The past, present, and future of the molten core method of fiber fabrication

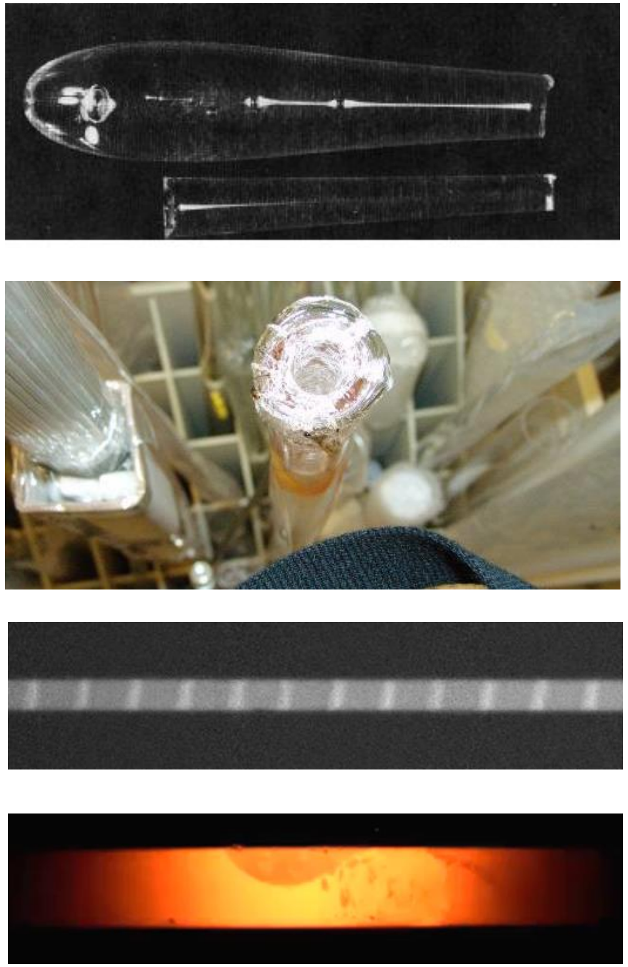
John Ballato

Department of Materials Science and Engineering, Clemson University, Clemson, SC USA

Optica Webinar - Optical Fabrication and Testing (FM) Technical Group

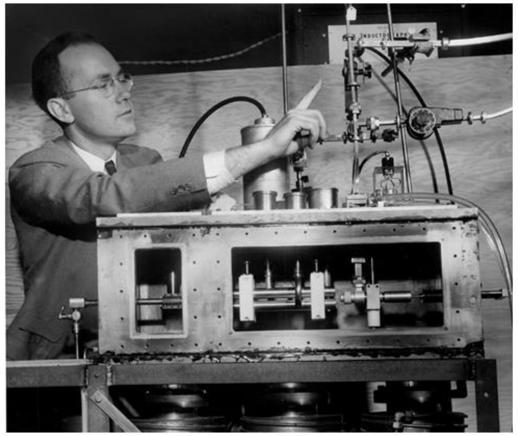
July 2022

- How did we get here?
- Where’s here?
- No. No. No. Maybe. OK. Boom. Whoa.
- What’s next?!?!

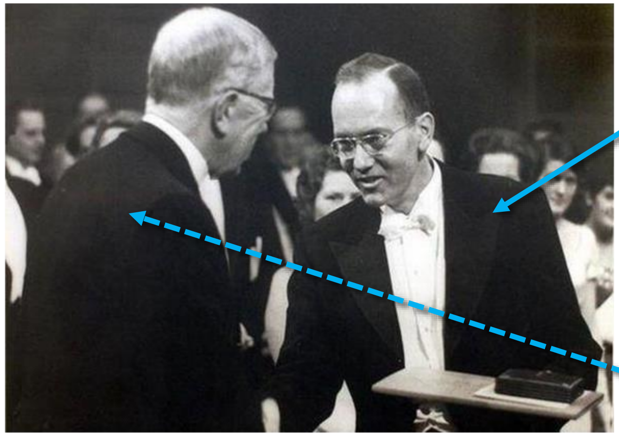


The Past

1955: Townes (and Gordon and Zeiger)



10 December 1964: Charles Townes and King Gustaf of Sweden



Father of the laser

1966: Kao (and Hockham)

10 December 2009: Charles Kao and King Carl of Sweden

Father of…

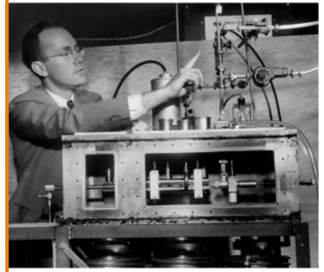
Father of optical fiber

Exactly 45 years later!

The Past

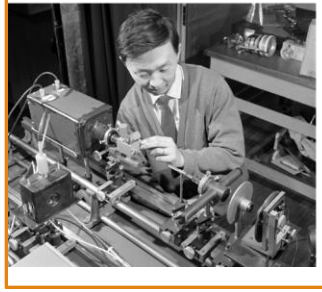
Necessary… but insufficient.

1955: Townes (and Gordon and Zeiger)

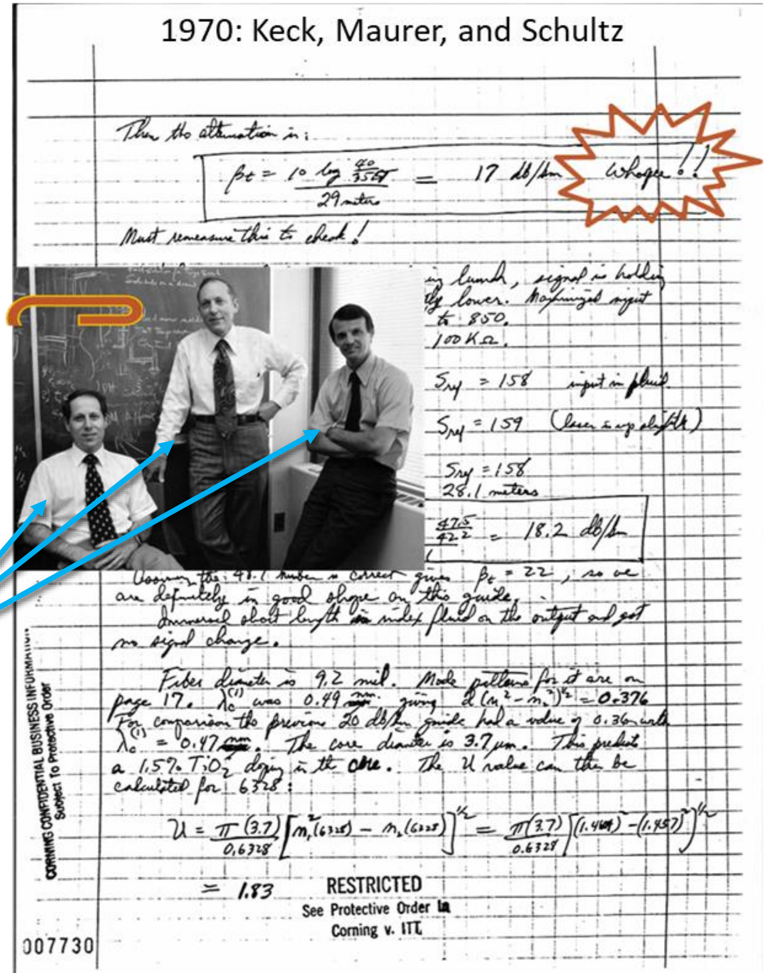


10 December 196 Ch es Townes and King Gustaf of Sweden

1966: Kao (and Hockham)



10 December 2009: Charles Kao and King Carl of Sweden



1970: Keck, Maurer, and Schultz

Then the attenuation is:

$$\beta_t = \frac{10 \log \frac{40}{3.5}}{29 \text{ meters}} = 17 \text{ db/km}$$

Must remeasure this to check!

ing lunch, signal is holding

ly lower. Maximized input

to 850.

100 KΩ.

$S_{ny} = 158$ input in fluid

$S_{ny} = 159$ (laser is up slightly)

$S_{ny} = 158$

28.1 meters

$\frac{47.5}{42.2} = 18.2$ db/km

Assuming the 41.1 number is correct gives $\beta_t = 22$, so we are definitely in good shape on this guide.

Immersed short length in index fluid on the output and got no signal change.

Fiber diameter is 9.2 mil. Mode patterns for it are on page 17. $\lambda_c^{(1)}$ was 0.49 mm giving $d(n_1^2 - n_2^2)^{1/2} = 0.376$. For comparison the previous 20 db/km guide had a value of 0.36 with $\lambda_c^{(1)} = 0.47$ mm. The core diameter is 3.7 μm. This predicts a 1.5% TiO_2 doping in the core. The V value can then be calculated for 6328:

$$V = \frac{\pi (3.7)}{0.6328}\left[n_1^2(6328) - n_2(6328)\right]^{1/2} = \frac{\pi(3.7)}{0.6328}\left[(1.4604)^2 - (1.457)^2\right]^{1/2}$$

$$= 1.83$$

RESTRICTED
See Protective Order in
Corning v. ITT

CORNING CONFIDENTIAL BUSINESS INFORMATION
Subject To Protective Order

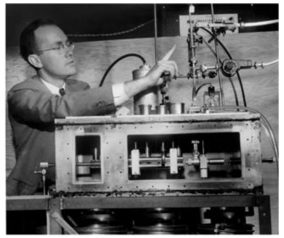
007730

Fathers of actual / useable fiber.

Images c/o Peter Schultz.

The Past. . . into… the Present

1955: Townes (and Gordon and Zeiger)



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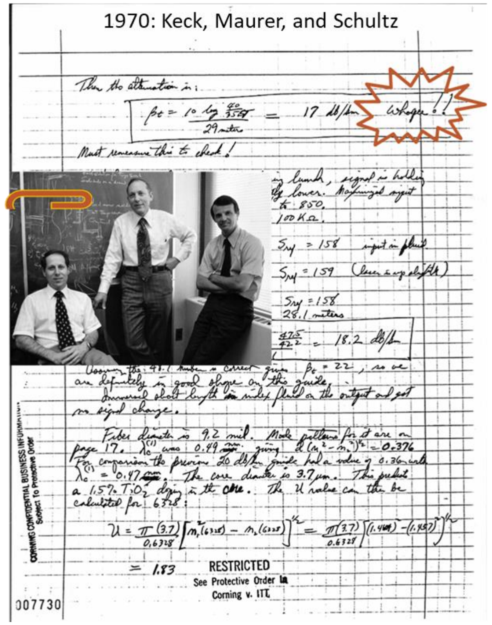

1970: Keck, Maurer, and Schultz

Then the attenuation is:

$\beta_t = \frac{10 \log \frac{40}{3.56}}{29 \text{ meters}} = 17$ db/km Whoopee!!

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…ing lunch, signal is holding …ly lower. Maximized input to 850. 100 KΩ.

$S_{ref} = 158$ input in fluid

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$S_{ref} = 158$

28.1 meters

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Fiber diameter is 9.2 mil. Mode patterns for it are on page 17. $\lambda_c^{(1)}$ was 0.49 nm giving $a(n_1^2 - n_2^2)^{1/2} = 0.376$. For comparison the previous 20 db/km guide had a value of 0.36 with $\lambda_c^{(1)} = 0.47$ nm. The core diameter is 3.7 μm. This predicts a 1.5% TiO_2 doping in the core. The U value can then be calculated for 6328:

$$U = \frac{\pi(3.7)}{0.6328}\left[n_1^2(6328) - n_2^2(6328)\right]^{1/2} = \frac{\pi(3.7)}{0.6328}\left[(1.4604)^2 - (1.457)^2\right]^{1/2}$$

$= 1.83$

RESTRICTED
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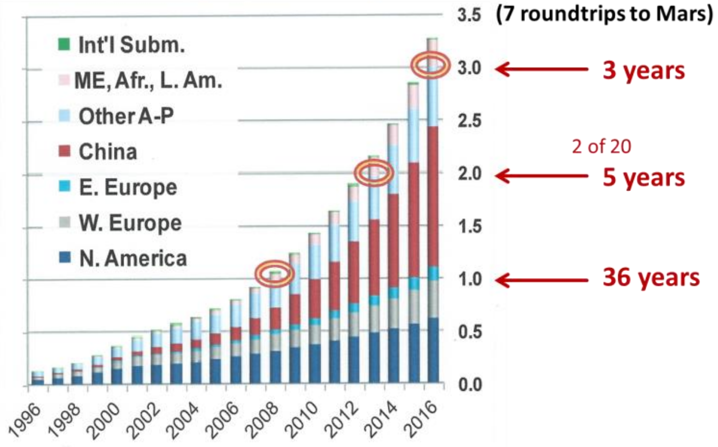
Cumulative total of cabled fiber installed worldwide
(billion fiber-km)



