2018 CROSSCUTTING
Research Project Review
Omni William Penn Hotel
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INVESTIGATION OF HIGH TEMPERATURE SILICA BASED FIBER OPTIC SENSOR MATERIALS

DE-FE0027891

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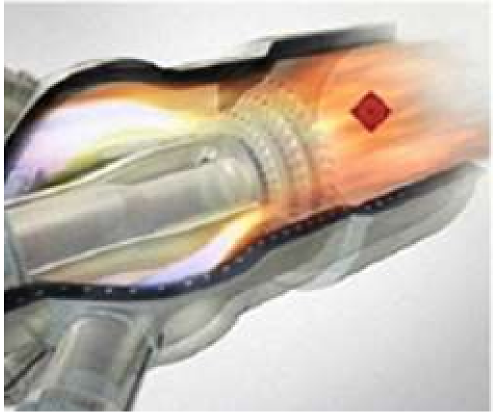
Overview

- Motivation, Objectives, and Technical Challenges
- Research Approach and Technology
  - Optical and Mechanical Reliability of Commercial Fused Silica Fibers
  - Thermally Tolerant Optical Fibers
  - Tube Encapsulated FBG Temperature Sensor

- Milestones and Schedule
  - Project Duration: 2 years
  - Current Status: 2nd year
- Next Steps

Motivation

- The lack of commercial sensing and monitoring solutions for next generation energy conversion systems, coupled with current drivers such as improved energy efficiency, and reduced emissions, has created a growing market opportunity that is anticipated to reach $4.5 billion by 2018
- The extremely high temperature and harsh environments has limited the use of mature fiber optic sensing technologies based on fused silica optical fibers and have slowed implementation in power generation system
- Detailed investigations of silica based optical fibers and their stability and interactions with various chemical constituents in high temperatures to clearly understand the limitations and opportunities for applications of silica based fibers in power generation related atmospheres.



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Power Generation Technology Needs

	Coal Gasifiers	Combustion Turbines	Solid Oxide Fuel Cells	Advanced Boiler Systems
Temperature	< 1600° C	< 1300°C	< 900° C	< 1000° C
Pressures	< 1000 psi	Ratios 30:1	Atmospheric	Atmospheric
Atmosphere(s)	Highly Reducing, Erosive, Corrosive	Oxidizing	Oxidizing and Reducing	Oxidizing
Examples of Important Gas Species	H_2, O_2, CO, CO_2, H_2O, H_2S, CH_4	O_2, Gaseous Fuels (Natural Gas to High Hydrogen), CO, CO_2, NO_x, SO_x	Hydrogen from Gaseous Fuels and Oxygen from Air	Steam, CO, CO_2, NO_x, SO_x

Ohodnicki, Jr., Paul R. "Embedded Sensors for Extreme Temperature and Harsh Environments." NETL-RUA Commercial Opportunity Summary, (2013)

Project Objectives

- **Goal**: Develop design strategies to assure reliable performance of deployed optical fibers and sensors
- **Objective:** Investigate and characterize the performance of commercially available optical fibers at elevated temperatures
- **Objective**: Conduct a comprehensive evaluation of fused silica optical fiber sensor materials by elucidating performance dependencies on the stoichiometry of fiber fabrication, incorporated chemical species, thermal history, material grades, dopants, and fiber design.
- **Benefit**: The successful appraisal of the operating boundary conditions of fused silica based optical fibers will drive the implementation of silica based fiber optic sensors into the power generation systems.

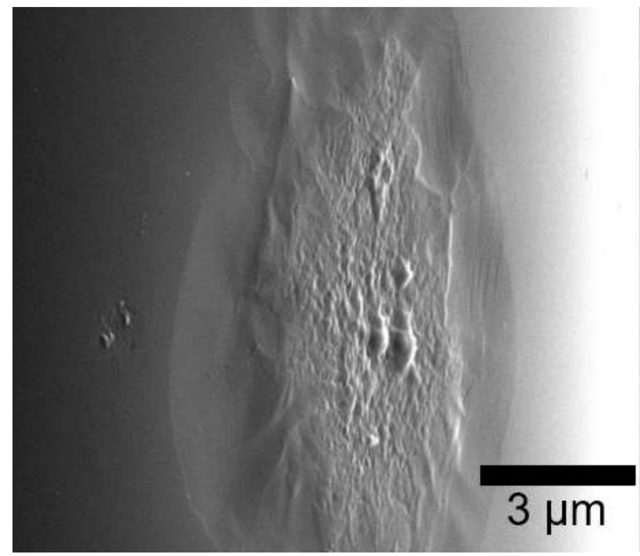
Technical Challenges

- Complex material interactions
  - Crystallization
  - Viscosity
  - Defect chemistry
  - Susceptibility to gaseous species
  - Dopants and migration
- Large array of commercial optical fiber types
  - Optical fiber vendors: OFS, Corning, Thorlabs, Nufern, Sumitomo
  - Chemical compositions: Ge, F, P, OH, etc.
  - Fiber geometries: core diameter, graded/step index
  - Manufacturing techniques: MCVD, OVD, PCVD, VAD
- Many types of fiber optic sensors
  - Numerous optical and materials phenomena that are uniquely configured to sense unique environmental parameters

TECHNOLOGY AND APPROACH

Crystallization

- Devitrification observed on the fiber surface
  - Conversion to cristobalite
- Heterogeneous nucleation
  - Impurities, scratches, dust
- Crystal growth is inversely related to glass viscosity
- Extremely sensitive to surface and environment conditions
  - Moisture is known to induce crystallization at elevated temperatures
  - Proper coating removal is critical to reliability at elevated temperatures
- Induces mechanical and optical failure



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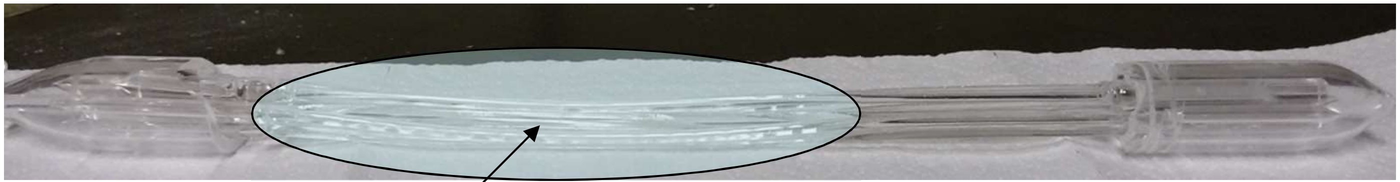
Glass Viscosity

Fused silica optical fibers

- Viscosity is defined in terms of a resistance to flow of a medium
- Fictive temperature of optical fibers is typically higher than bulk
  - Fused silica optical fibers: $T_f \approx$1600–1700ºC
  - Bulk fused silica: $T_f \approx$1200–1300ºC
- Strength decrease at elevated temperatures (~5GPa to ~1.5 GPa)
  - Package fibers and sensors with zero strain and avoid moisture
- Sensitive to impurities and dopants
  - Chlorine, fluorine, hydroxyl, etc..
- Relaxation and deformation must be accounted for at elevated temperatures (i.e. > 900ºC)



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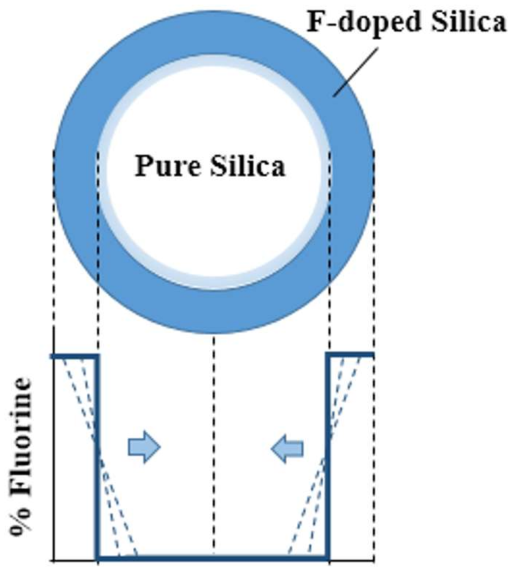
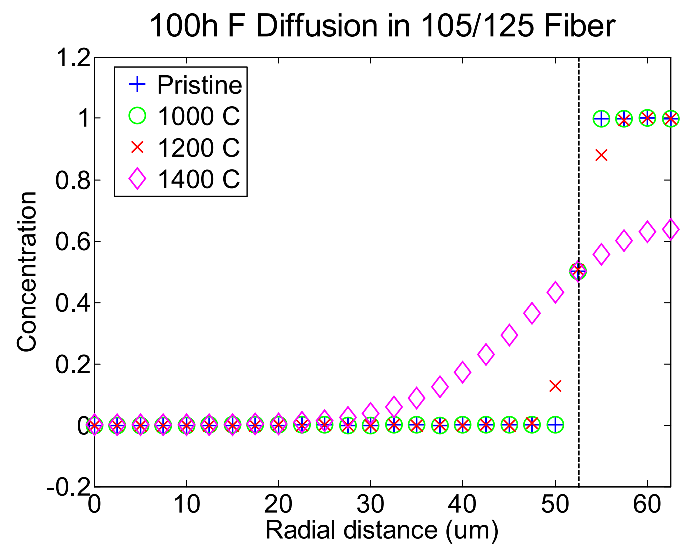
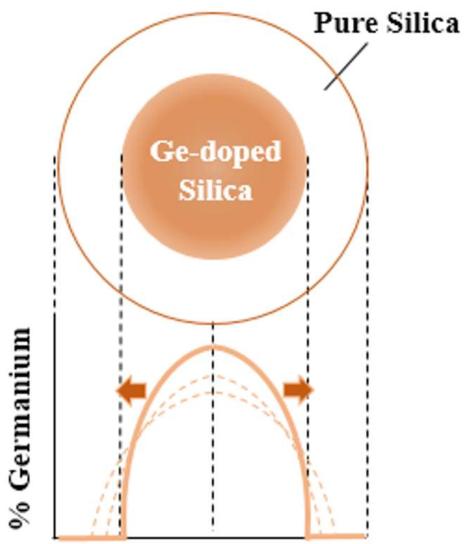
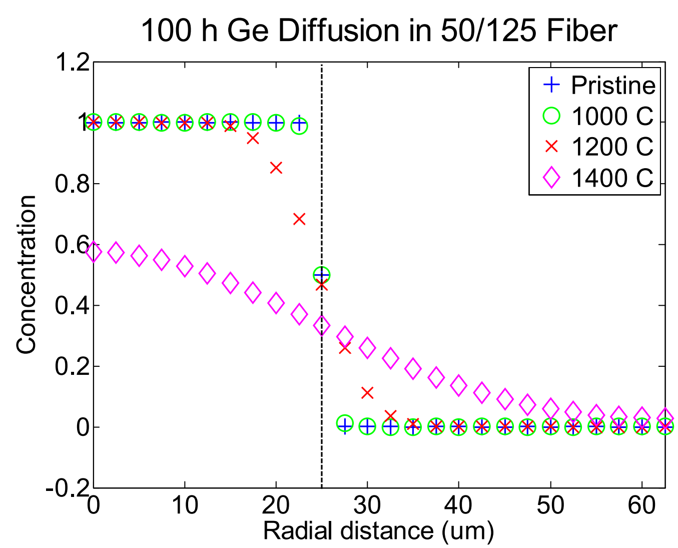
Dopant Migration



