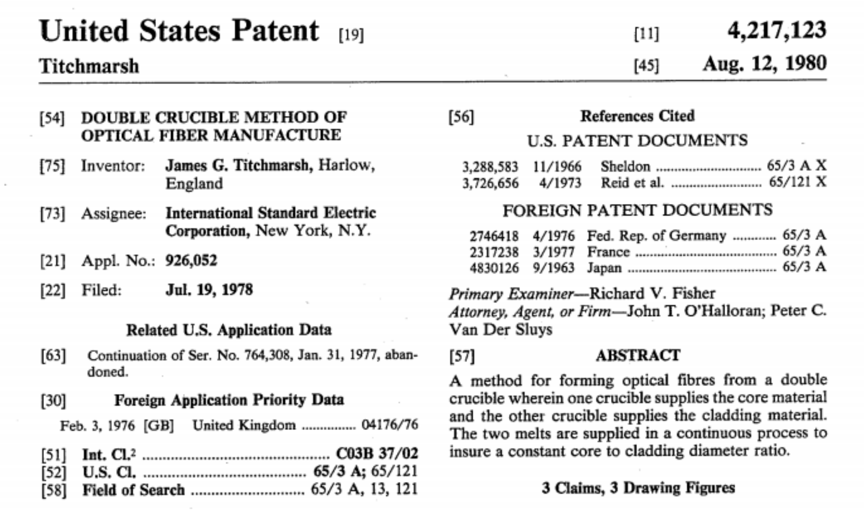
- + Growth rate < mm / min
- + Chemical and melt homogeneity
- + Lower cost
- – Larger diameter fibers
- – Melt zone stability
- – Difficulty cladding

Valery I. Chani "Micro-Pulling-Down (***μ***-PD) and Related Growth Methods", Shaped Crystals, Ed: Springer Berlin Heidelberg, 2007; L. Wang, et al., "Growth of single crystal fibers for 1.3 μm optical amplifiers by the laser-heated pedestal growth method," Materials Research Bulletin **33**, 1793 – 1799 (1998).

Double crucible fiber fabrication

- An approach to fiberizing compositions that are unstable and cannot be formed into conventional bulk samples (rods + tubes).
- Was once more common for chalcogenide fibers but not used in practice today.




United States Patent [19] [11] **4,217,123**
Titchmarsh [45] **Aug. 12, 1980**

[54] **DOUBLE CRUCIBLE METHOD OF OPTICAL FIBER MANUFACTURE**

[75] Inventor: **James G. Titchmarsh,** Harlow, England

[73] Assignee: **International Standard Electric Corporation,** New York, N.Y.

[21] Appl. No.: **926,052**

[22] Filed: **Jul. 19, 1978**

Related U.S. Application Data

[63] Continuation of Ser. No. 764,308, Jan. 31, 1977, abandoned.

[30] **Foreign Application Priority Data**

Feb. 3, 1976 [GB] United Kingdom 04176/76

[51] **Int. Cl.**^{2} **C03B 37/02**
[52] **U.S. Cl.** .... **65/3 A;** 65/121
[58] **Field of Search** .... 65/3 A, 13, 121

[56] **References Cited**

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3,726,656 4/1973 Reid et al. .... 65/121 X

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2746418 4/1976 Fed. Rep. of Germany .... 65/3 A
2317238 3/1977 France .... 65/3 A
4830126 9/1963 Japan .... 65/3 A

Primary Examiner—Richard V. Fisher
Attorney, Agent, or Firm—John T. O'Halloran; Peter C. Van Der Sluys

[57] **ABSTRACT**

A method for forming optical fibres from a double crucible wherein one crucible supplies the core material and the other crucible supplies the cladding material. The two melts are supplied in a continuous process to insure a constant core to cladding diameter ratio.