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

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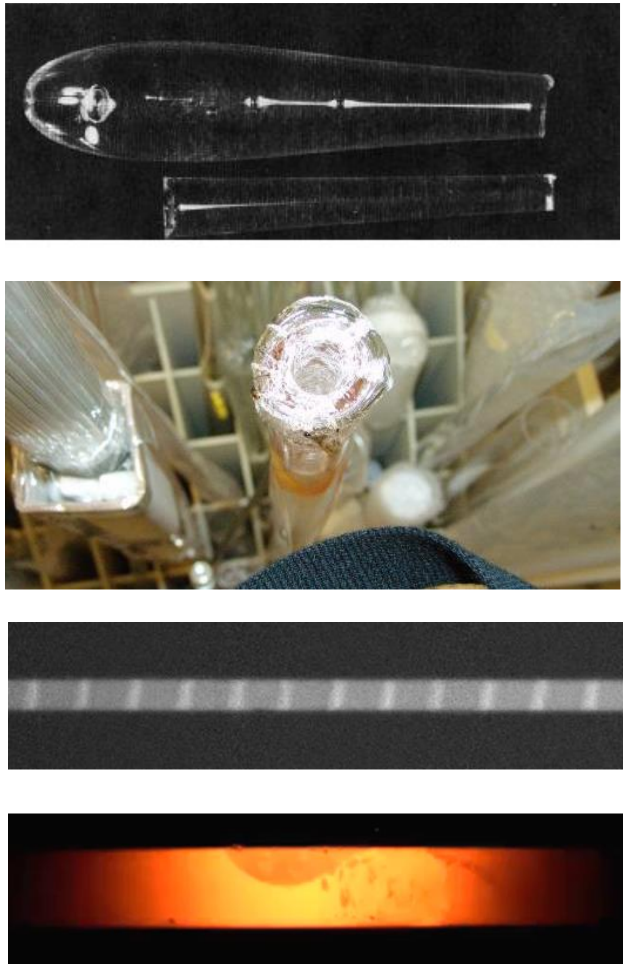
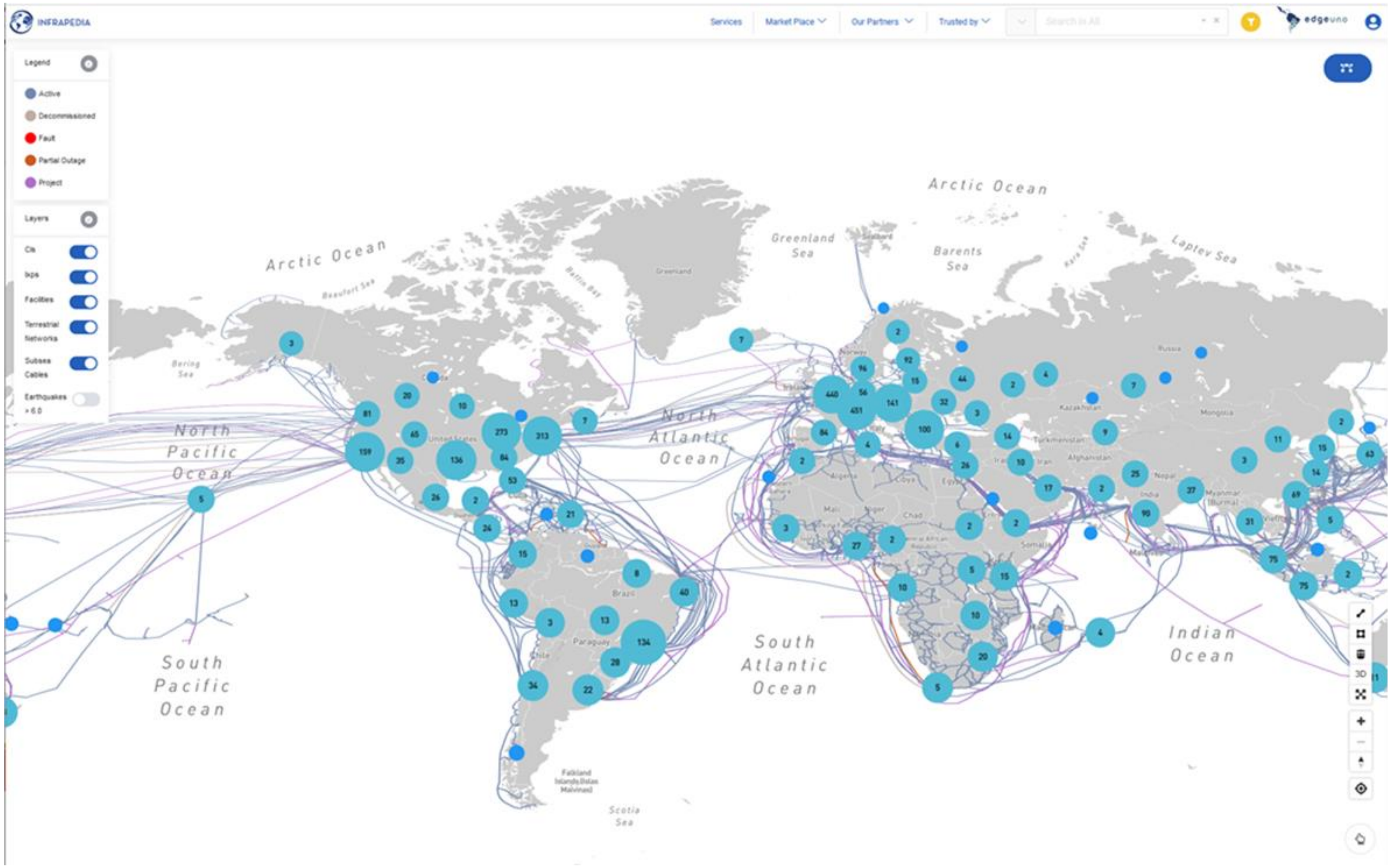


The Present



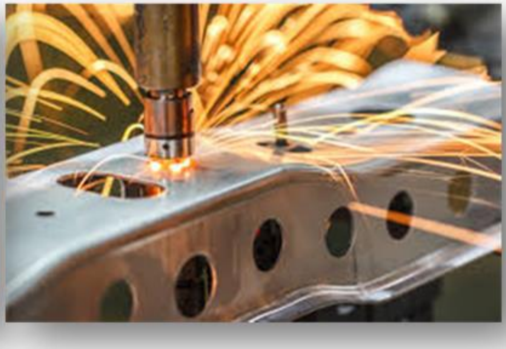
https://www.infrapedia.com/app, https://www.youris.com/energy/gallery/undersea-hvdc-cables-discovering-some-of-the-worlds-top-power-interconnections.kl
https://www.thefoa.org/tech/ref/appln/datacenters.html

The Present… but…

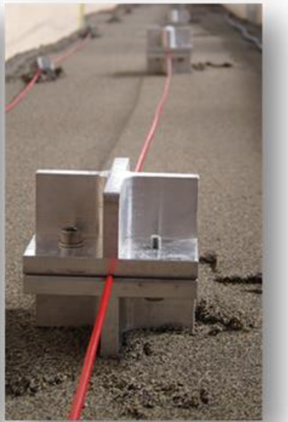
- Always more… growing demand for ever-more sophisticated fibers and lasers.

Communications

Machining / Manufacturing



Energy / Sensing / Medicine



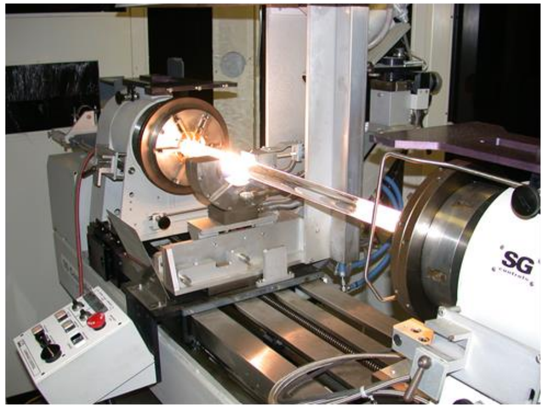
Ranging / Science

Directed Energy

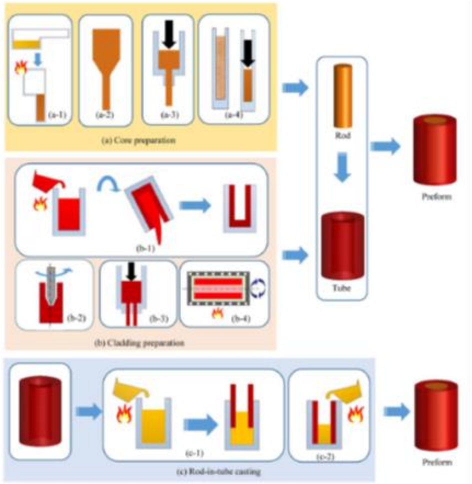
The Present… but…

- Two <u>primary practical methods</u> for making optical fibers.

Form preform via CVD processes (telecom)



Melt and form core and clad glasses (specialty)



- Both require the formation of a (core / clad) preform.
- Both force the glass to go through multiple thermal cycles, thus risking compositional flexibility, due to immiscibilities or glass forming limitations, hence performance limitations.

G. Tao, H. Ebendorff-Heidepriem, A. M. Stolyarov, S. Danto, J. V. Badding, Y. Fink, J. Ballato, and A. F. Abouraddy, “Infrared fibers,” *Advances in Optics and Photonics* **7**, 379-458 (2015).

The Present… but…

- Fibers drawn from a preform; either consolidated or as rods / tubes.
- In both cases, compositions are limited by glass-forming ranges, which depend on time and temperature.
- One really needs to pay attention to the underlying materials science to unleash the full potential of the periodic table on fiber properties and performance.

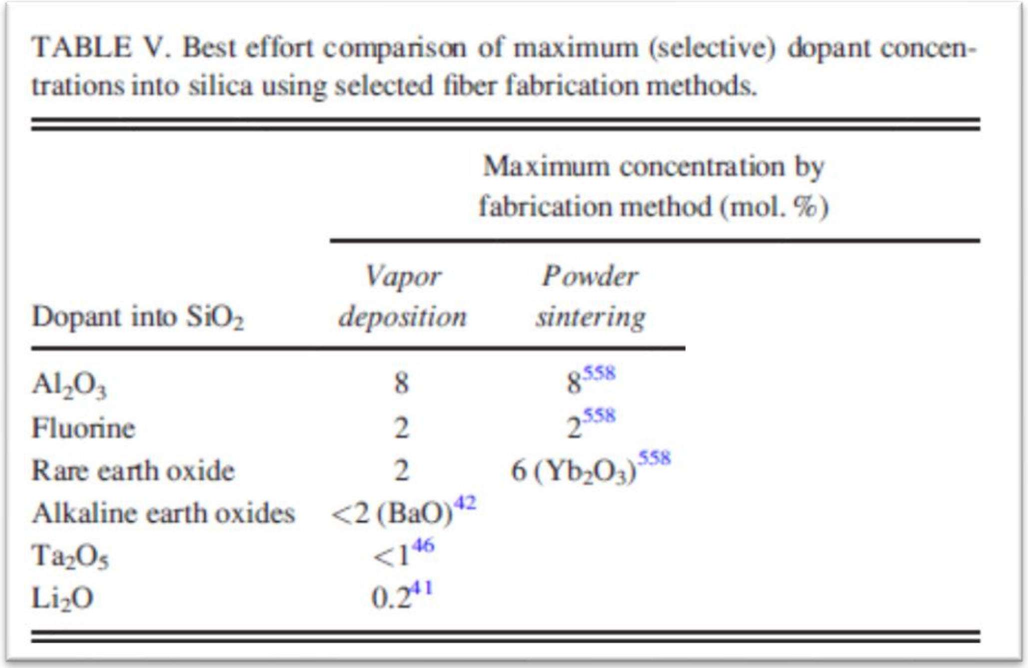


TABLE V. Best effort comparison of maximum (selective) dopant concentrations into silica using selected fiber fabrication methods.

	Maximum concentration by fabrication method (mol. %)	
Dopant into SiO_2	*Vapor deposition*	*Powder sintering*
Al_2O_3	8	8[558]
Fluorine	2	2[558]
Rare earth oxide	2	6 (Yb_2O_3)[558]
Alkaline earth oxides	<2 (BaO)[42]	
Ta_2O_5	<1[46]	
Li_2O	0.2[41]	

S. H. Risbud and J. A. Pask, "Calculated thermodynamic data and metastable immiscibility in the system SiO_2-Al_2O_3," *Journal of the American Ceramic Society* **60**, 418-424 (1977);
P. Dragic, M. Cavillon, and J. Ballato, "Materials for optical fiber lasers: A review," *Applied Physics Reviews* **5**, 041301 (2018).

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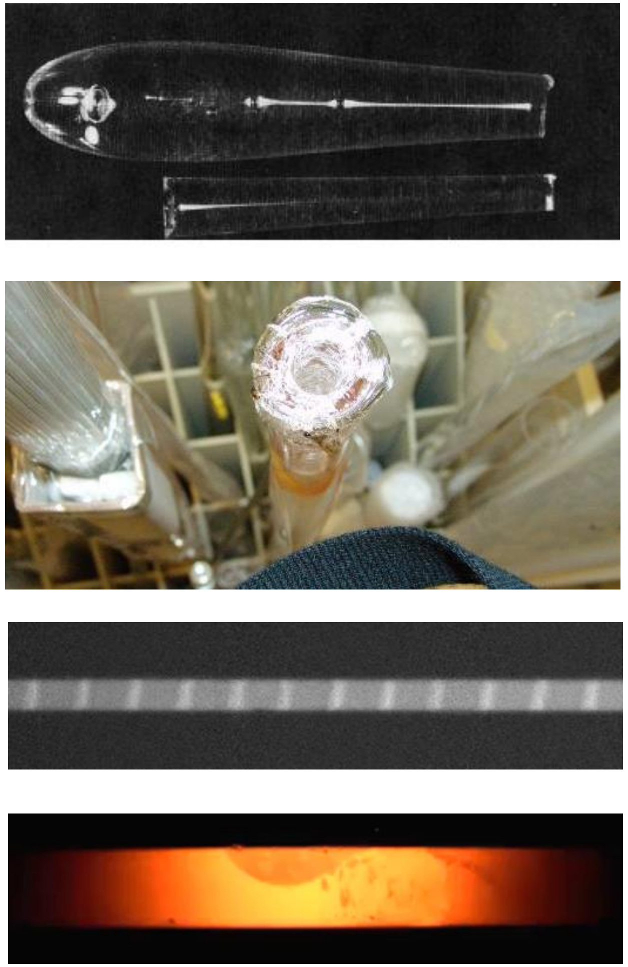
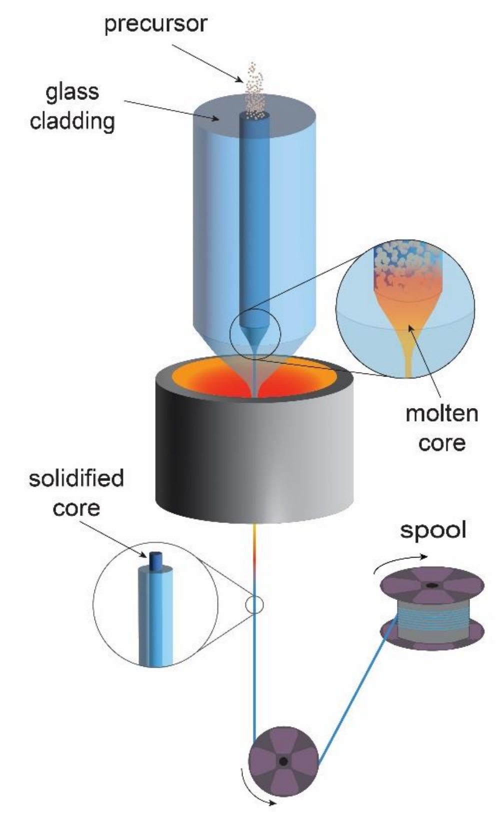


The molten core method

aka "melt-in-tube," "powder-in-tube," granulated powder," etc. methods.