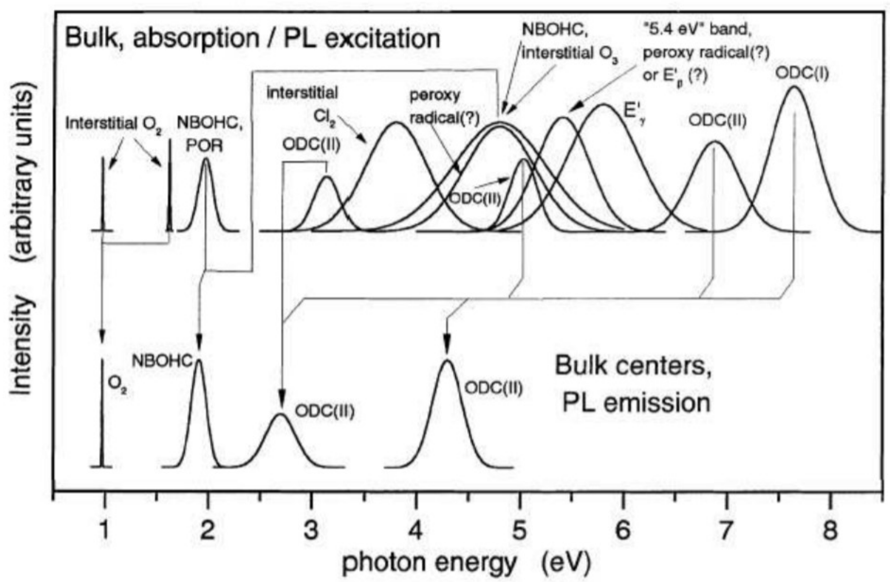


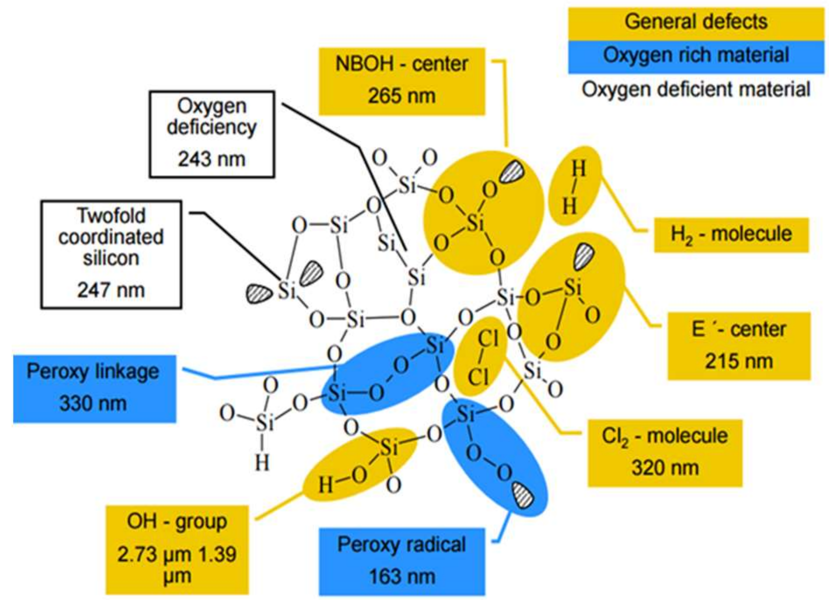




Susceptibility to Gaseous Species

Defects, Optical Absorption and Thermal Stability

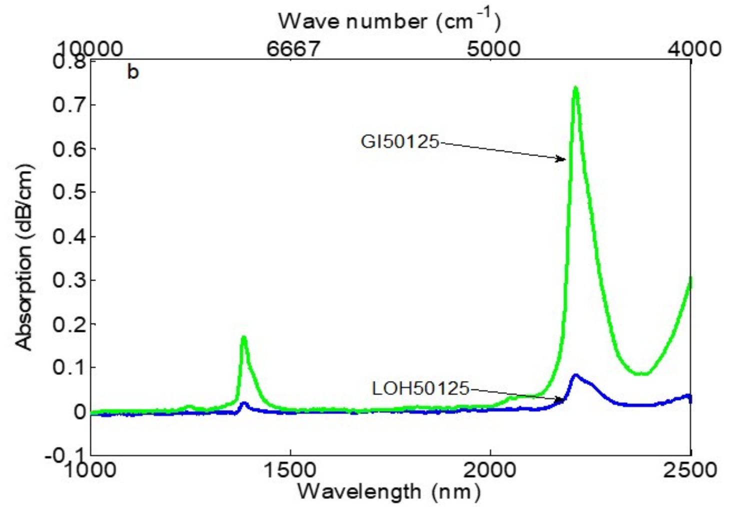


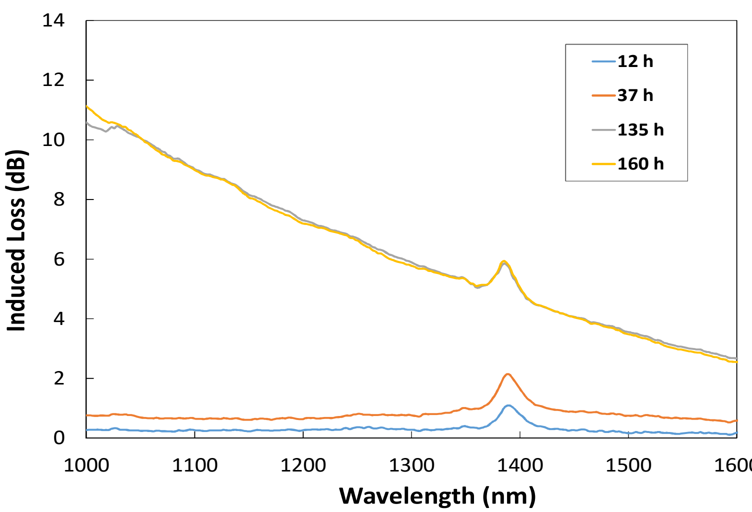


Susceptibility to Gaseous Species

Chemical Reactions and Optical Absorptions

- Optically active defects will induce absorptions at specific wavelengths and act as reaction sites for impurities during and post fabrication.
- The defects sites are thermally active and, the distribution of the defect population can become transient upon exposure to an energy source, such as UV nuclear radiation, and temperature
- The most prevalent induced absorption is due to exposure to hydrogen gas, moisture, and/or water
- Hydrogen induced loss mechanisms have been studied extensively in the low temperature regime (<300ºC)
  - ***Germanium doped fibers are generally more susceptible to hydrogen induced optical losses***