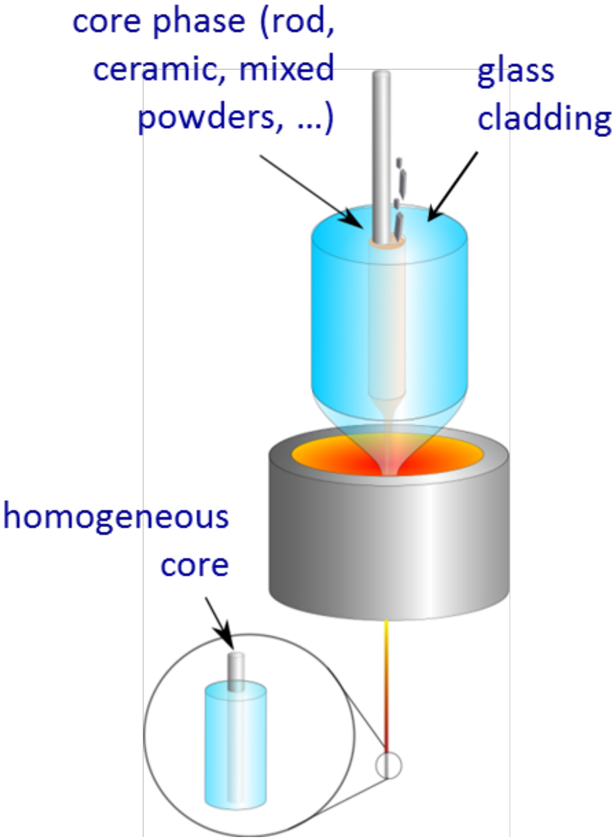
3 Claims, 3 Drawing Figures

- Disadvantages
  - High losses due to precursors and contamination from crucibles.
  - Little control over index profiles
  - Want core / clad glasses pre-fabricated and homogeneous.

J. MacChesney, et al., Chapter 3: Overview of Materials and Fabrication Technologies in Specialty Optical Fibers Handbook, T. F. Morse (eds), Elsevier, 2011.

Molten core method (MCM)

- **Molten-core technique:**
  - Core phase melts at temperature where cladding glass draws (directly) into fiber.
  - Originally… High quench rates permit unstable glasses to be directly fiberized.



Advantages

- Straight-forward
- Long lengths (> km)
- High speed manufacturing (> m/s)
- Amendable to very wide range of materials
- Can be reactive (liquid-phase chemistry)
- **Low temperature** (compared to CVD…)
- Industry-accepted manufacturing (fiber draw) used; no lathe deposition.

Disadvantages (?)

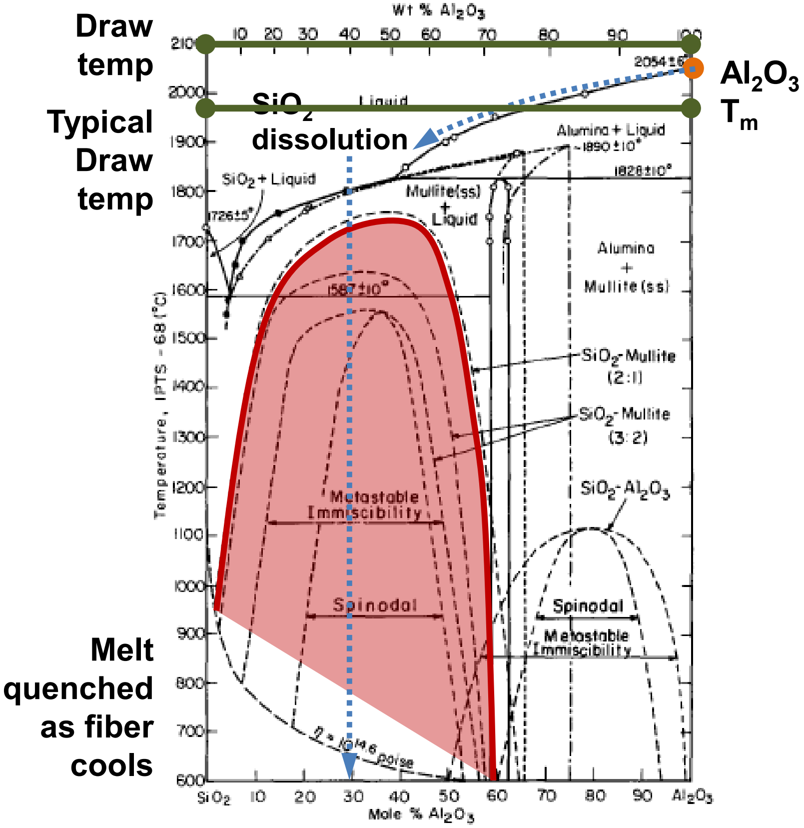
- **High temperature** (diffusion/dissolution)
- *One must understand materials/glass science*