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



Advantages

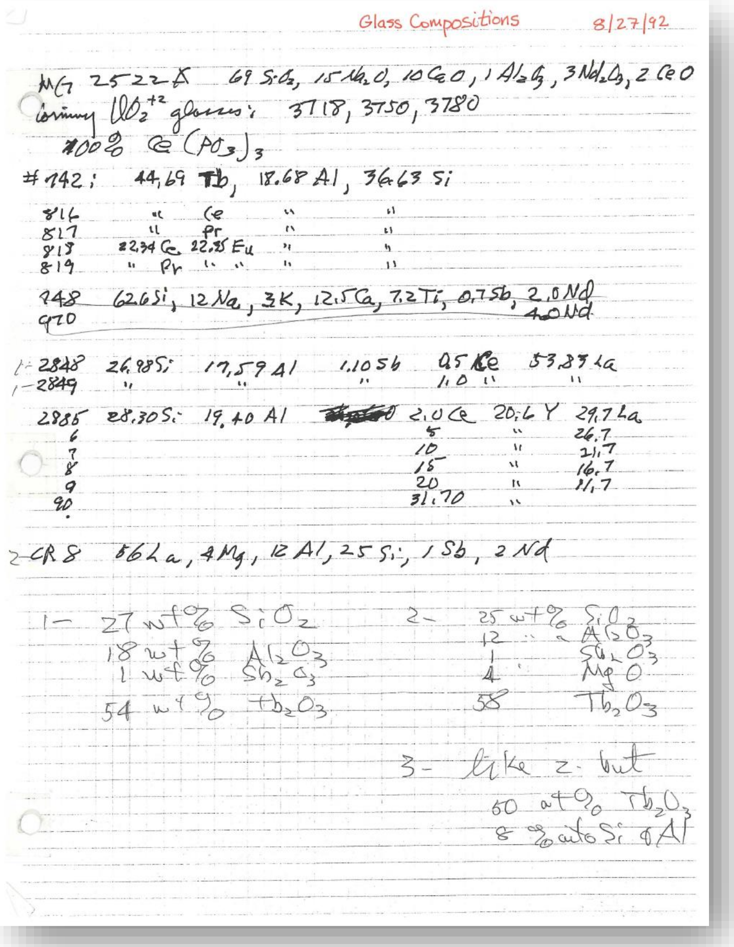
- Straight-forward
- Industry-accepted manufacturing (fiber draw) used; no lathe deposition.
  - Long lengths (> km)
  - High speed manufacturing (> m/s)
- **Low temperature** (compared to CVD…)
- Can be reactive (liquid-phase chemistry), we'll get to this…
- Amendable to very wide range of materials

Disadvantages (?)

- **High temperature** (diffusion/dissolution)
- Non-volatile cores, we'll get to this…
- *One must understand materials / glass science*

J. Ballato and P. Dragic, "Rethinking Optical Fiber: New Demands, Old Glasses," *Journal of the American Ceramic Society* **96**, 2675 – 2692 (2013).

The Past. . . again (a quick walk down memory lane…)



Glass Compositions 8/27/92

MG 2522A 69 SiO_2, 15 Na_2O, 10 CaO, 1 Al_2O_3, 3 Nd_2O_3, 2 CeO
Corning UO_2^{+2} glasses: 3718, 3750, 3780
100% $Ce(PO_3)_3$
#742: 44.69 Tb, 18.68 Al, 36.63 Si
816 " Ce " "
817 " Pr " "
818 22.34 Ce 22.35 Eu " "
819 " Pr " " " "
748 62.6Si, 12 Na, 3K, 12.5 Ca, 7.2 Ti, 0.7 Sb, 2.0 Nd
920 4.0 Nd

1-2848 26.98 Si 17.59 Al 1.10 Sb 0.5 Ce 53.83 La
1-2849 " " " 1.0 " "
2885 28.30 Si 19.40 Al [illegible] 2.0 Ce 20.6 Y 29.7 La
6 5 " 26.7
7 10 " 21.7
8 15 " 16.7
9 20 " 11.7
90 31.70 "

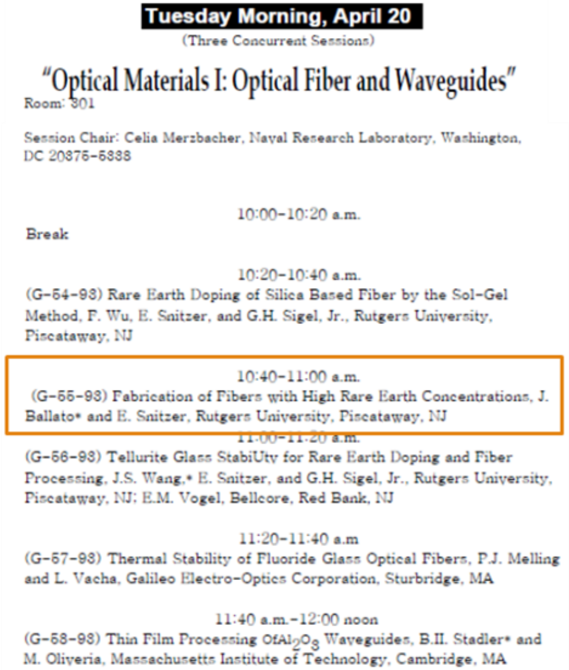
2-CR8 56 La, 4 Mg, 12 Al, 25 Si, 1 Sb, 2 Nd

1– 27 wt% SiO_2
18 wt% Al_2O_3
1 wt% Sb_2O_3
54 wt% Tb_2O_3

2– 25 wt% SiO_2
12 " " Al_2O_3
1 Sb_2O_3
4 MgO
58 Tb_2O_3

3– like 2 but
60 at% Tb_2O_3
8 % at% Si & Al

First report of molten core optical fiber



Tuesday Morning, April 20

(Three Concurrent Sessions)

"Optical Materials I: Optical Fiber and Waveguides"

Room: 301

Session Chair: Celia Merzbacher, Naval Research Laboratory, Washington, DC 20375-5338

10:00-10:20 a.m.

Break

10:20-10:40 a.m.

(G-54-93) Rare Earth Doping of Silica Based Fiber by the Sol-Gel Method, F. Wu, E. Snitzer, and G.H. Sigel, Jr., Rutgers University, Piscataway, NJ

10:40-11:00 a.m.

(G-55-93) Fabrication of Fibers with High Rare Earth Concentrations, J. Ballato* and E. Snitzer, Rutgers University, Piscataway, NJ

11:00-11:20 a.m.

(G-56-93) Tellurite Glass StabiUty for Rare Earth Doping and Fiber Processing, J.S. Wang,* E. Snitzer, and G.H. Sigel, Jr., Rutgers University, Piscataway, NJ; E.M. Vogel, Bellcore, Red Bank, NJ

11:20-11:40 a.m

(G-57-93) Thermal Stability of Fluoride Glass Optical Fibers, P.J. Melling and L. Vacha, Galileo Electro-Optics Corporation, Sturbridge, MA

11:40 a.m.-12:00 noon

(G-58-93) Thin Film Processing Of Al_2O_3 Waveguides, B.II. Stadler* and M. Oliveria, Massachusetts Institute of Technology, Cambridge, MA

Fabrication of fibers with high rare-earth concentrations for Faraday isolator applications

John Ballato and Elias Snitzer

The Faraday effect provides a mechanism for achieving unidirectional light propagation in optical isolators; however, miniaturization requires large Verdet constants. High rare-earth content glasses produce suitably large Verdet values, but intrinsic fabrication problems remain. The novel powder-in-tube method, or a single-draw rod-in-tube method, obviates these difficulties. The powder-in-tube method was used to make silica-clad optical fibers with a high terbium oxide content aluminosilicate core. Core diameters of 2.4 µm were achieved in 125-µm-diameter fibers, with a numerical aperture of 0.35 and a Verdet constant of −20.0 rad/(T m) at 1.06 µm. This value is greater than 50% for crystals found in current isolator systems. This development could lead to all-fiber isolators of dramatically lower cost and ease of fabrication compared with their crystalline competitors. © 1995 Optical Society of America

1. Introduction

Modern photonic devices for optical computing, telecommunications, etc., require classes of elements that exhibit nonreciprocal behavior. One such class is based on the Faraday effect,[1] in which the rotation of plane-polarized light is dependent on only the applied magnetic field and is not dependent on the direction of light propagation. This provides unidirectional propagation of light in an optical fiber. In this paper we briefly describe this effect to illustrate the factors that influence the Verdet constant,[2] characterizing the magnitude of the effect, and our choice of the high rare-earth content glass composition for its attainment. This is followed by a short discussion of a novel method of fabricating optical fibers with these constituents and the experimental realization of fibers with large Verdet constants.

2. Faraday Effect

The Faraday effect in glass is a well-understood phenomenon and has been intensively studied and documented.[3–10] It is present in all materials and is closely related to the magnetic behavior of the component ions. The rotation varies with temperature in paramagnetic and ferromagnetic materials, but is temperature independent in diamagnetic materials. Its magnitude also tends to decrease with increasing wavelength. The Faraday effect is a magnetic-field-induced circular birefringence, providing a means of controlling the polarization state of light. The effect is distinct from intrinsic circular birefringence (optical chiralty or activity) in that its rotation direction depends on only the direction of the magnetic field along the path of light propagation and not on the direction of light propagation. The optical rotation arises from the inequality of the refractive indices for right- and left-circularly polarized light; these, in turn, stem from the ground- and excited-state splitting in the medium when an external magnetic field is applied.

At a more fundamental level, Faraday rotation can be implicitly inferred from the time-reversal asymmetry of Maxwell's equations. These are

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t},$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J},$$

$$\nabla \cdot \mathbf{D} = \rho,$$

$$\nabla \cdot \mathbf{B} = 0.$$

When (t) is replaced with $(-t)$ for $\mathbf{E}$ and $\mathbf{D}$, this is equivalent to replacing x, y, and z by $(-x)$, $(-y)$, and $(-z)$, respectively [similarly, $\mathbf{r}$ by $(-\mathbf{r})$]. The physical

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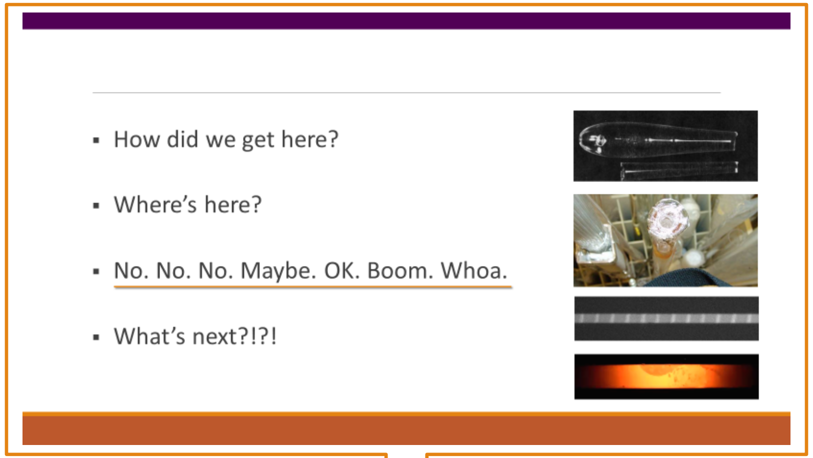
The authors are with the Fiber Optic Materials Research Program, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08855-0909.

Received 21 November 1994; revised manuscript received 31 March 1995.
0003-6935/95/306848-07$06.00/0.

6848 APPLIED OPTICS / Vol. 34, No. 30 / 20 October 1995

J. Ballato and E. Snitzer, "Fabrication of fibers with high rare-earth concentrations for Faraday isolator applications," *Applied Optics* **34**, 6848-6854 (1995).

The Past. . . into... the Present (again)



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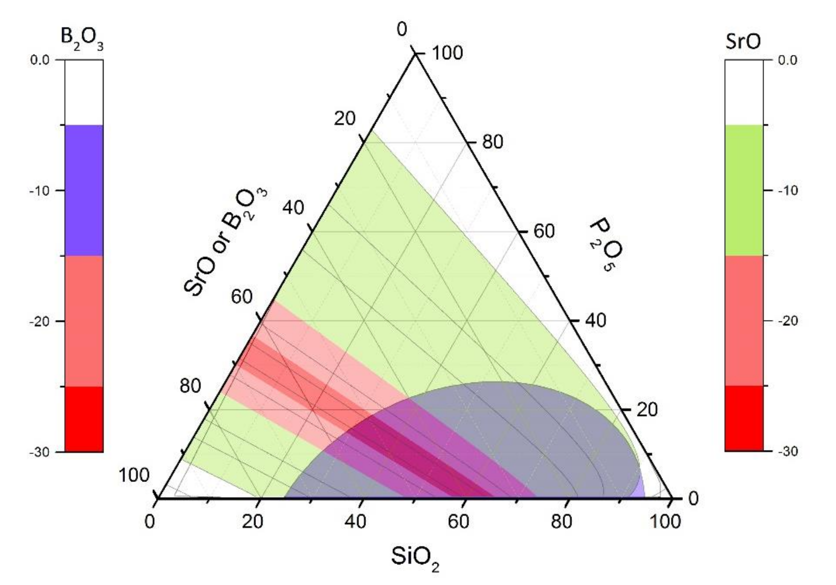
Examples…

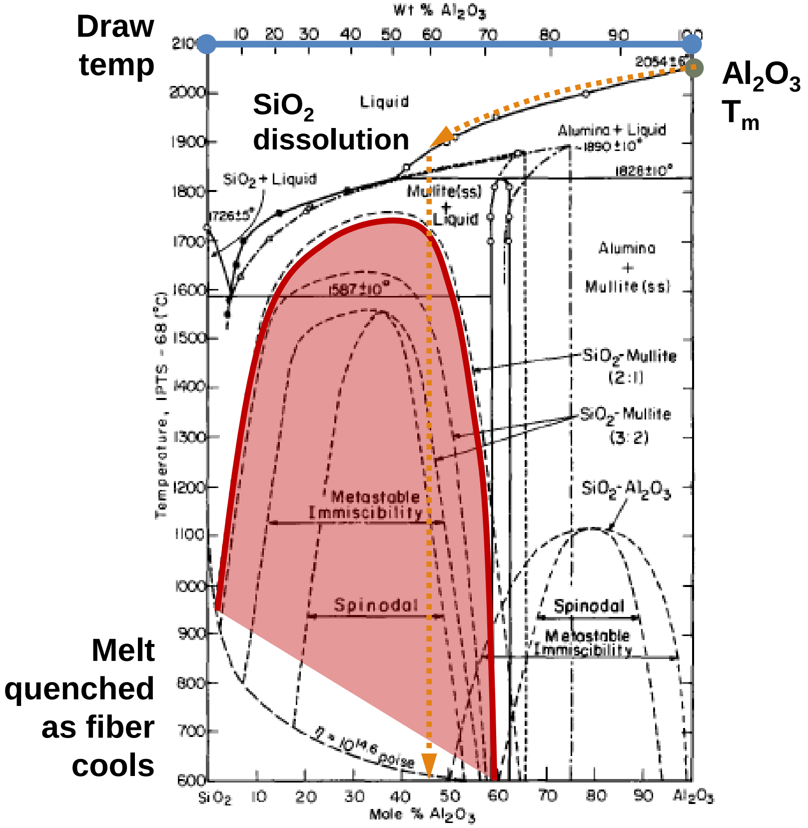
1. Intrinsically low nonlinearity all-glass fibers
2. Crystalline semiconductor core fibers



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

What’s new about the Al_2O_3 – SiO_2 system?