FUSED SILICA OPTICAL FIBERS

Generalized Types of Optical Fiber

Germanium Doped
Core: GeO_2-SiO_2
Clad: F-SiO_2

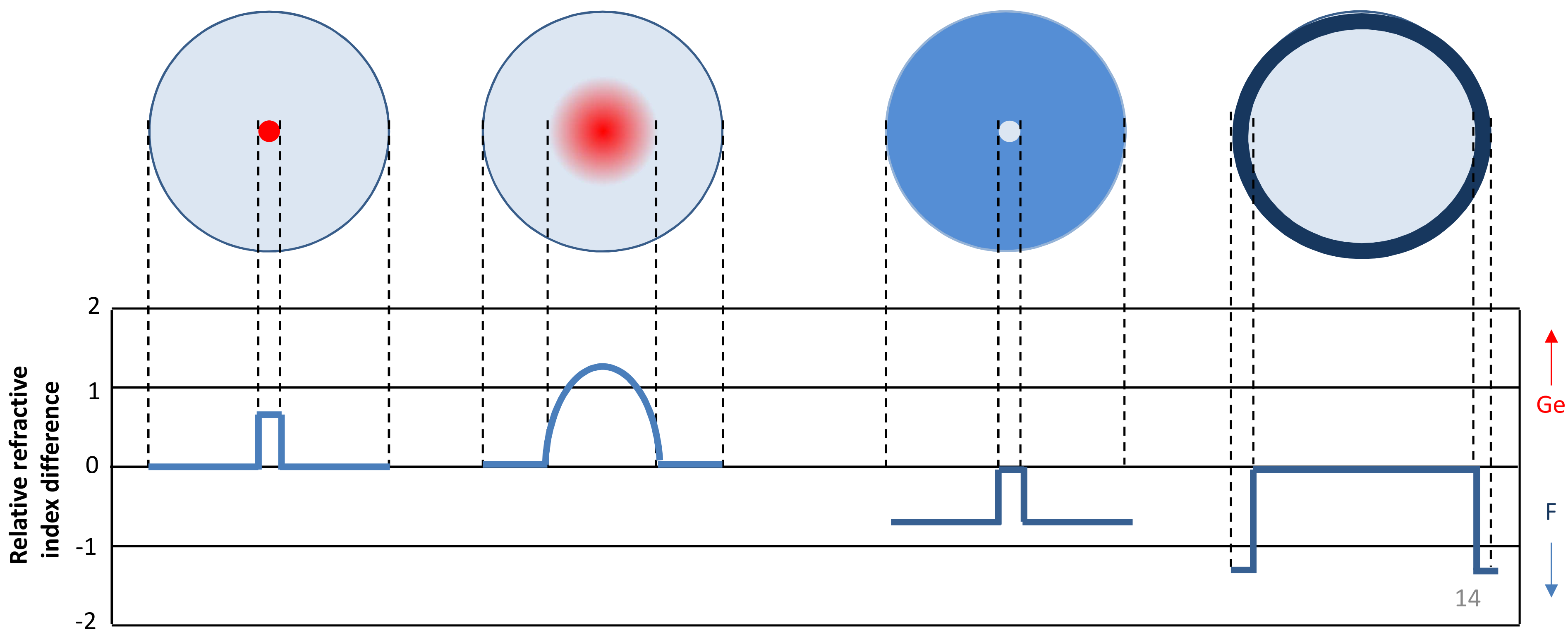
Single Mode Fiber
Core: ~ 9μm
RIP: Step Index

Multimode Fiber
Core: 50μm
RIP: Graded Index

Pure Silica Core
Core: SiO_2
Clad: F-SiO_2

Single Mode Fiber
Core: ~10 μm
RIP: Step Index

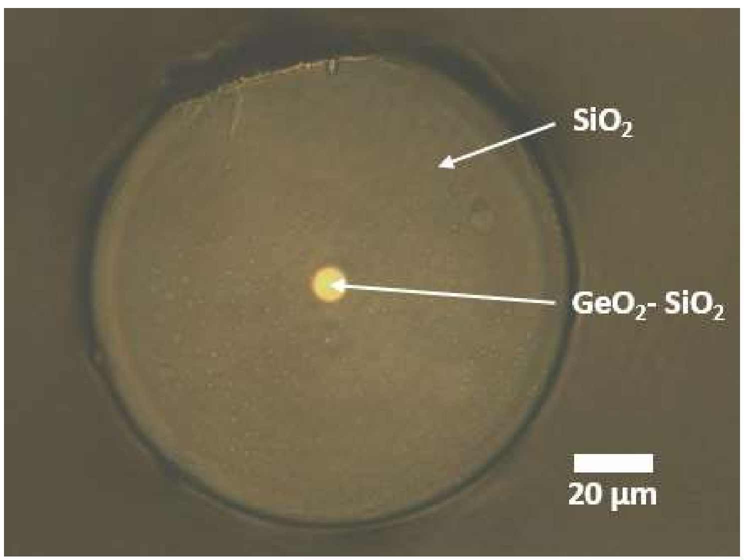
Multimode Fiber
Core: ~105 μm
RIP: Step Index

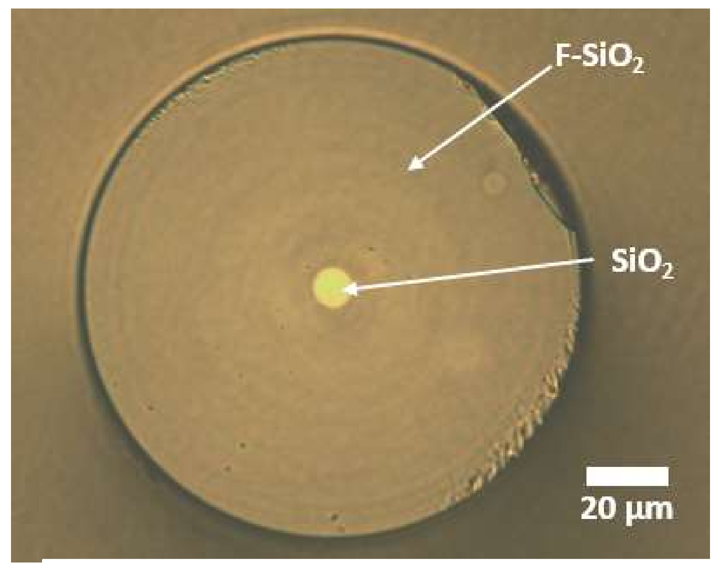


Selected Fused Silica Optical Fibers

Single Mode

- Germanium doped
  - Core: GeO_2-SiO_2
  - Clad: SiO_2
  - Corning: "SMF28"
- Pure silica core
  - Core: SiO_2
  - Clad: F-SiO_2
  - Sumitomo: "Z-fiber"

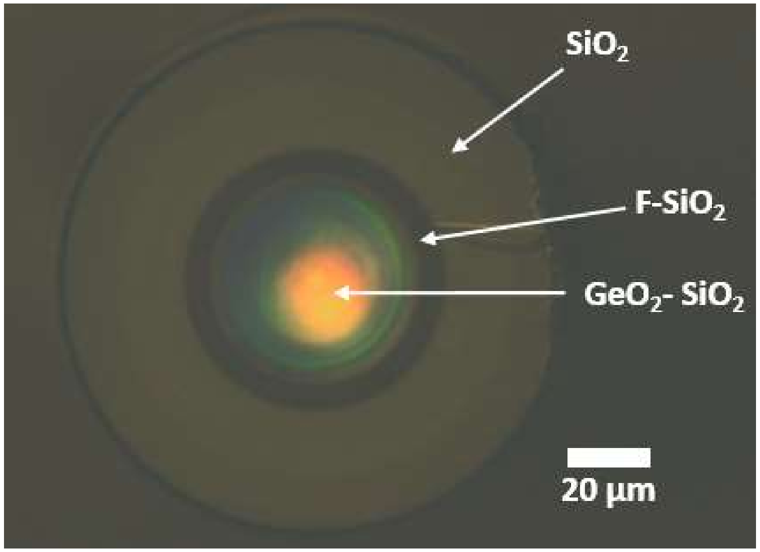




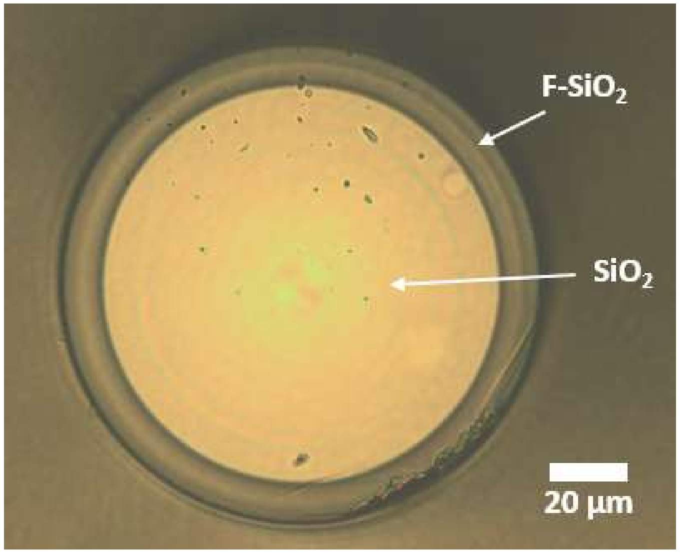
Selected Fused Silica Optical Fibers

Multimode

- Germanium doped
  - Core: GeO_2-SiO_2
  - Inner clad: F-SiO_2
  - Outer clad: SiO_2
  - Corning: Graded Index