J. Ballato and A. C. Peacock, "Perspective: Molten core optical fiber fabrication—A route to new materials and applications," APL Photonics **3**, 120903 (2018).

Molten core method (MCM)

An illustrative case is that of sapphire-derived aluminosilicate optical fibers

- The addition of alumina (Al_2O_3) to silica (SiO_2) glass is known to reduce the Brillouin gain coefficient and "solubilize" active dopants into the glass.
- However, the use of alumina in silica has historically been limited for two reasons:
  1. conventional CVD processes are not as amenable to the addition of alumina as they are other dopants (e.g., GeO_2) and
  2. there is a limitation in amount of alumina (~ 12 weight %) that can be added into silica prior to phase-separation.
  3. **Issue here is T_{melt} (Al_2O_3) > T_{draw} (SiO_2)**



Draw temp

Typical Draw temp

SiO_2 dissolution

Al_2O_3 T_m

Melt quenched as fiber cools

P. D. Dragic, T. W. Hawkins, P. Foy, S. Morris, and J. Ballato, "Sapphire-derived all-glass optical fibres," Nature Photonics **6**, 627 (2012).

Fiber material and process comparisons

Material type	Pros	Cons
Glass fibers	+ Long-haul (long length + low loss) + Highly spread and manufactured + Novel/specialized fibers	- Flexibility (for home networks) - Expensive (relative)
Crystalline fibers	+ Single crystals + Good quality	- Small length of “fiber” - Unclad - Hard to manufacture
Plastic fibers	+ Cheap, lightweight, and robust + Ease for network integration + Low temperature processing	- Acceptable for short-haul networks - Generally multimode (or GI) fibers

Process	Pros	Cons
Vapor Phase	+ Extremely high purity / low loss + High homogeneity + Industrial process	- Relatively low concentration limits - Precursor (hence composition) limits
Liquid phase (melting)	+ Wide range of precursors + High final concentrations + Chemical reactions allowed	- Impurities - Dynamic processes (dissolution)
Specialty fabrication	+ Precise / complex microstructures	- Extremely tedious

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    - Semiconductor core fibers
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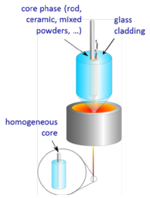
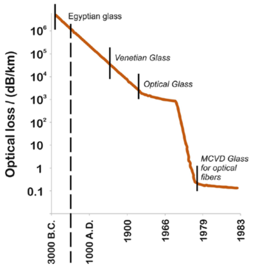
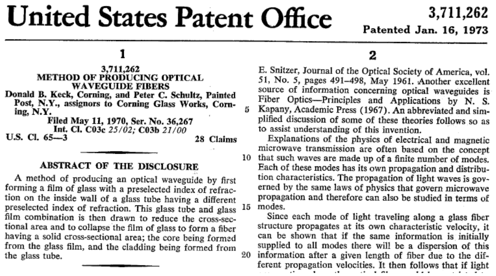
    - Material family basics
    - Fiber fabrication approaches
    - *Suggested reading*







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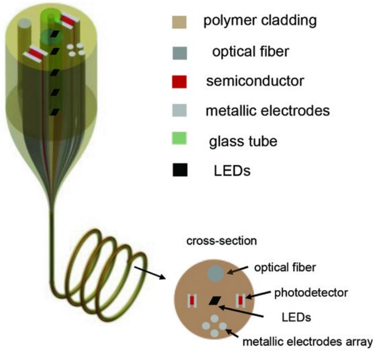

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