- The addition of alumina (Al_2O_3) to silica (SiO_2) glass is known to raise the refractive index and to “solubilize” active dopants into the glass.
- However, the doping of alumina in silica is limited for two reasons:
  1. CVD not as amenable to the addition of alumina as they are other dopants (e.g., vapor-phase GeO_2).
  2. Limitation in amount of alumina (~ 10 wt. %) that can be added into silica prior to phase-separation.



S. Risbud and J. Pask, “Calculated thermodynamic data and metastable immiscibility in the system SiO_2-Al_2O_3,” *Journal of the American Ceramic Society* **60**, 418 - 424 (1977).

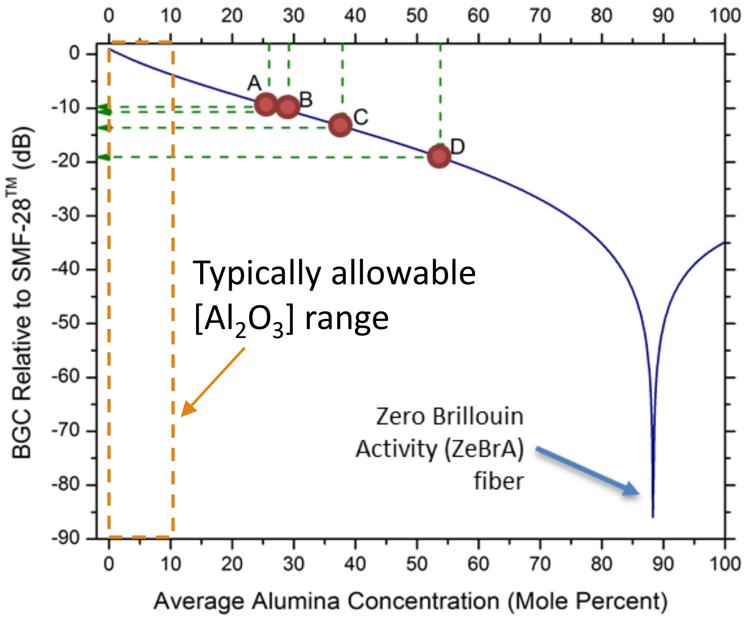
What's new about the Al_2O_3 – SiO_2 system?

- Transverse photoelastic coefficients!

$$\mathbf{p}_{12}^{Al_2O_3} < 0 \qquad \mathbf{p}_{12}^{SiO_2} > 0$$

- Balance to greatly reduce Brillouin scattering; possibly negate completely!

$$BGC = \frac{2\pi n^7 \mathbf{p}_{12}^{2}}{c\lambda^2 \rho V_a \Delta\nu_B}$$



Typically allowable $[Al_2O_3]$ range

Zero Brillouin Activity (ZeBrA) fiber

- Measured BGC was ~ 100× lower than commercial single mode fiber.
- **Immensely useful: not just reduce… but completely eradicate SBS!**

What else now possible?

P. Dragic, T. Hawkins, S. Morris, and J. Ballato, "Sapphire-derived all-glass optical fibers," *Nature Photonics* **6**, 627 – 633 (2012).

What's new about the BaO – SiO_2 system?

- Well… $\mathbf{p}_{\mathbf{12}}^{\mathbf{BaO}} \sim \mathbf{10} \times \mathbf{p}_{\mathbf{12}}^{\mathbf{Al_2O_3}}$ … but

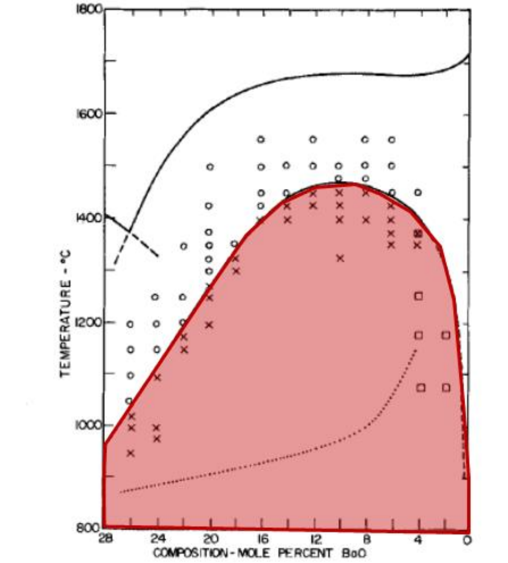
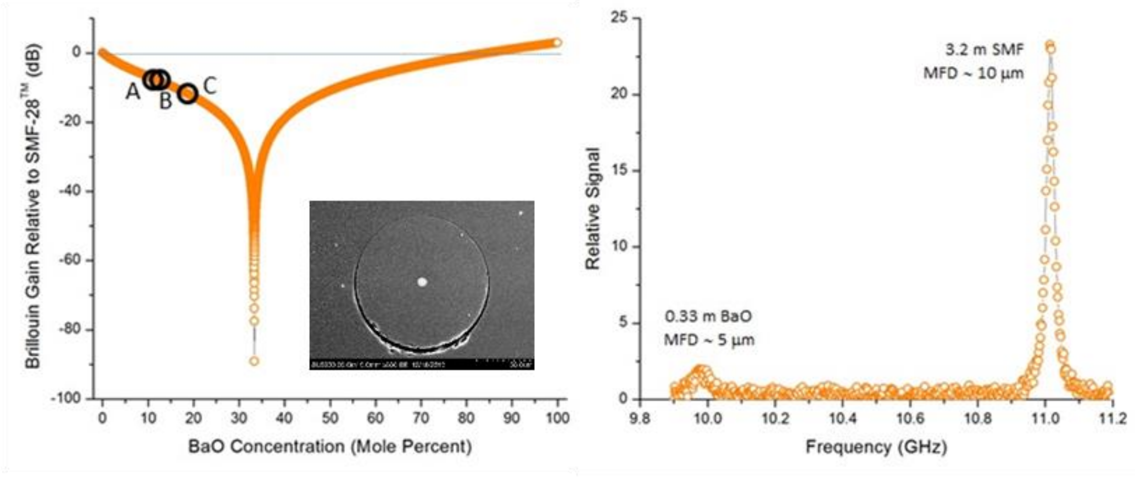


Fig. 2. Metastable miscibility gap in the system BaO–SiO_2. ○ = clear glasses, × = opalescent glasses, □ = electron microscope immiscibility data (no visible opalescence), *dotted line* = approximate temperatures below which samples could be held for 30 sec without visible opalescence.

- Perfect for MCM since $T_m^{BaO} < T_{draw}^{SiO_2}$

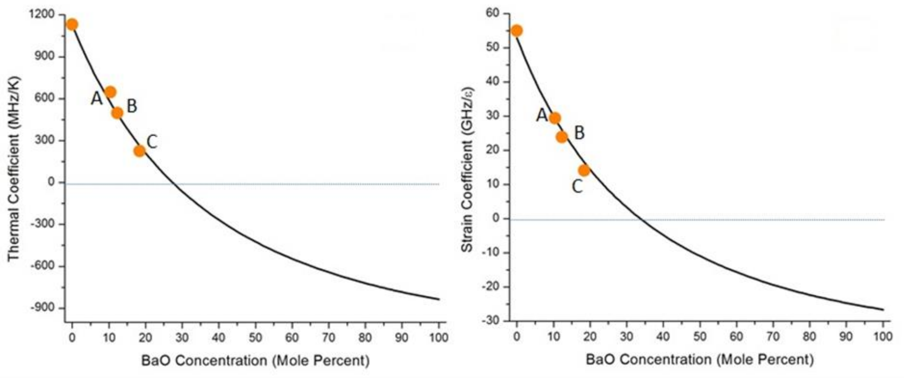


- This compositional balancing of + / – p_{12} greatly reduced Brillouin scattering. But can be done to other (selected) properties too!
- Counter-balancing thermo-acoustic and strain-acoustic coefficients yield *athermal and atensic Brillouin fibers*.

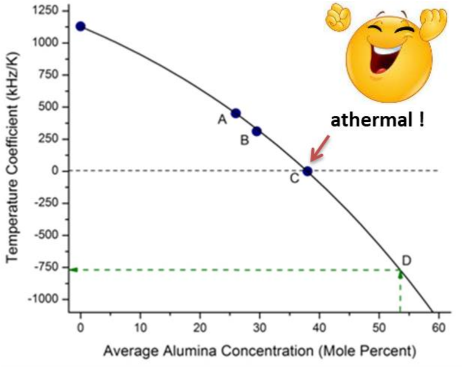
T. S. Seward, D. R. Uhlmann, and D. Turnbull, "Development of two-phase structure in glasses, with special reference to the system BaO-SiO_2," *Journal of the American Ceramic Society* **51**, 634 – 642 (1968).
P. Dragic, C. Kucera, J. Furtick, J. Guerrier, T. Hawkins, and J. Ballato, "Brillouin spectroscopy of a novel baria-doped silica glass optical fiber," *Optics Express* **21**, 10924 – 10941 (2013).

a-“X”-ic (atenstic, athermal) fibers

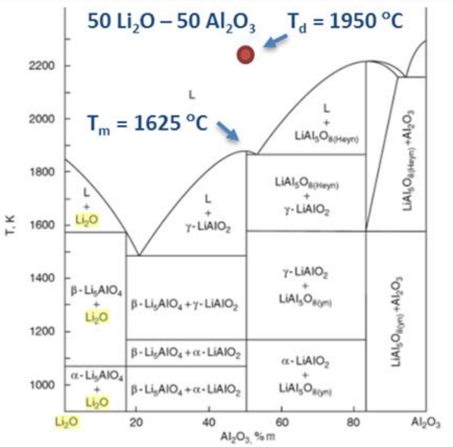
- $BaO – SiO_2$



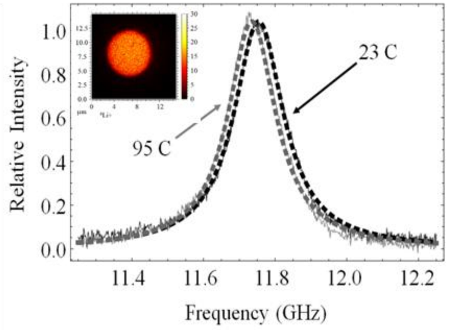
- $Al_2O_3 – SiO_2$



- $Li_2O – Al_2O_3 – SiO_2$



  - $v_{\mathrm{acoustic}}^{\mathrm{SiO_2}}$ increases with increasing temperature <u>but</u> decreases with increasing pressure; SiO_2 is anomalous.
  - Large core CTE relative to cladding, restricts thermal expansion; equivalent to a positive pressure.
  - Increasing T (increasing v_A) increases pressure (decreasing velocity); which can cancel at the proper composition.

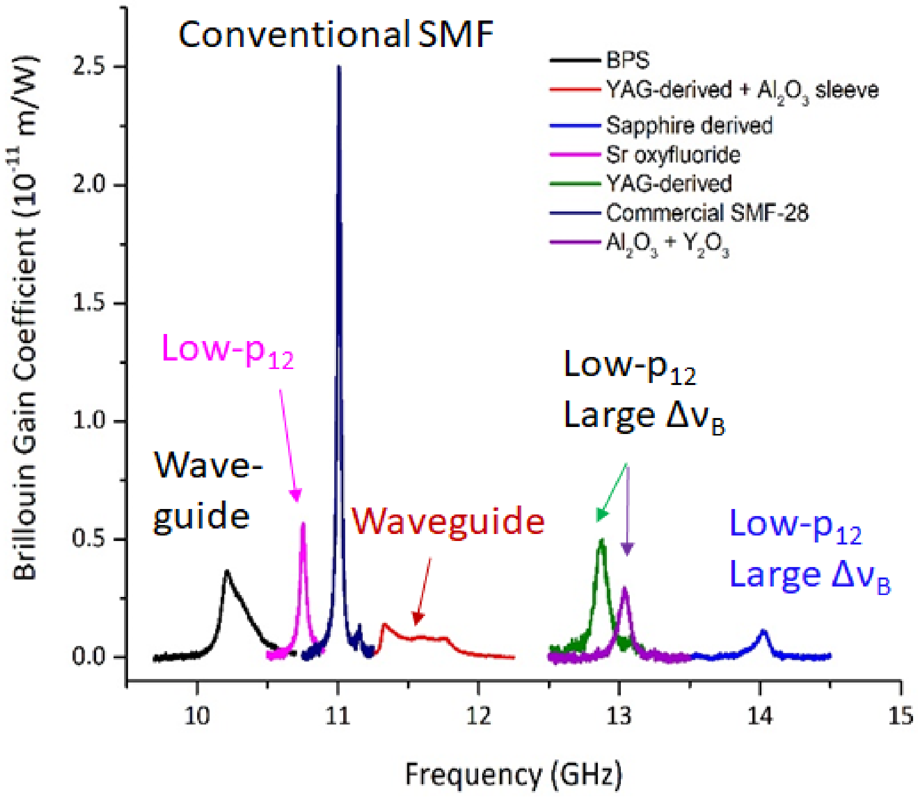


  - **Large CTE of Li_2O used as design parameter for a Brillouin-athermal <u>single mode</u> optical fiber.**

P. Dragic, C. Ryan, C. Kucera, M. Cavillon, M. Tuggle, R. Stolen, and J. Ballato, “Novel single- and few-moded optical fiber for athermal Brillouin strain sensing based on lithium aluminosilicates,” *Optics Letters* **40**, 5030 – 5033 (2015).

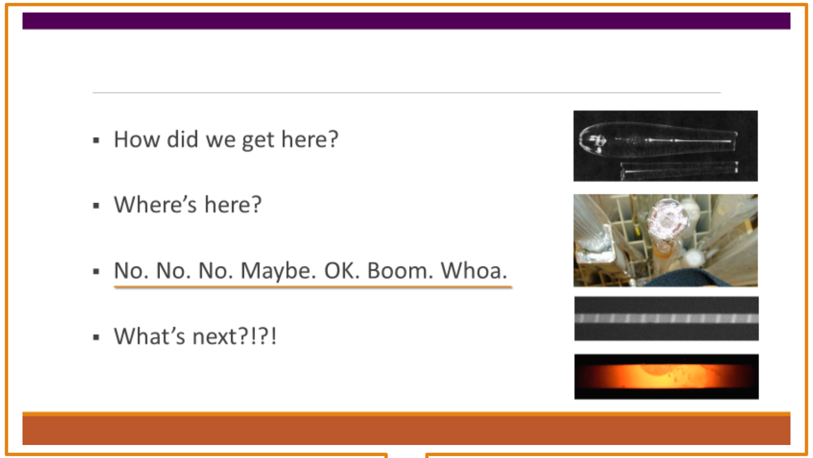
The Present…

- More compositions = more fun!
- Exploration of novel phenomena, such as intrinsically low (< SiO_2) multicomponent glass fibers.
- Can make fiber perform in ways never thought possible or permissible by design alone.
- But there's more!!!