- Pure silica core
  - Core: SiO_2
  - Clad: F-SiO_2
  - Thorlabs: Step Index



MECHANICAL STABILITY

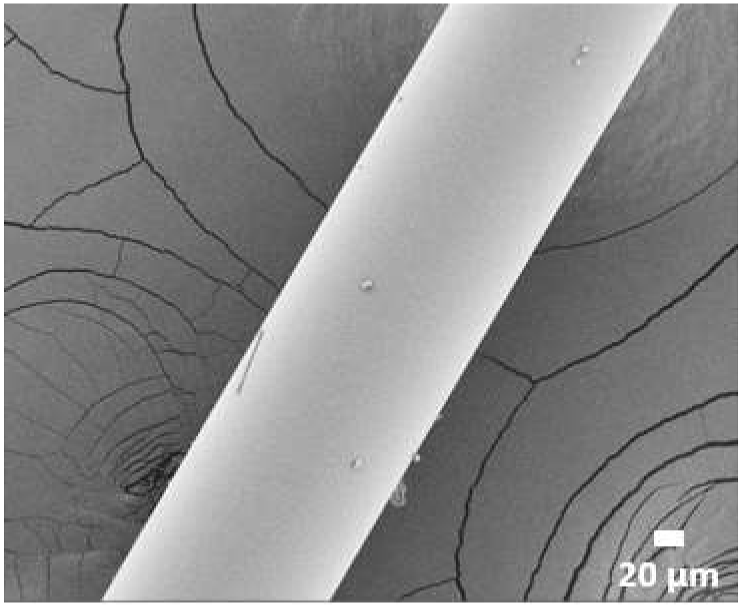
SURFACE CHARACTERIZATION

Surface Characterization

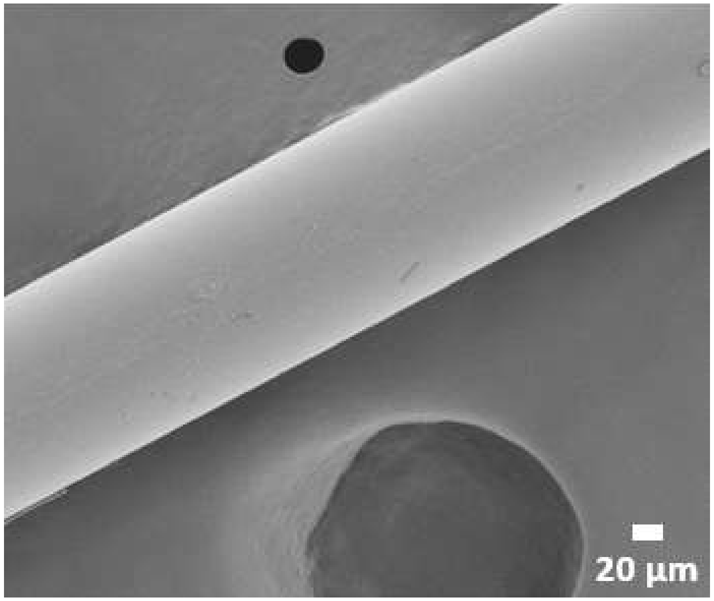
Pure silica core vs. germanium doped single mode fibers

- Exposure Conditions
  - Temperature: 1200ºC
  - Environment: 100% N_2
  - Duration: 48 hours

"Z-fiber"



"SMF-28"

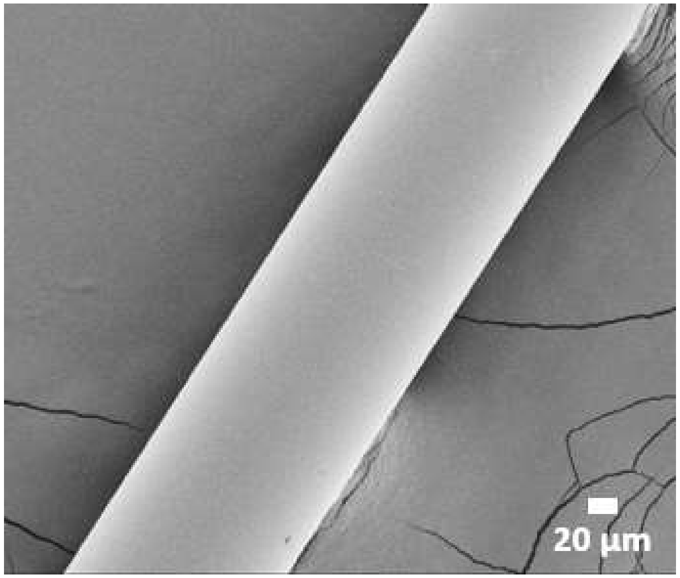


Surface Characterization

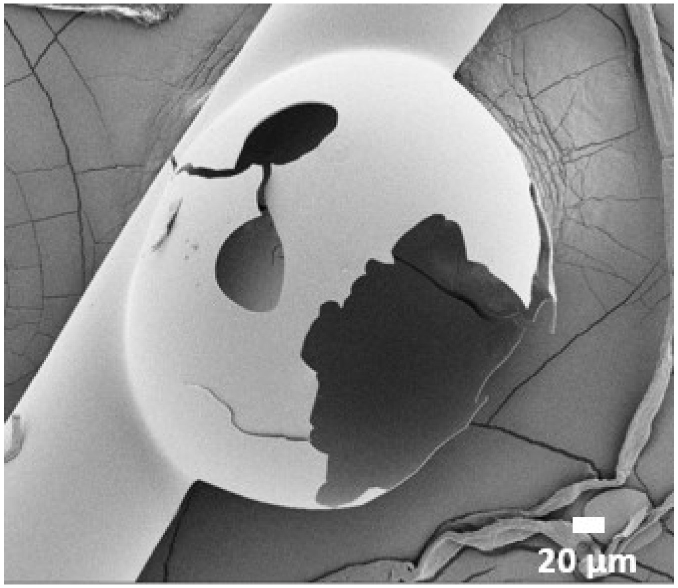
Pure silica core vs. germanium doped multimode fibers

- Exposure Conditions
  - Temperature: 1200ºC
  - Environment: 100% N_2
  - Duration: 48 hours

Ge-doped Core (50 µm/125 µm)



Pure Silica Core (105 µm /125 µm)

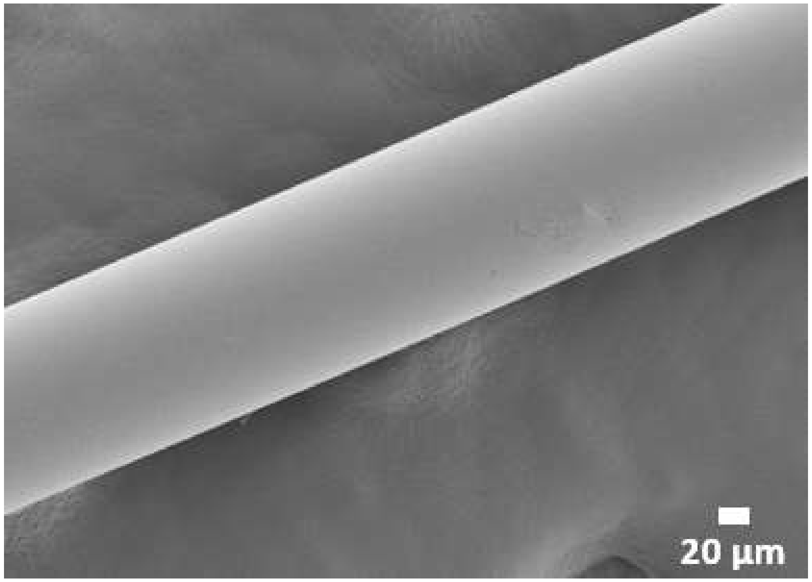


Surface Characterization

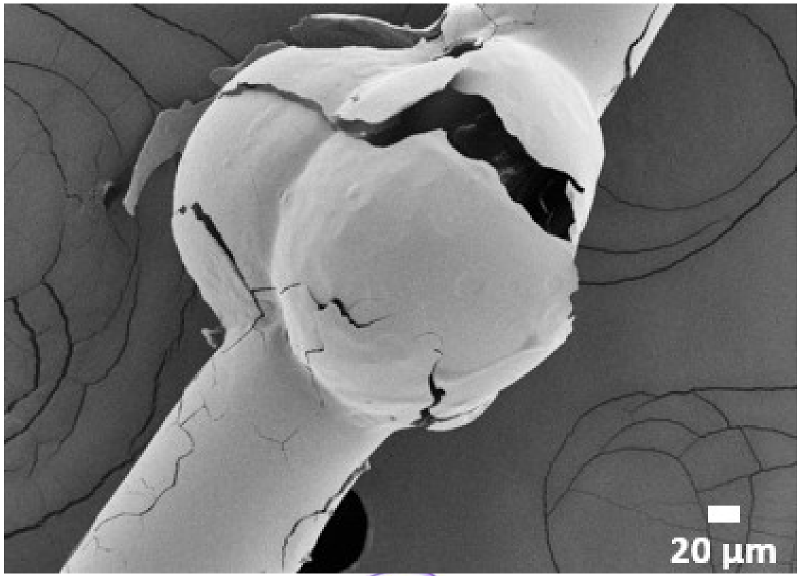
Pure silica multimode fiber: High NA vs. Low NA

- Exposure Conditions
  - Temperature: 1200ºC
  - Environment: 100% N_2
  - Duration: 48 hours