P. Dragic, M. Cavillon, and J. Ballato, "Materials for optical fiber lasers: A review," *Applied Physics Reviews* **5**, 041301 (2018).

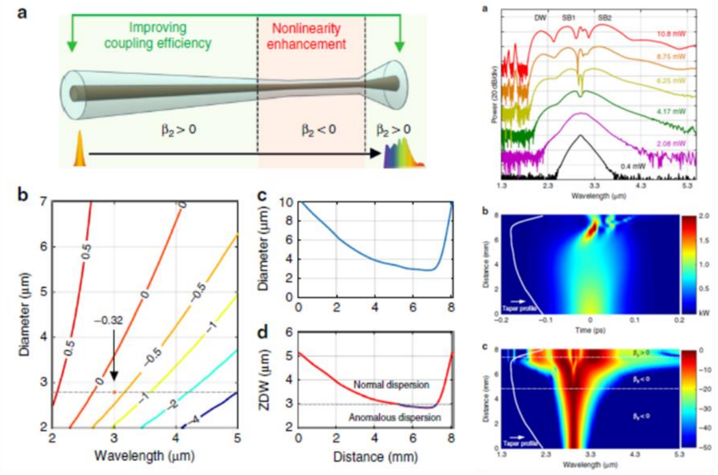
The Past… into… the Present (again)



- How did we get here?
- Where's here?
- No. No. No. Maybe. OK. Boom. Whoa.
- What's next?!?!

Examples…

1. Intrinsically low nonlinearity all-glass fibers
2. Crystalline semiconductor core fibers

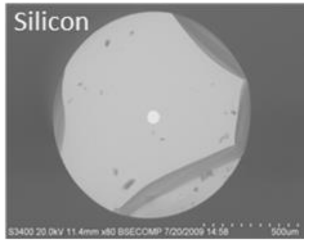


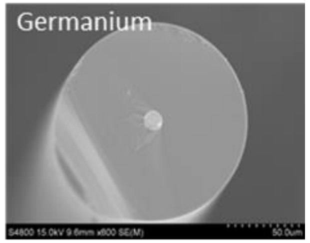
- Compact SCF platform achieves low loss transmission across the mid-IR spectral regime. Exploiting a novel asymmetric taper design, coherent SC span of 1.74 octaves was generated from 1.6 to 5.3 μm, which is the broadest SC reported in a silicon core/silica-clad waveguide.

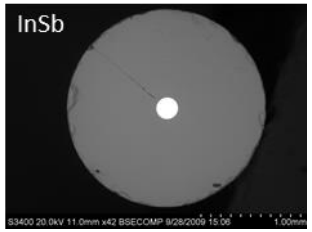
J. Ballato and A. C. Peacock, "Perspective: Molten core optical fiber fabrication - A route to new materials and applications," *APL Photonics* **3**, 120903 (2018); H. Ren, L. Shen, A. F. J. Runge, T. W. Hawkins, J. Ballato, U. J. Gibson, and A. C. Peacock, "Low-loss silicon core fibre platform for mid-infrared nonlinear photonics," (Nature) *Light: Science & Applications* **8**, 105 (2019).

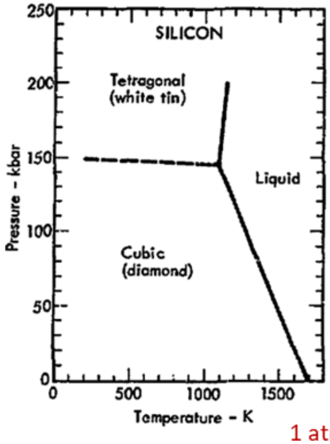
The role of phase diagrams…

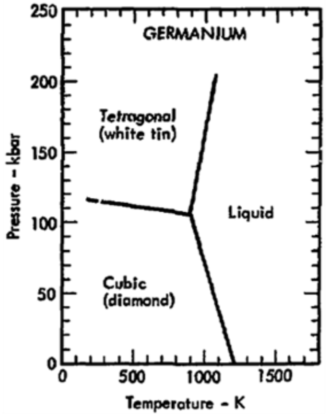
- **Optical fibers are (<u>normally</u>) made of glass… why consider (equilibrium) phase diagrams?**
  - Phase diagrams can inform dopant / additive solubility limits AND glass forming compositions.
- **For crystalline core fibers, they are invaluable…But not always appreciated**…
  - **Gen 0** (2008 – 2010): Unary, e.g., **Si** and **Ge**, and line compounds, e.g., **InSb** and **GaSb**… phase diagrams inform melting points, phase transitions, and phases immediately off stoichiometry.



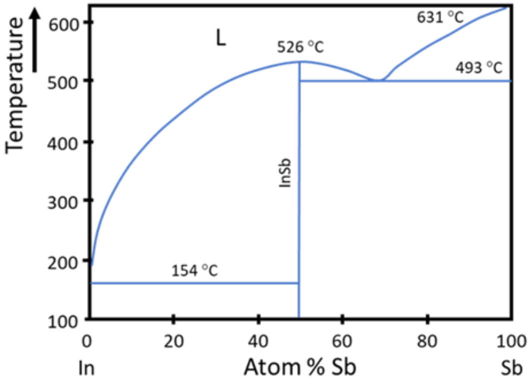








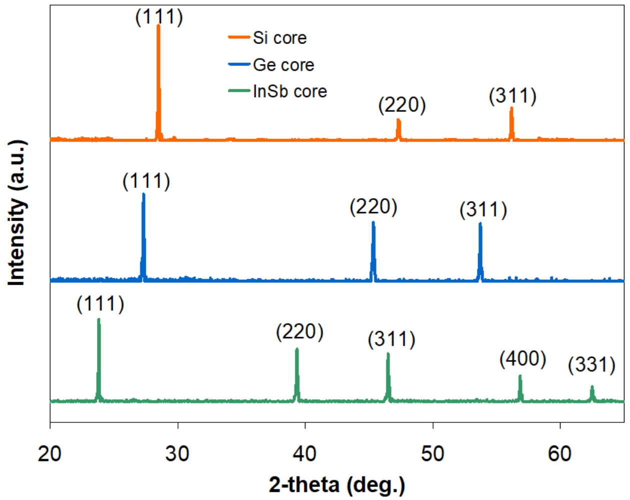
1 atm = 0.001 kbar

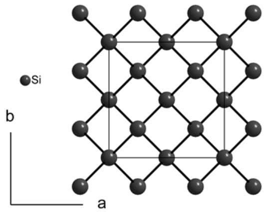


Young, David A. *Phase diagrams of the elements*. No. UCRL--51902. California Univ., 1975.
A. Peacock, U. Gibson, and J. Ballato, "Silicon Optical Fiber – Past, Present, and Future," *Advances in Physics: X* (APX) **1**, 114 – 127 (2016).

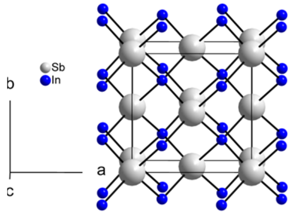
Gen 0: Unary phases and line compounds

- As drawn… highly crystalline!! But polycrystalline.



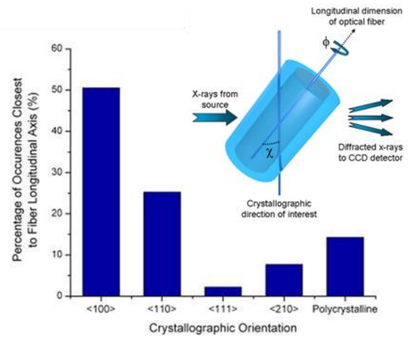


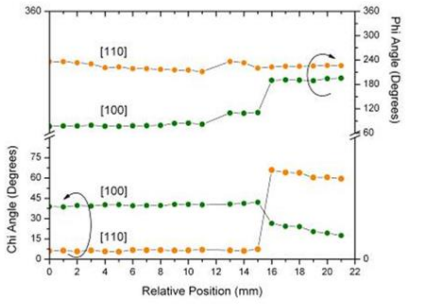
Fd-3m (Diamond)



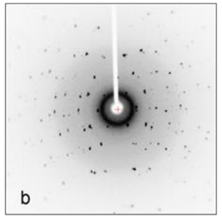
F-43m (Zinc Blende)

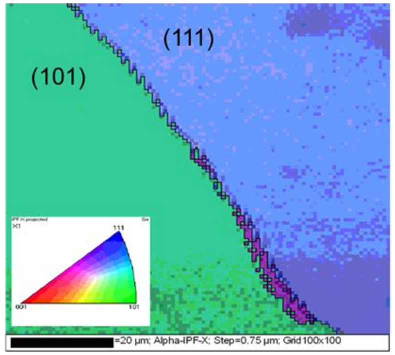
Over longer distances (> cm) , the orientation is found to change along length of fiber so technically poly-crystalline but with large grain size in comparison to fiber dimensions (> 1000:1).





polycrystallinity



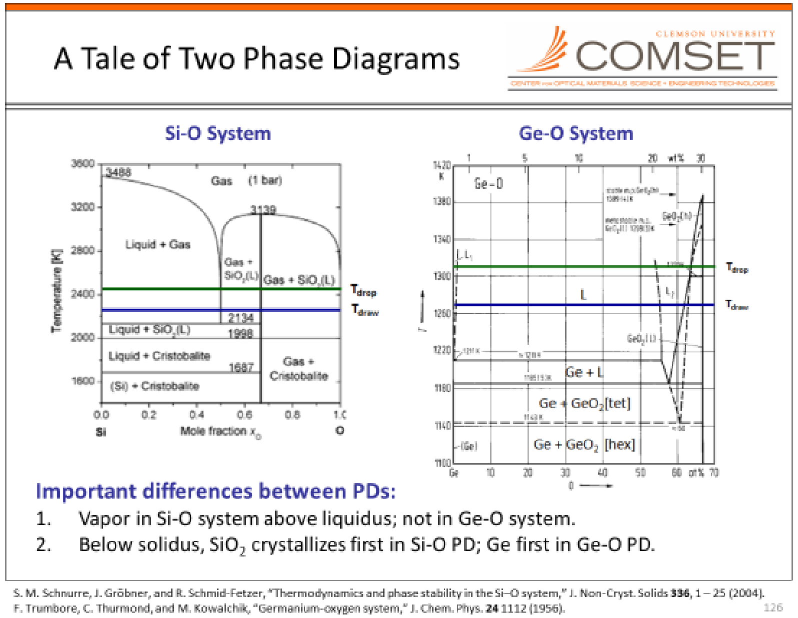


Electron backscatter diffraction (EBSD) micrograph of grain boundary [side-polished sample]

- *N.B.*: Crystalline nature of cores implies equilibrium processes despite high draw speeds. In reality, kinetics of crystallization of semiconductors from melt extremely fast.

Gen 1: Reactive molten core

- **Gen 1** (2011)… used only for managing oxygen contamination.
  - Understand the Si-O and Ge-O systems (did help realize zero oxide content Ge:SiO_2 fibers)
  - Taught oxygen gettering by reactive molten core: $SiO_2 + SiC \rightarrow Si + SiO_g + CO_g$.
  - MCM permits *in-situ* chemistry! Will be very important later...



A Tale of Two Phase Diagrams

Important differences between PDs:

1. Vapor in Si-O system above liquidus; not in Ge-O system.
2. Below solidus, SiO_2 crystallizes first in Si-O PD; Ge first in Ge-O PD.

S. M. Schnurre, J. Gröbner, and R. Schmid-Fetzer, "Thermodynamics and phase stability in the Si–O system," J. Non-Cryst. Solids **336**, 1 – 25 (2004).
F. Trumbore, C. Thurmond, and M. Kowalchik, "Germanium-oxygen system," J. Chem. Phys. **24** 1112 (1956).

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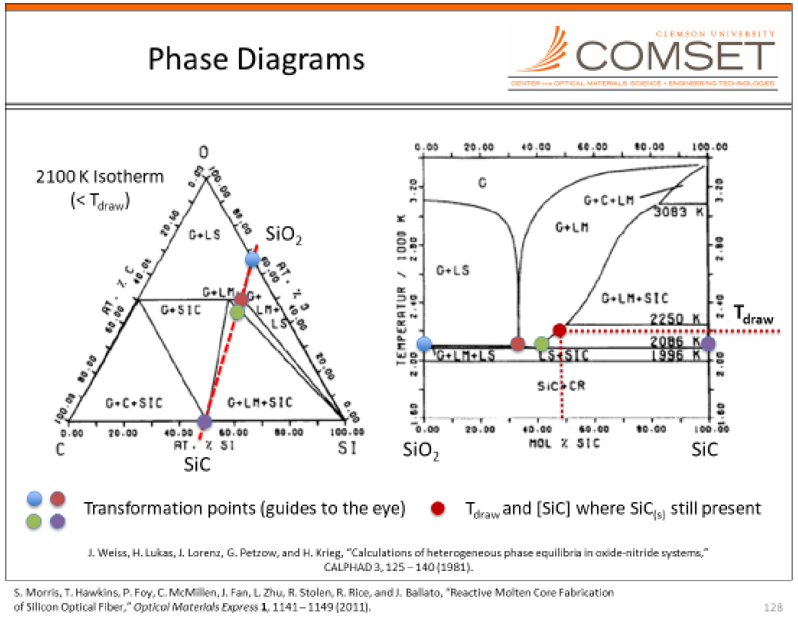

Phase Diagrams

● ● ● ● Transformation points (guides to the eye) ● T_{draw} and [SiC] where $SiC_{(s)}$ still present

J. Weiss, H. Lukas, J. Lorenz, G. Petzow, and H. Krieg, "Calculations of heterogeneous phase equilibria in oxide-nitride systems," CALPHAD 3, 125 – 140 (1981).

S. Morris, T. Hawkins, P. Foy, C. McMillen, J. Fan, L. Zhu, R. Stolen, R. Rice, and J. Ballato, "Reactive Molten Core Fabrication of Silicon Optical Fiber," *Optical Materials Express* **1**, 1141 – 1149 (2011).

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S. Morris, T. Hawkins, P. Foy, C. McMillen, J. Fan, L. Zhu, R. Stolen, R. Rice, and J. Ballato, "Reactive molten core fabrication of silicon optical fiber," *Optical Materials Express* **1**, 1141 – 1149 (2011).

Gen 1.5: Reactive (interfacial) molten core

- **Gen 1.5** (2013)… still used only for managing oxygen contamination… but better…
  - Interfacial modifiers… based on CaO – SiO_2… silicon / slag literature…
  - Critical advance in achieving long lengths of oxygen-free silicon core fibers.

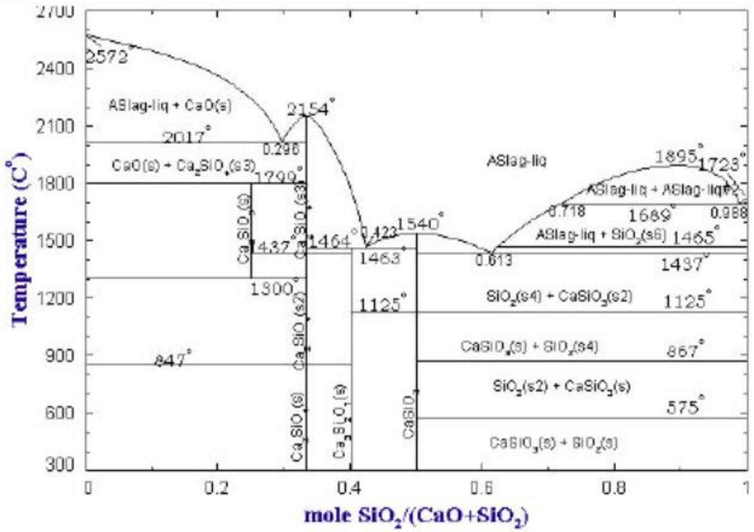
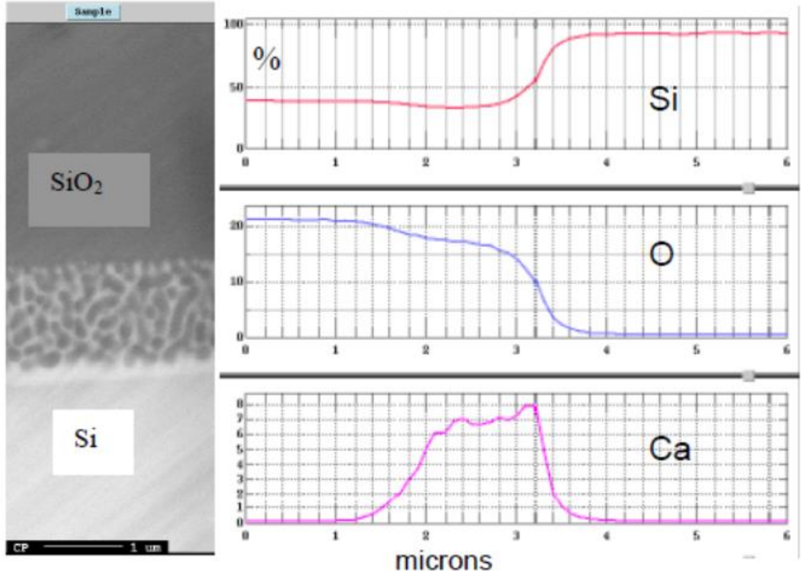


Fig. 2 Phase diagram of the CaO – SiO_2 system [20]

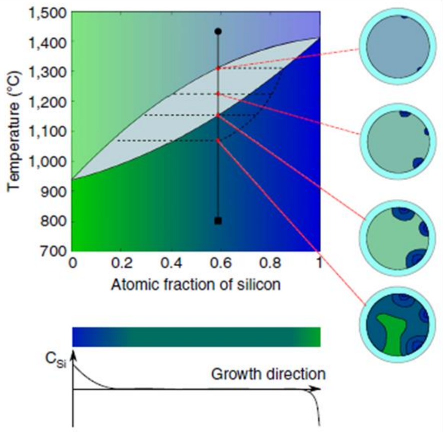


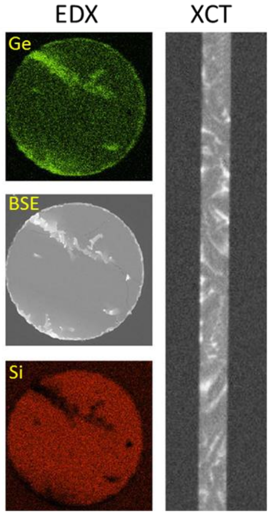
E. F. Nordstrand, A. N. Dibbs, A. J. Eraker, and U. J. Gibson, “Alkaline oxide interface modifiers for silicon fiber production,” *Optical Materials Express* **3**, 651 – 657 (2013).

Gen 2: Isomorphic molten core…

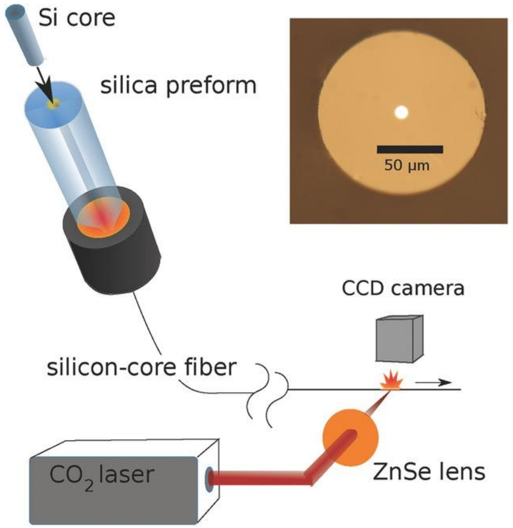
- **Gen 2** (2016)… Two critical advances:
  1. Isomorphic systems, e.g., Si-Ge.
  2. Laser post-processing to zone recrystallize / repurify and create in-fiber structures and tapers.

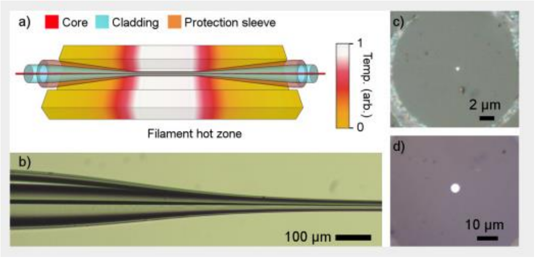
As-drawn fibers have compositional variations due to non-equilibrium cooling.





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. J. Gibson, "Laser recrystallization and inscription of compositional microstructures in crystalline SiGe-core fibres," *Nature Communications* **7**, 13265 (2016).

Gen 2: Isomorphic molten core… and laser post-processing

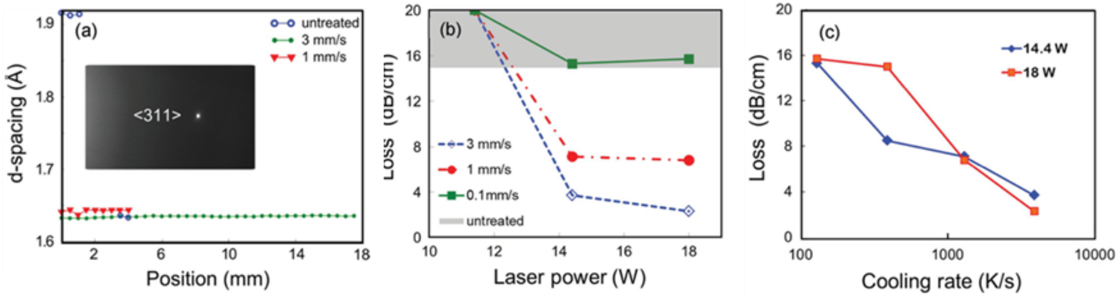
2. Laser post-processing to zone recrystallize / repurify and create in-fiber structures and tapers.

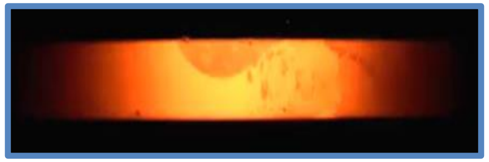
Example 1: Si

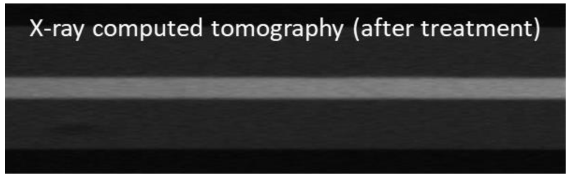
- High speed translational annealing: establish melt zone, translate fiber.
- Nucleation suppressed, single crystalline over entire length and preferential segregation of impurities.
- Loss reduction, now routinely ~ 0.1 dB/cm.

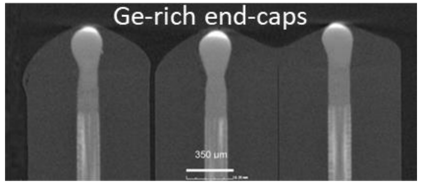
Example 2: Si-Ge

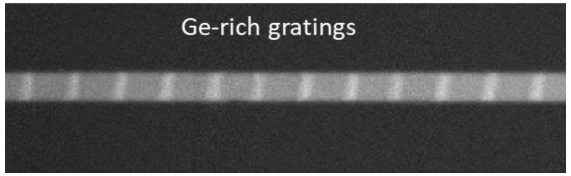
- Ge-rich material accumulates in the high temperature region.
- Establish melt zone – translate through fiber. Competition between nucleation suppression and unstable growth front.







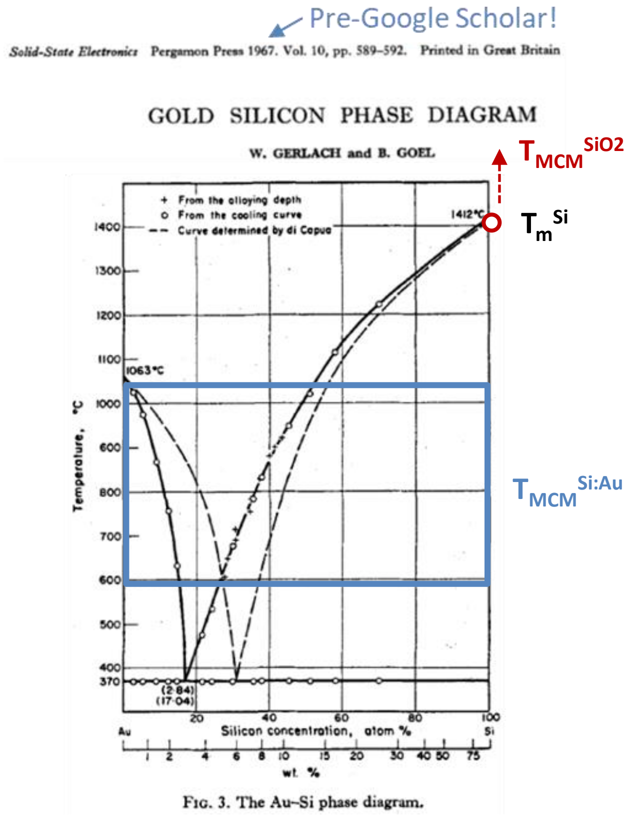




N. Healy, et al., “CO_2 laser-induced directional recrystallization to produce single crystal silicon-core optical fibers with low loss,” Advanced Optical Materials **4**, 1004 – 1008 (2016); Y. Franz, et al., “Material properties of tapered crystalline silicon core fibers,” *Optical Materials Express* **7**, 2055 – 2061 (2017).

Gen 3: Eutectic molten core…

- **Gen 3** (2018)… Eutectic systems



Pre-Google Scholar!

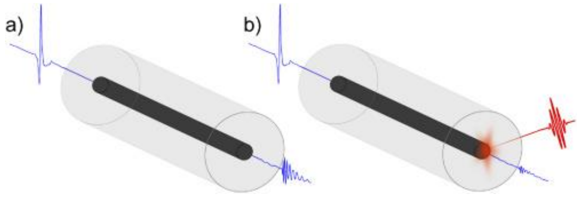
Solid-State Electronics Pergamon Press 1967. Vol. 10, pp. 589–592. Printed in Great Britain

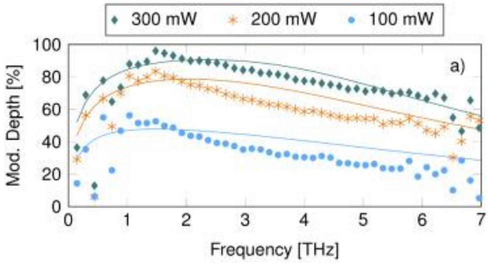
GOLD SILICON PHASE DIAGRAM

W. GERLACH and B. GOEL

FIG. 3. The Au–Si phase diagram.

- e.g., eutectic Si-Au system
  - Draw homogeneous mixture in eutectic region, spatially post-process below melting point of either end-member, and then transition (L + S) field to solidify desired phase.
  - Facilities low temperature fabrication, less contamination, AND better zone refinement / recrystallization.
  - Employed for high-speed all-optical modulation of broadband THz signals within a SCF with low levels of gold.

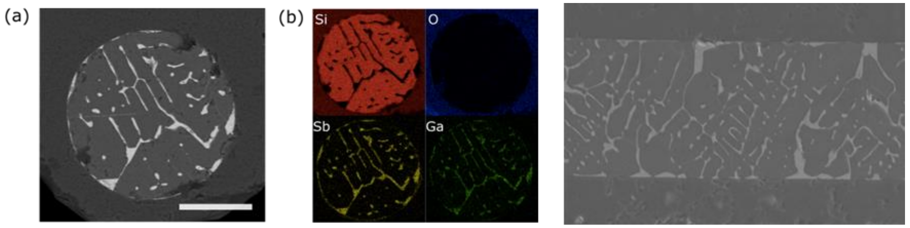




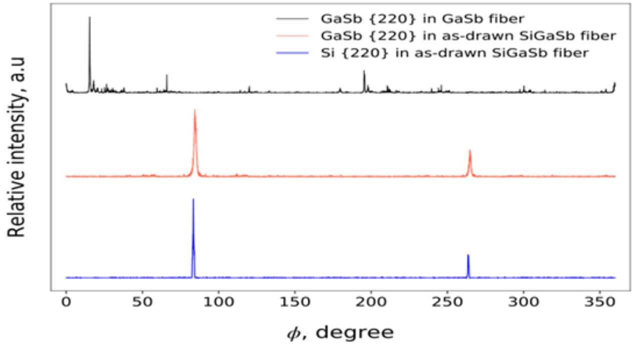
T. Sørgård, et al., "Broadband infrared and THz transmitting silicon core optical fiber," *Optical Materials Express* **10**, 2491 – 2499 (2020); T. Sørgård, et al., "All-optical high-speed modulation of THz transmission through silicon core optical fibers," *Optics Express* **29**, 3543 – 3552 (2021).