Low NA



High NA



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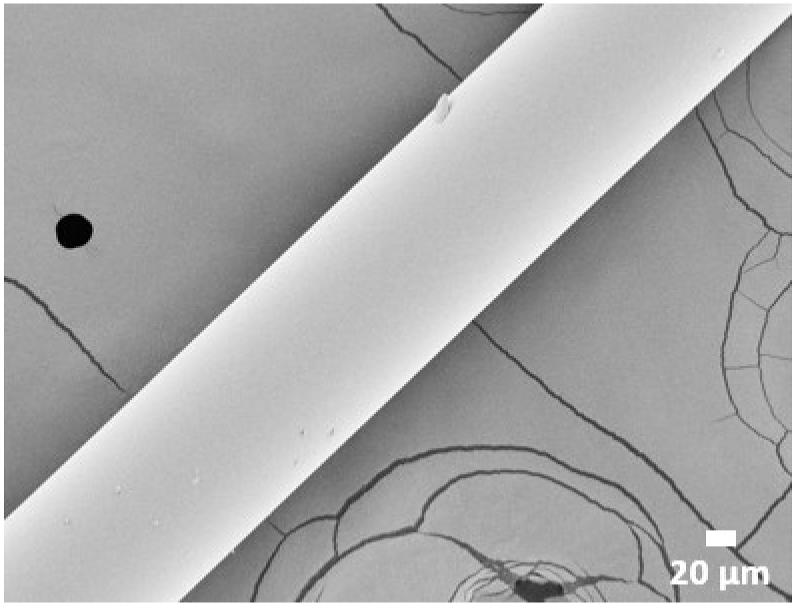
Surface Characterization

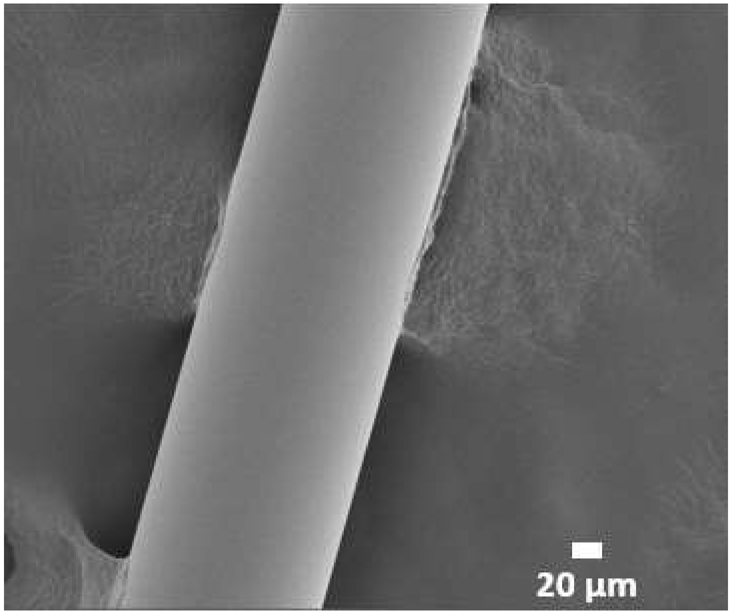
Pure silica core vs. germanium doped multimode fibers

- Exposure Conditions
  - Temperature: 1000ºC
  - Environment: 100% N_2
  - Duration: 2 weeks

Ge-doped Core (50 µm/125 µm)



Pure Silica Core (105 µm /125 µm)

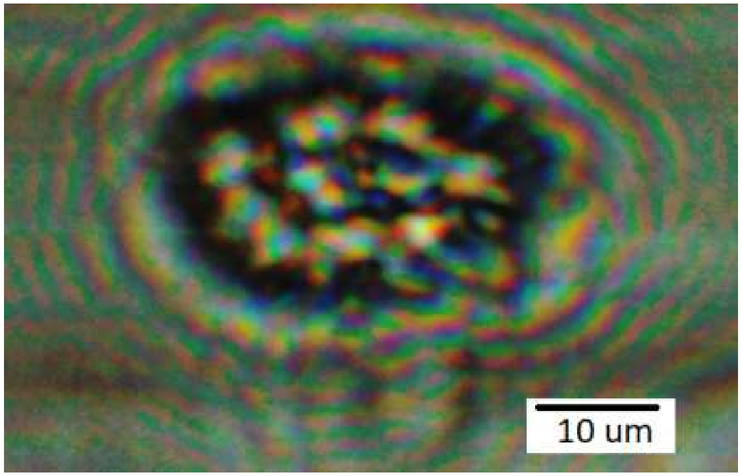


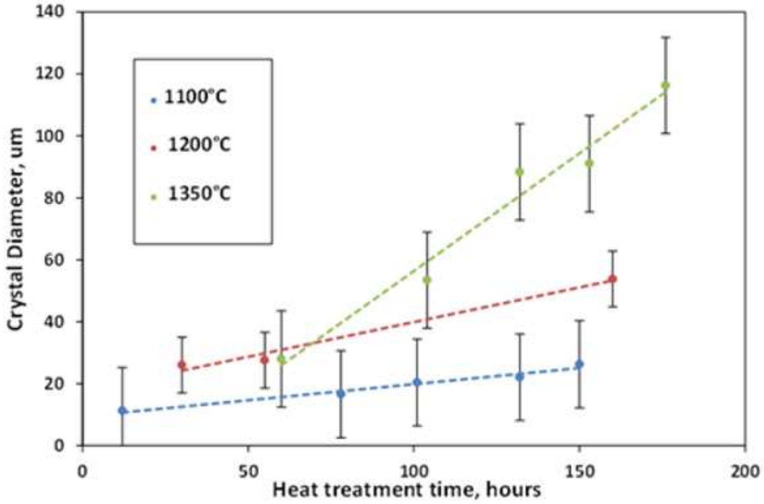
SURFACE CRYSTALLIZATION

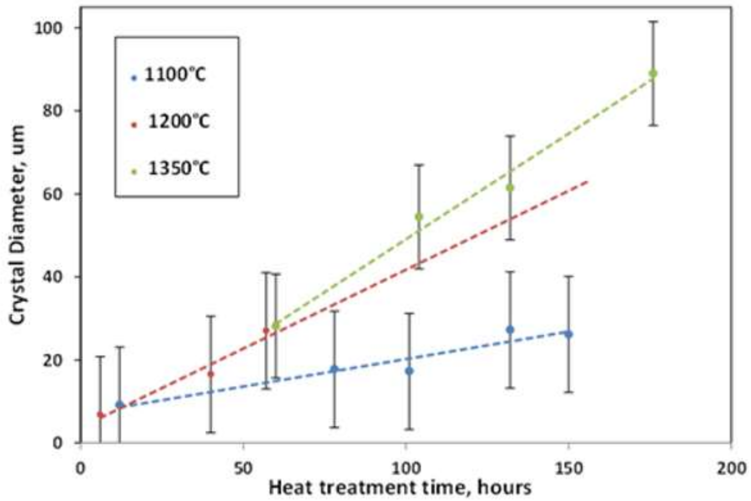
Surface Crystallization

Exposure to ambient air

Temperature = 1200ºC



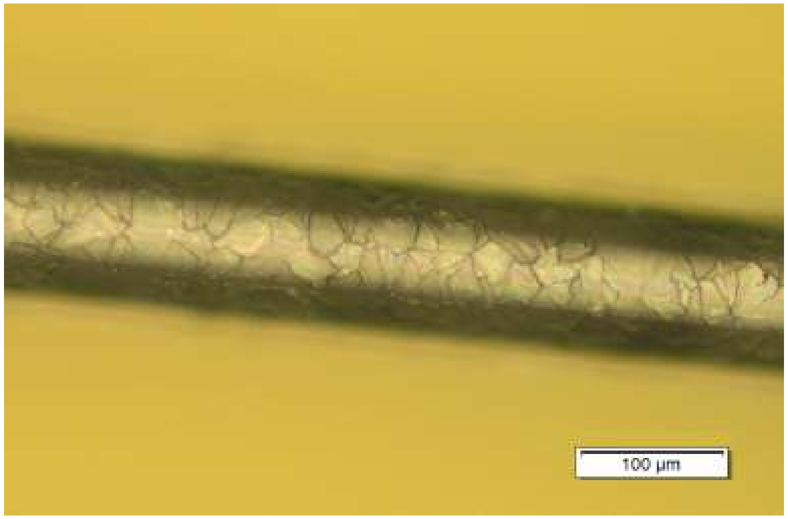


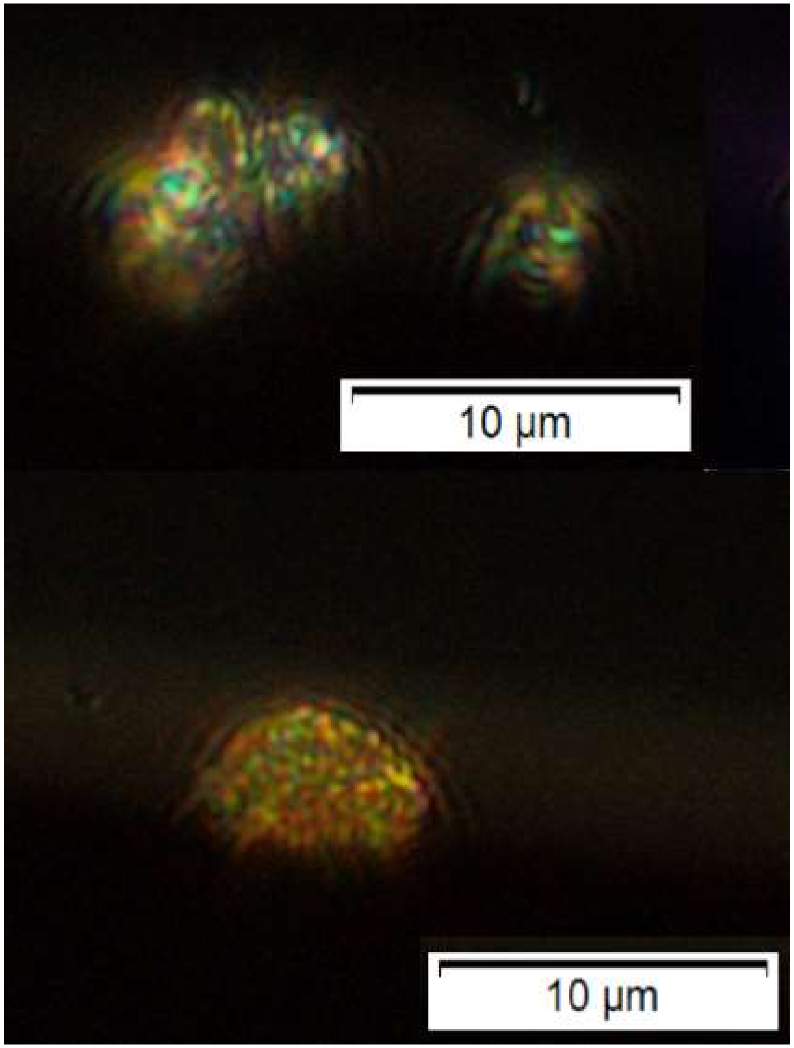


Surface Crystallization

Exposure to ambient air

Temperature = 1300°C





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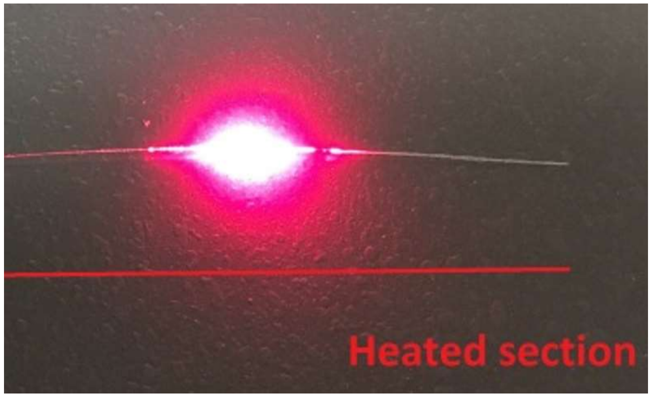
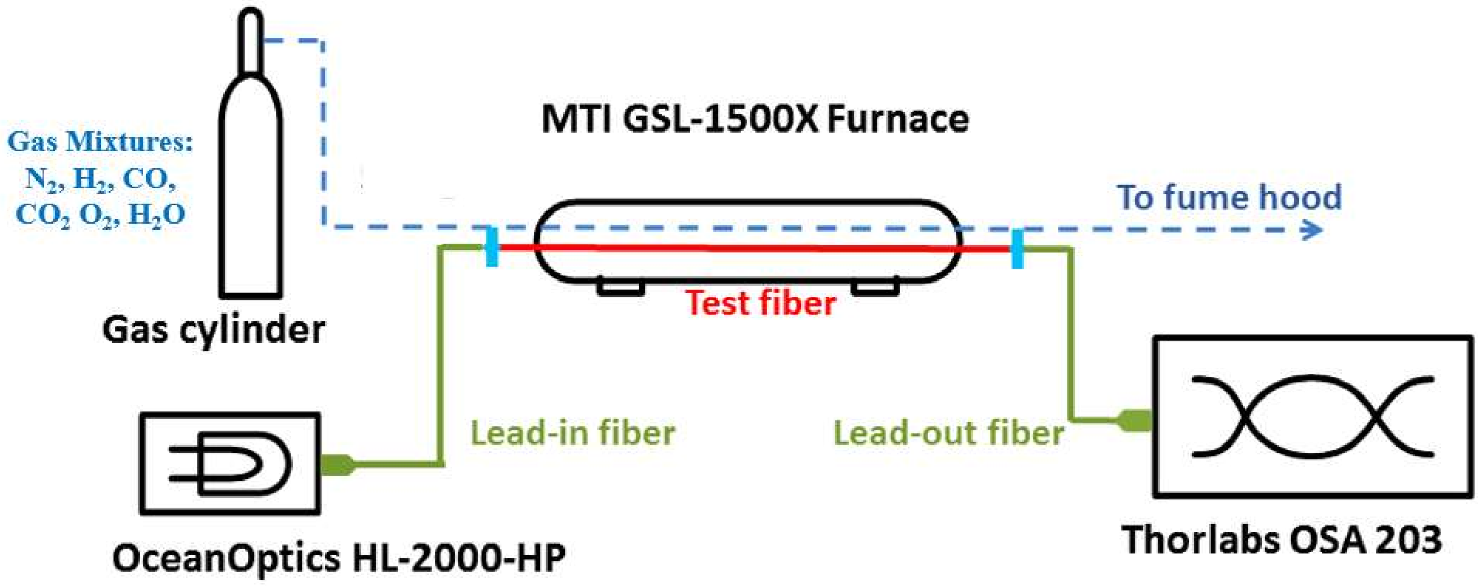
OPTICAL STABILITY

Optical Performance Testing

- Optical Stability
  - Temperatures up to 1300ºC
  - Fiber lengths ~ 1m
  - $\lambda = 400\ nm\ - 2500\ nm$
  - In-situ measurements

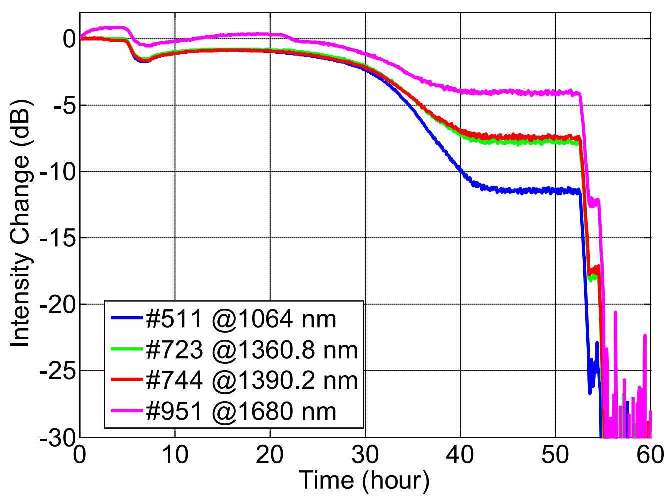




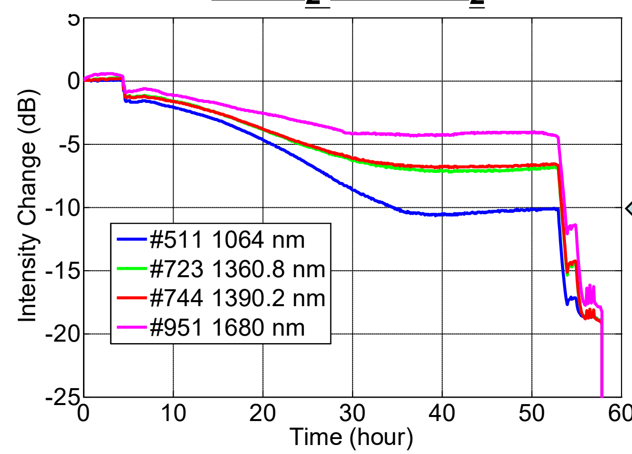
Optical Susceptibility to Gaseous Species