Gen 3: Eutectic molten core…

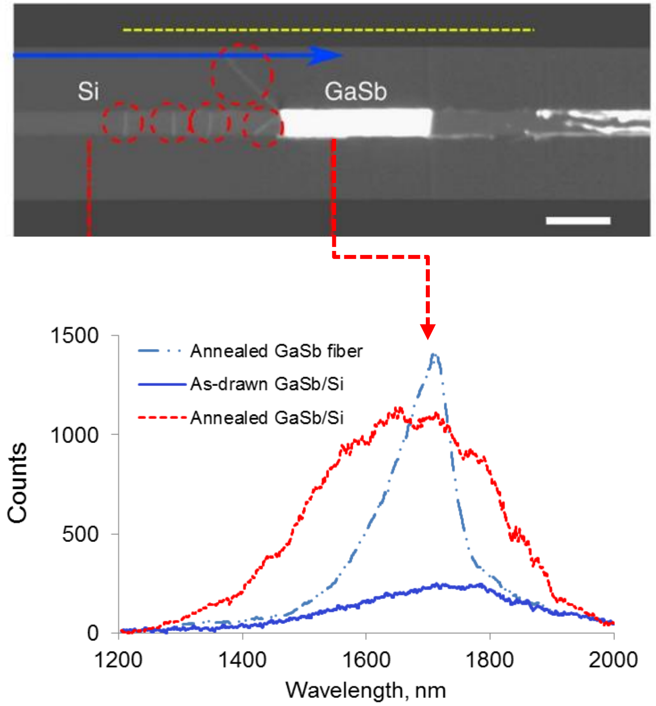
- **Gen 3** (2018)… Eutectic systems
  - e.g., Si and III-V core: GaSb as solvent



  - Heterogeneous as-drawn fiber but with Si / GaSb phases co-aligned.



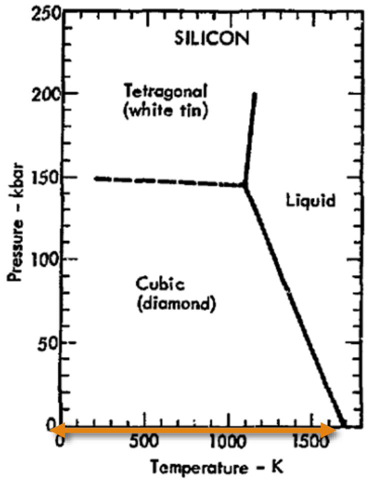
- Laser post-processing…



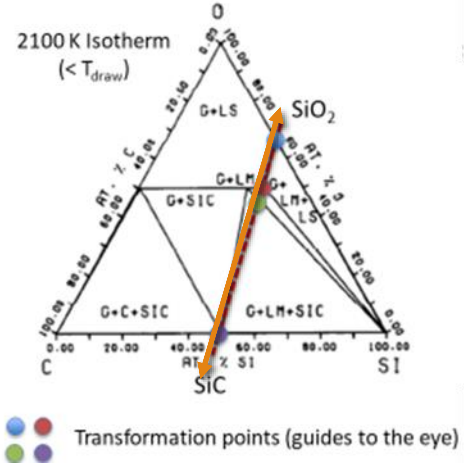
S. Song, et al., "Crystalline GaSb-core optical fibers with room-temperature photoluminescence," *Optical Materials Express* **8**, 1435 – 1440 (2018).

The role of phase diagrams… becoming more appreciated

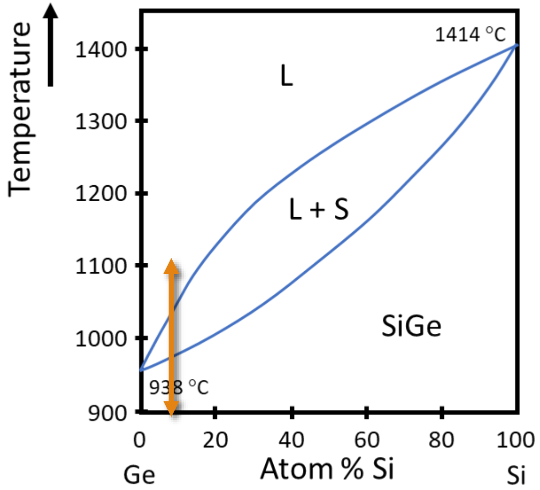
Gen 0
(2008)



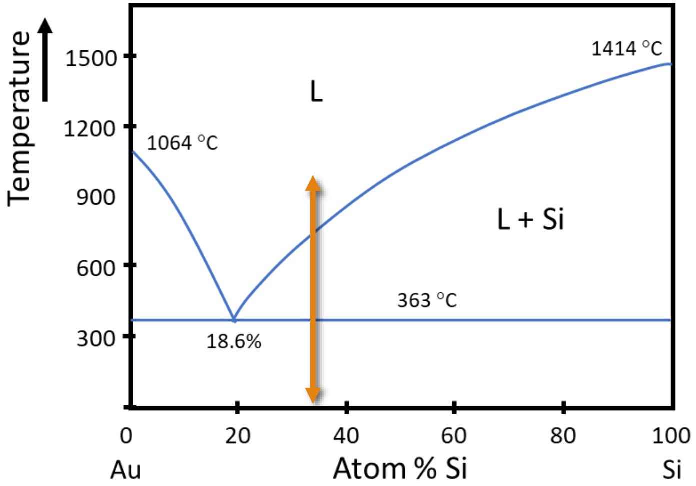
Gen 1
(2011)

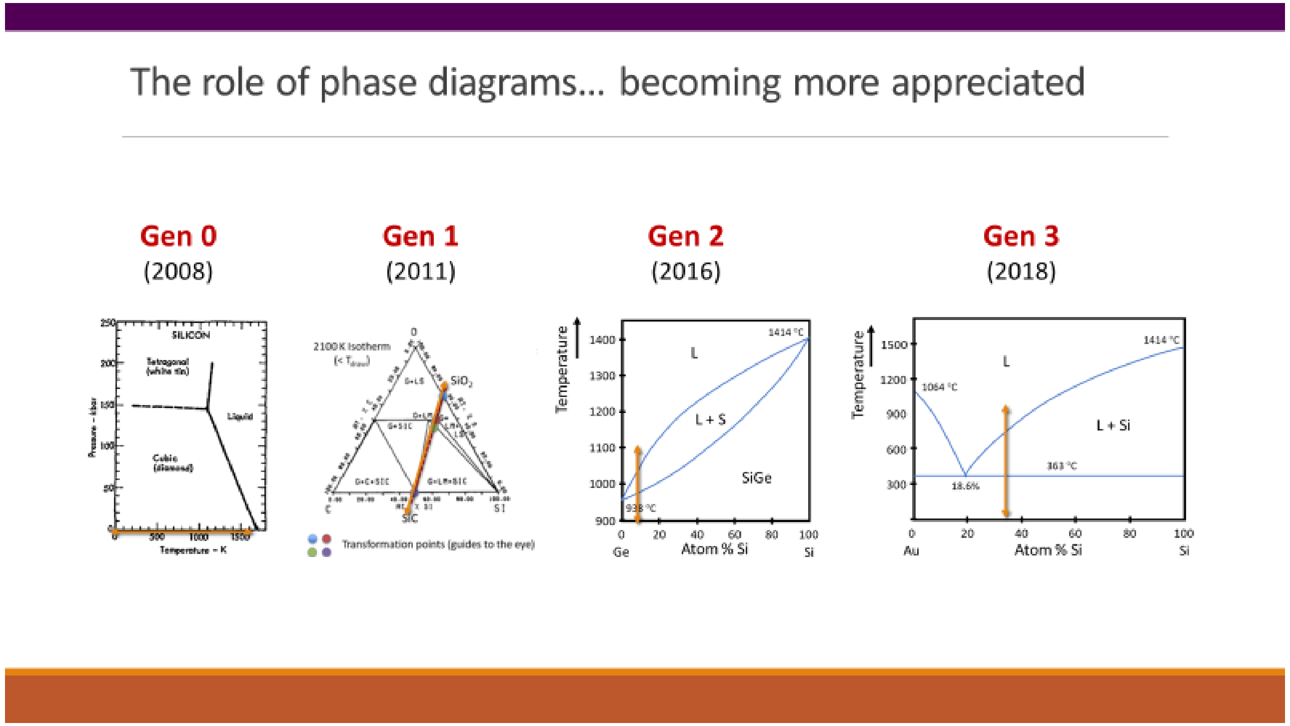


Gen 2
(2016)



Gen 3
(2018)





The role of phase diagrams… becoming more appreciated

Gen 0
(2008)

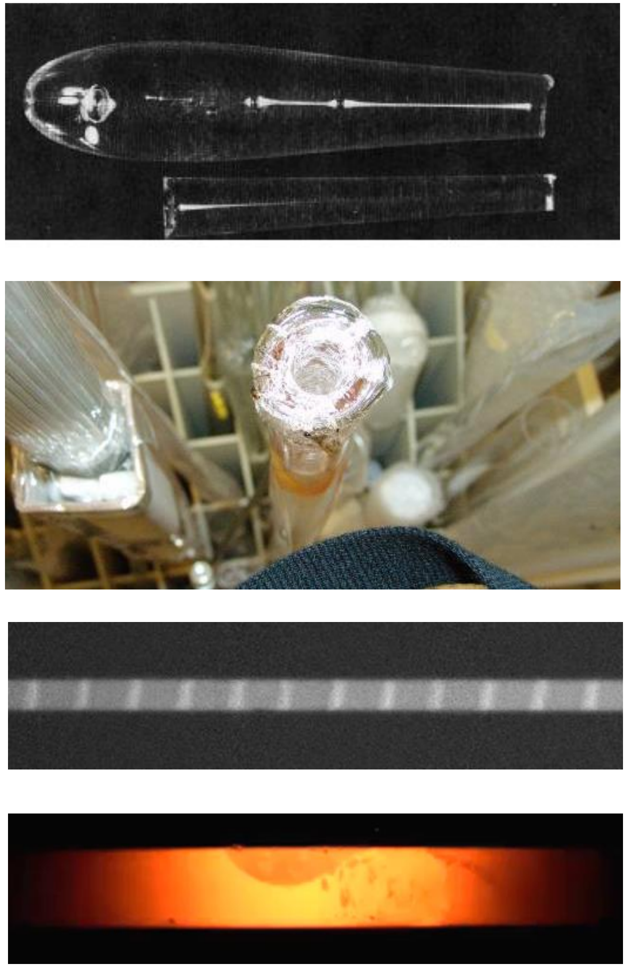
Gen 1
(2011)

Gen 2
(2016)

Gen 3
(2018)

Gen 4
(2022…)

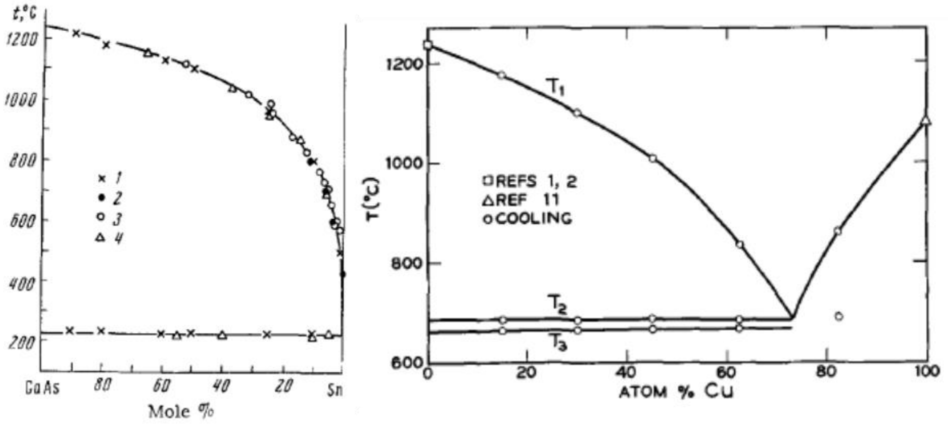
- How did we get here?
- Where’s here?
- No. No. No. Maybe. OK. Boom. Whoa.
- What’s next?!?!



The **FUTURE** … doing the impossible…

- **Gen 4** (now!)
    - Established that the molten core is limited to phases exhibiting low / no vapor pressure at the melting point...

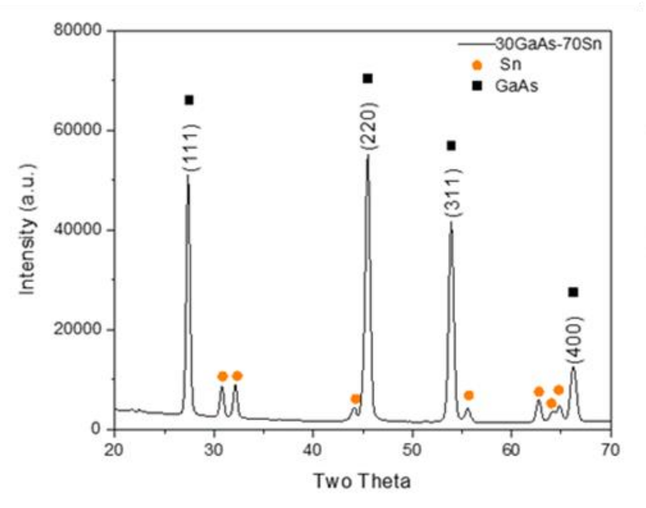
- **But…**
    - Volatility depends on temperature, which can be greatly reduced using the now-established flux approaches!