Pure silica core step index multimode fiber

100% Nitrogen

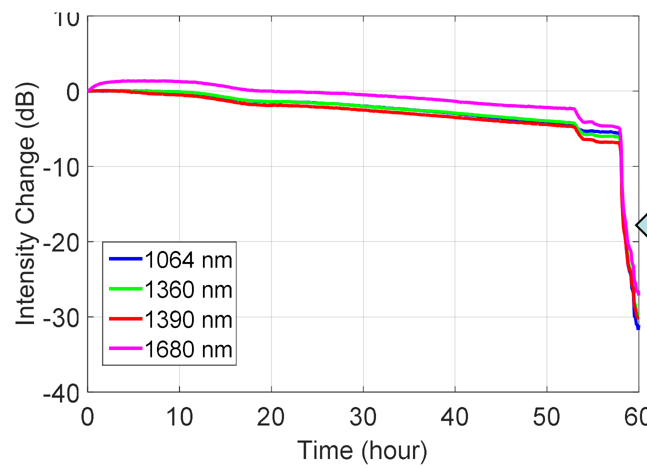


$5\%O_2$ / $95\%N_2$



No measurable change

Ambient Air

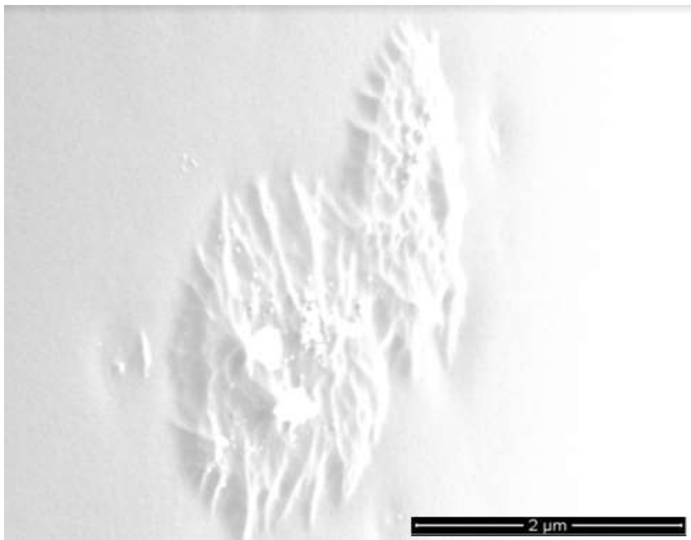


Lower induced loss

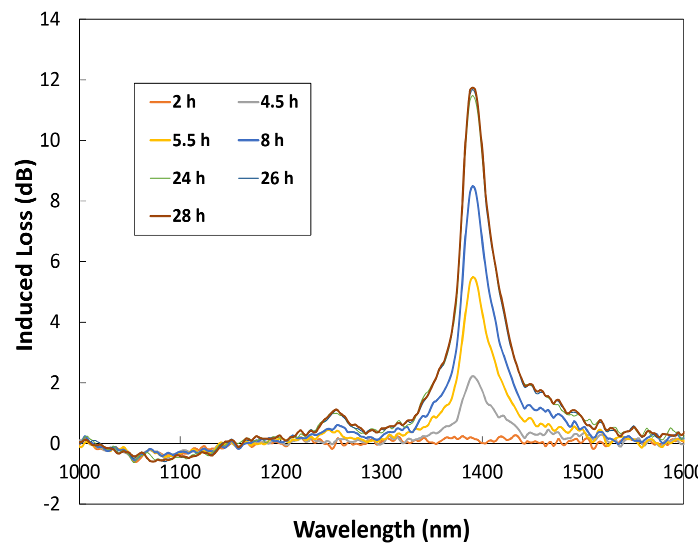
Optical Fiber Selection Methodology

Exposure to moisture

Devitrification



Induced Attenuation



Fused silica optical fibers are very susceptible to moisture

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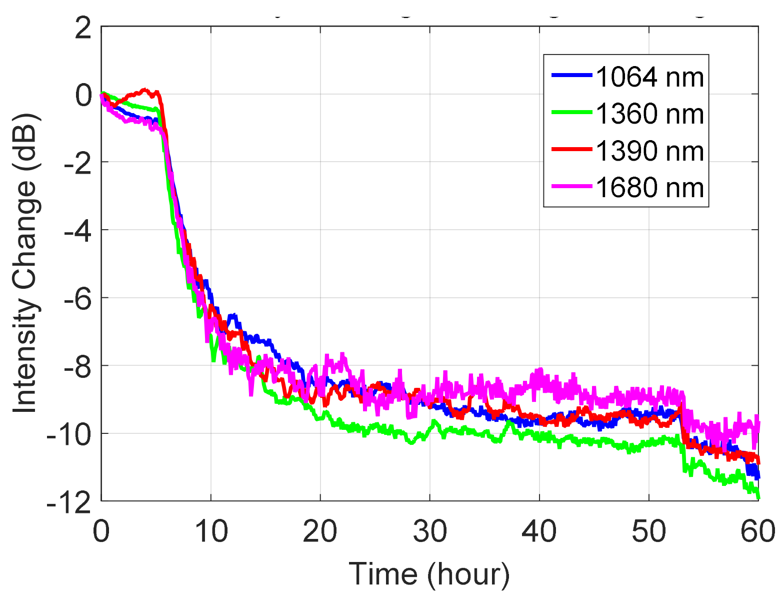
Optical Fiber Selection Methodology

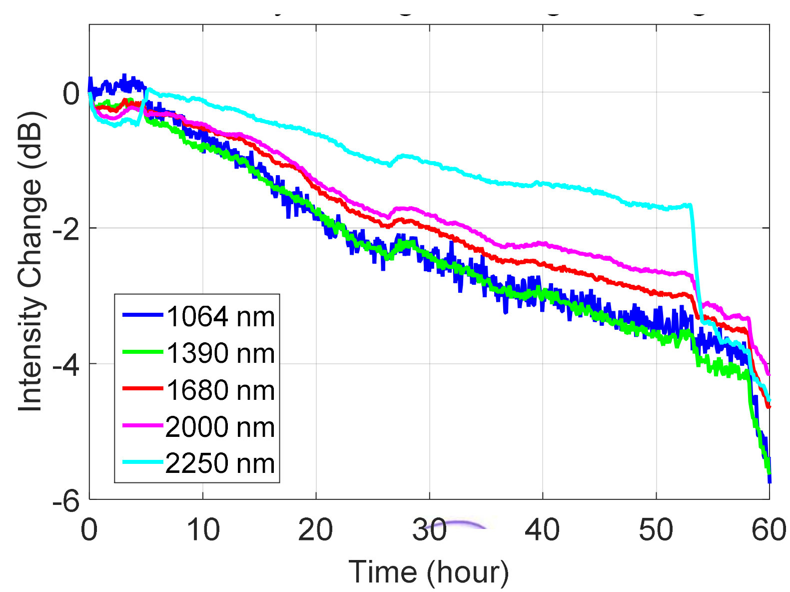
Single Mode Fibers

- Exposure Conditions
  - Temperature: 1200ºC
  - Environment: 100% N_2
  - Duration: 48 hours

Pure Silica Core (Z-fiber)



Germanium Doped Core (SMF28)

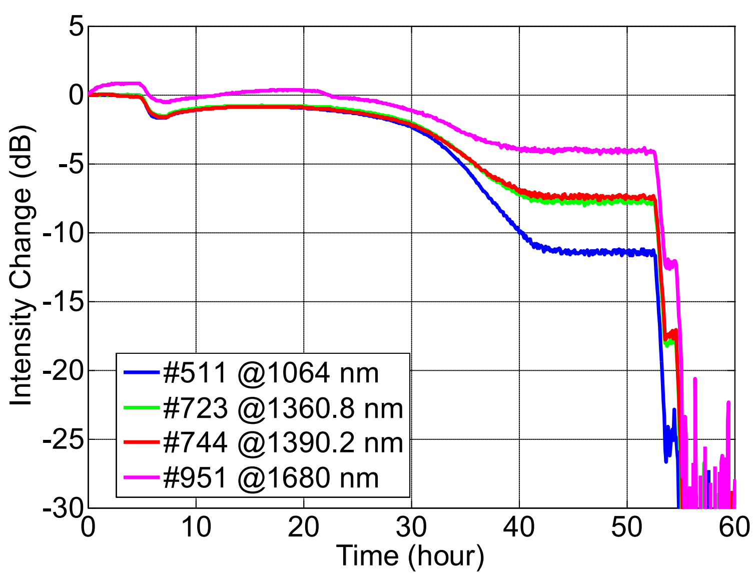


Optical Fiber Selection Methodology

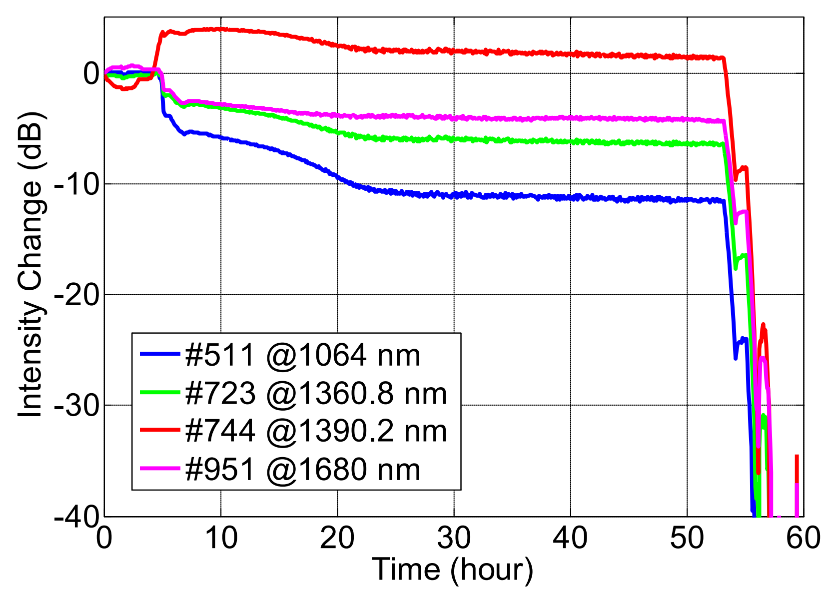
Pure silica core multimode fibers – Low OH vs. High OH

- Exposure Conditions
  - Temperature: 1200ºC
  - Environment: 100% N_2
  - Duration: 48 hours