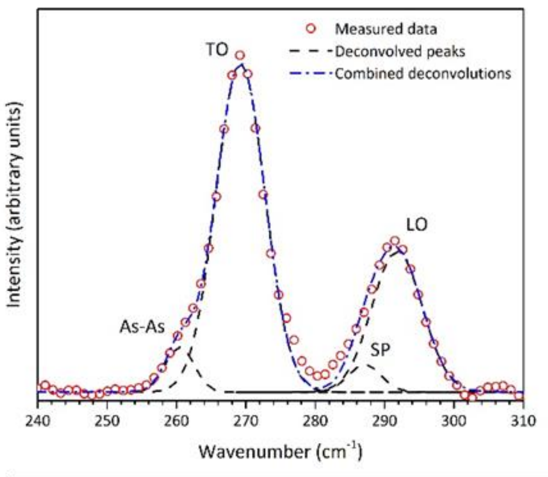


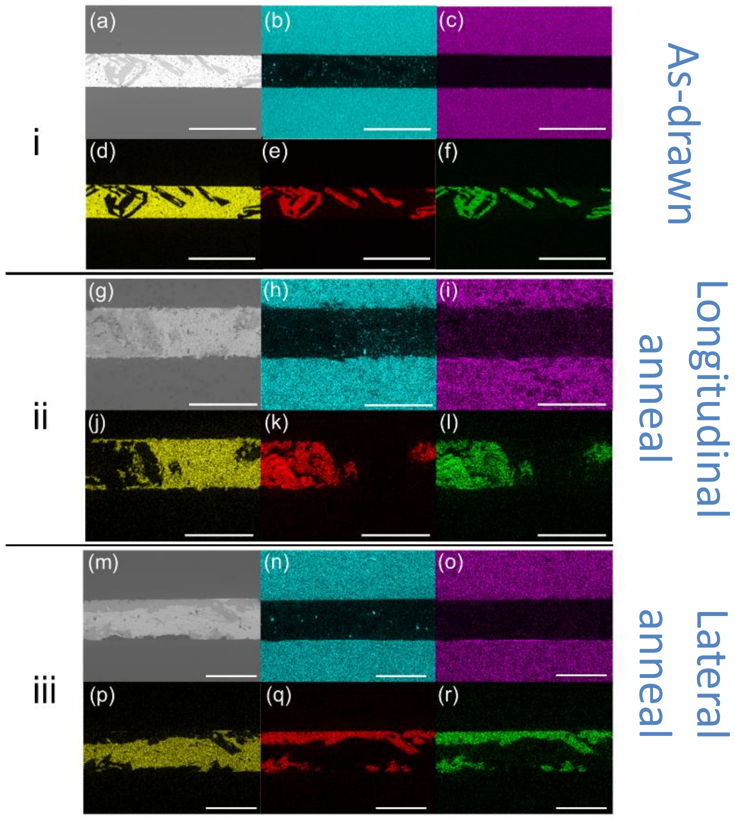
O. Pelevin, M. Milvidky, and B. Zherdev, "Phase diagram of the quasi-binary system GaAs-Sn," *Izvest Akad Nauk SSSR Neorg. Materialy* **8**, 446 (1972).
M. Panish "Ternary condensed phase systems of gallium and arsenic with Group IB elements," Journal of the Electrochemical Society **114**, 516 (1967).

Gen 4: Flux molten core…

- **Gen 4** (2022)… Volatile and incongruent melting cores, e.g., GaAs.
  - E.g., GaAs core optical fiber!
    - T_m = 1245°C… but very high VP…
    - Use fluxes to reduce liquidus and apply MCM below where volatility is problematic.





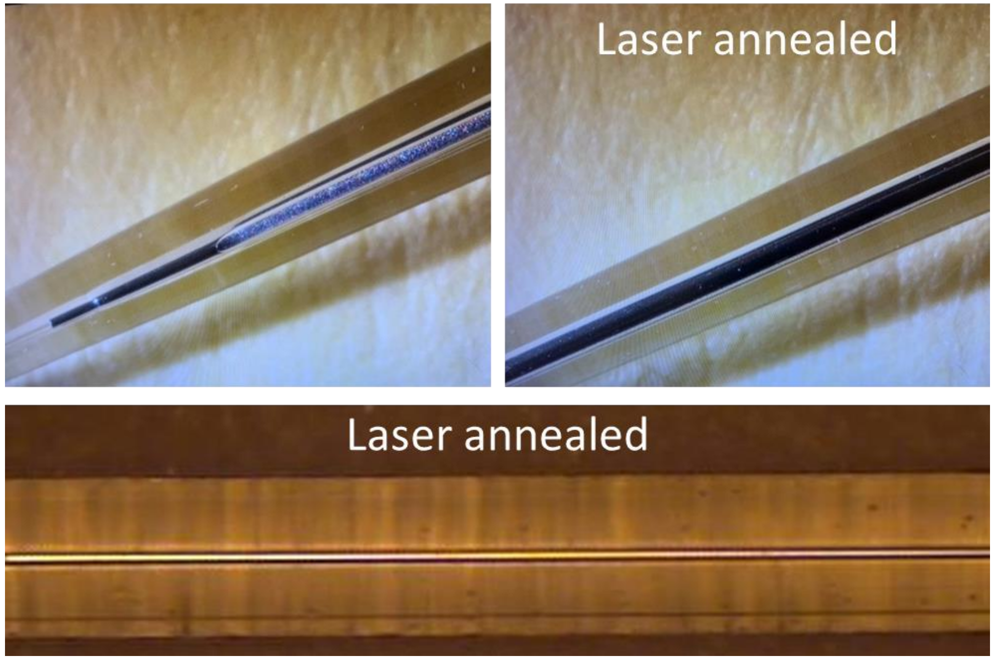


T. Zaengle, U. J. Gibson, T. W. Hawkins, C. McMillen, B. Ghimire, A. M. Rao, and J. Ballato, "A novel route to fibers with incongruent and volatile crystalline semiconductor cores: GaAs," *ACS Photonics* **9**, 1058 – 1064 (2022).

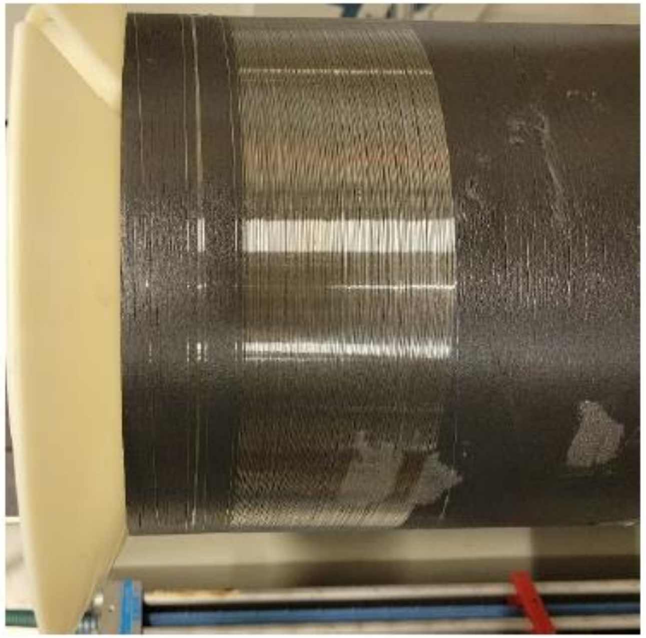
Gen 4: Flux molten core…

- **Gen 4** (2022)… Volatile and incongruent melting cores, e.g., GaAs.

1. Laser annealing and segregation.



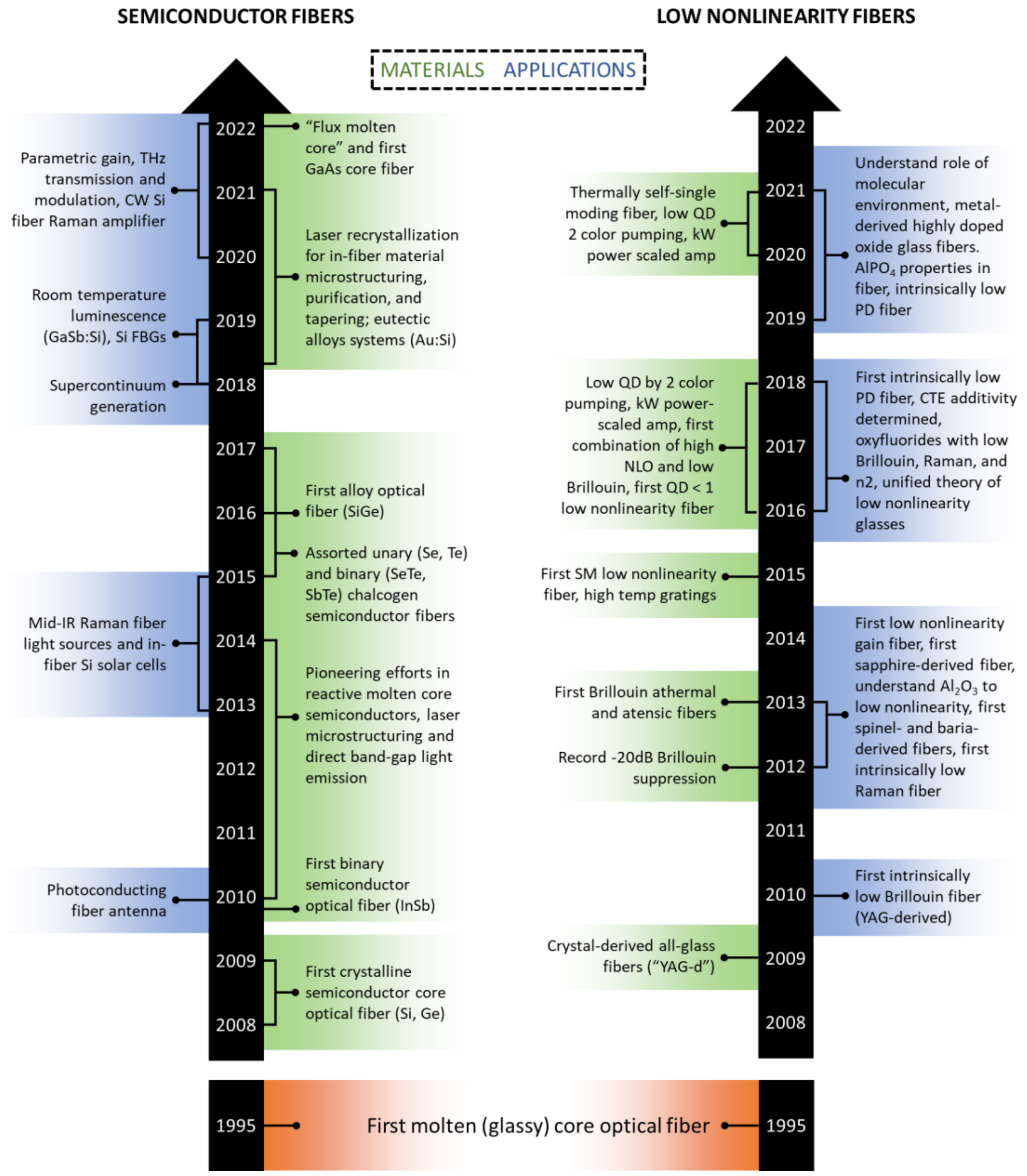
2. Scalable: 100 m of the as-drawn, DURAN® glass-clad, crystalline 30GaAs-70Sn core fiber.



Supplementary Data to: T. Zaengle, U. J. Gibson, T. W. Hawkins, C. McMillen, B. Ghimire, A. M. Rao, and J. Ballato, “A novel route to fibers with incongruent and volatile crystalline semiconductor cores: GaAs,” *ACS Photonics* **9**, 1058 – 1064 (2022).

Conclusions… for now!

- **The molten core method has opened the periodic table to advanced and multi-functional fibers.**
  - Commercially scalable; all sorts of fun, useful, and novel glass and crystal science!
  - Only process that yields amorphous and crystalline core fibers (depending on material family) over long lengths at practical speeds.
  - Employed globally (77 countries to-date) for the study and use of a wide range of novel in-fiber photonic and opto-electronic devices.



SEMICONDUCTOR FIBERS

LOW NONLINEARITY FIBERS

MATERIALS APPLICATIONS

Parametric gain, THz transmission and modulation, CW Si fiber Raman amplifier

Room temperature luminescence (GaSb:Si), Si FBGs

Supercontinuum generation

Mid-IR Raman fiber light sources and in-fiber Si solar cells

Photoconducting fiber antenna

"Flux molten core" and first GaAs core fiber

Laser recrystallization for in-fiber material microstructuring, purification, and tapering; eutectic alloys systems (Au:Si)

First alloy optical fiber (SiGe)

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

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

First binary semiconductor optical fiber (InSb)

First crystalline semiconductor core optical fiber (Si, Ge)

Thermally self-single moding fiber, low QD 2 color pumping, kW power scaled amp

Low QD by 2 color pumping, kW power-scaled amp, first combination of high NLO and low Brillouin, first QD < 1 low nonlinearity fiber

First SM low nonlinearity fiber, high temp gratings

First Brillouin athermal and atensic fibers

Record -20dB Brillouin suppression

Crystal-derived all-glass fibers ("YAG-d")

Understand role of molecular environment, metal-derived highly doped oxide glass fibers. $AlPO_4$ properties in fiber, intrinsically low PD fiber

First intrinsically low PD fiber, CTE additivity determined, oxyfluorides with low Brillouin, Raman, and n2, unified theory of low nonlinearity glasses

First low nonlinearity gain fiber, first sapphire-derived fiber, understand Al_2O_3 to low nonlinearity, first spinel- and baria-derived fibers, first intrinsically low Raman fiber

First intrinsically low Brillouin fiber (YAG-derived)

First molten (glassy) core optical fiber

Collaborators and $ponsors

CLEMSON UNIVERSITY

T. W. Hawkins, M. Cavillon, B. Faugas, S. Morris, B. Kokuoz, T. Zaengle, M. Stone, B. Meehan, C. McMillen, J. Kolis, R. Stolen, L. Zhu, M. Tuggle

ILLINOIS
UNIVERISTY OF ILLINOIS AT URBANA-CHAMPAIGN

P. D. Dragic, N. Yu

NTNU
Norwegian University of Science and Technology

U. J. Gibson, U. L. Osterberg, F. A. Martinsen, A. F. J. Runge

UNIVERSITY OF Southampton
Optoelectronics Research Centre

A. C. Peacock, G. Brambilla, H. N. Ren

RUTGERS
THE STATE UNIVERSITY OF NEW JERSEY

E. Snitzer, R. Riman, M. J. Matthewson

ARL

M. Dubinskiy

NORTHROP GRUMMAN

R. Rice, R. Davis

NANYANG TECHNOLOGICAL UNIVERSITY
SINGAPORE

L. Wei

華中科技大學
HUAZHONG UNIVERSITY OF SCIENCE AND TECHNOLOGY
HUST

L. Shen

Newcastle University

N. Healy

KTH
VETENSKAP OCH KONST

M. Fokine

Ucla

B. Jalali, R. Shori, O. Stafsudd

STATE

S. W. Martin

THE UNIVERSITY OF AUCKLAND
NEW ZEALAND

N. Broderick

Collaborators and $ponsors

NORTHROP GRUMMAN

DARPA

Raytheon

NSF

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
UNITED STATES AIR FORCE

DEPARTMENT OF DEFENSE
UNITED STATES OF AMERICA

UNDER SECRETARY OF DEFENSE FOR RESEARCH AND ENGINEERING
DEPARTMENT OF DEFENSE

JOINT TRANSITION OFFICE
DIRECTED ENERGY

Market Street, San Francisco

Thank You !!

John Ballato
jballat@clemson.edu