Pure Silica Core Multimode – Low OH



Pure Silica Core Multimode – High OH

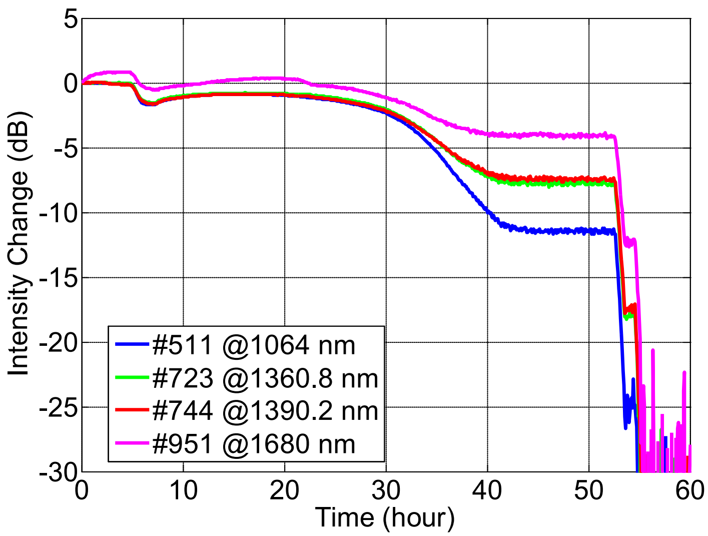


Optical Fiber Selection Methodology

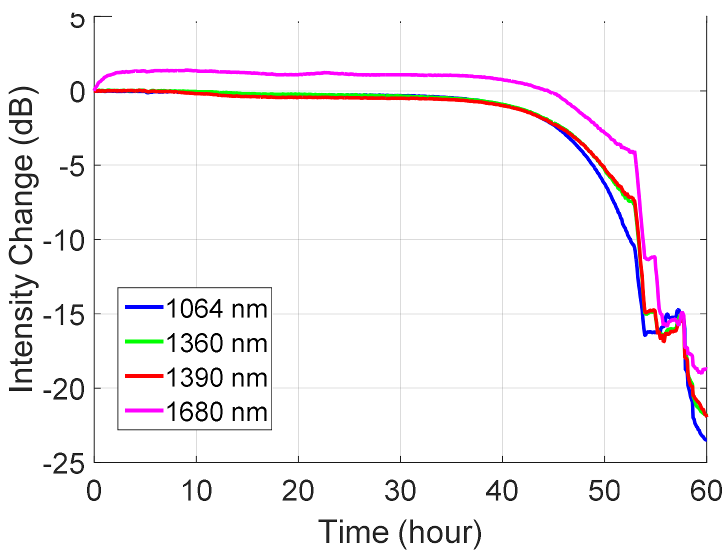
Pure silica core vs. germanium doped multimode fibers

- Exposure Conditions
  - Temperature: 1200ºC
  - Environment: 100% N_2
  - Duration: 48 hours

Pure Silica Core Multimode – Low OH

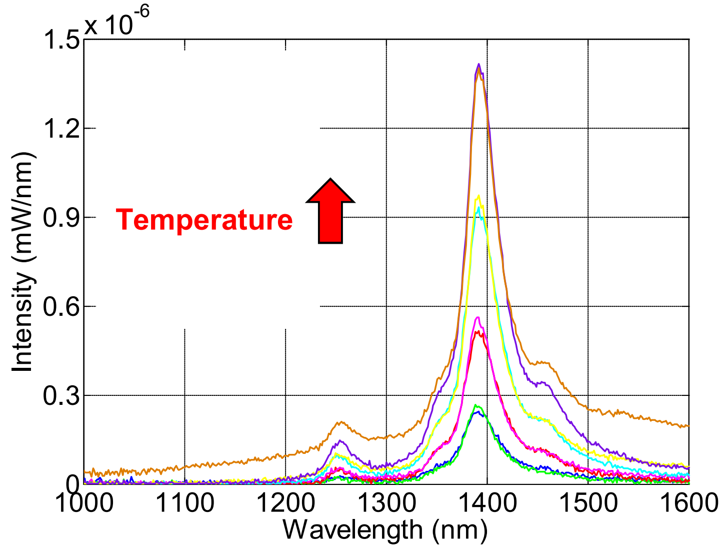


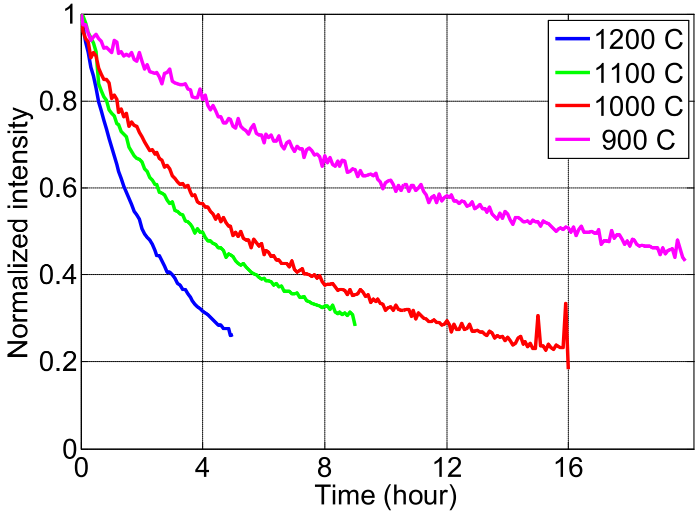
Germanium Doped Multimode – Low OH



"OH Thermal Emission"

- Emission centered at OH overtones (1.39 μm, 1.24 μm)
- Peak intensity increases with temperature
  - Radiant relaxation from the thermally excited vibrational energy levels.
- Isothermal decay of peak intensity
  - OH out-diffusion
- More prevalent in fibers with higher OH content



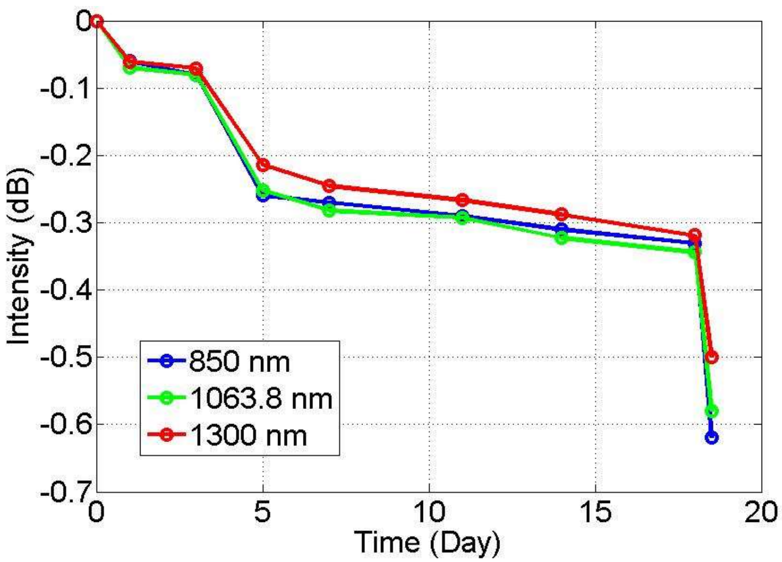


"Long Term" Testing: 1000ºC

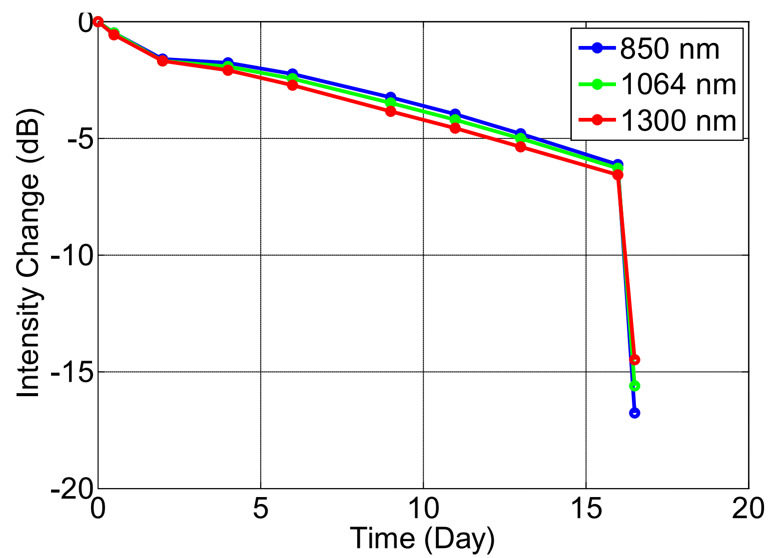
Performance in Nitrogen

- Germanium doped graded index multimode fiber
  - No significant increase in attenuation over 2 weeks
- Pure silica core step index multimode fiber
  - No significant increase in attenuation over 2 weeks

Pure Silica Core Multimode – Low OH



Germanium Doped Multimode –Low OH

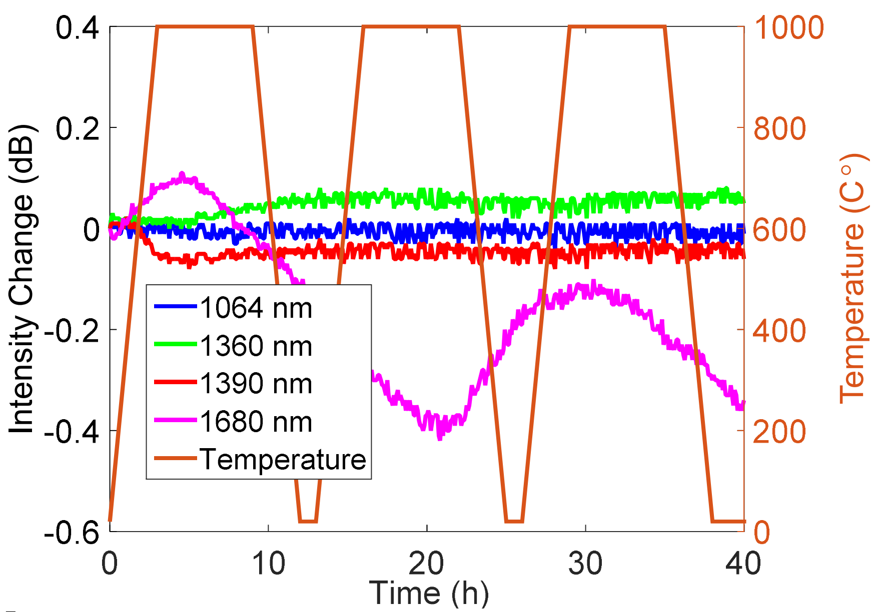


Thermal Cycling

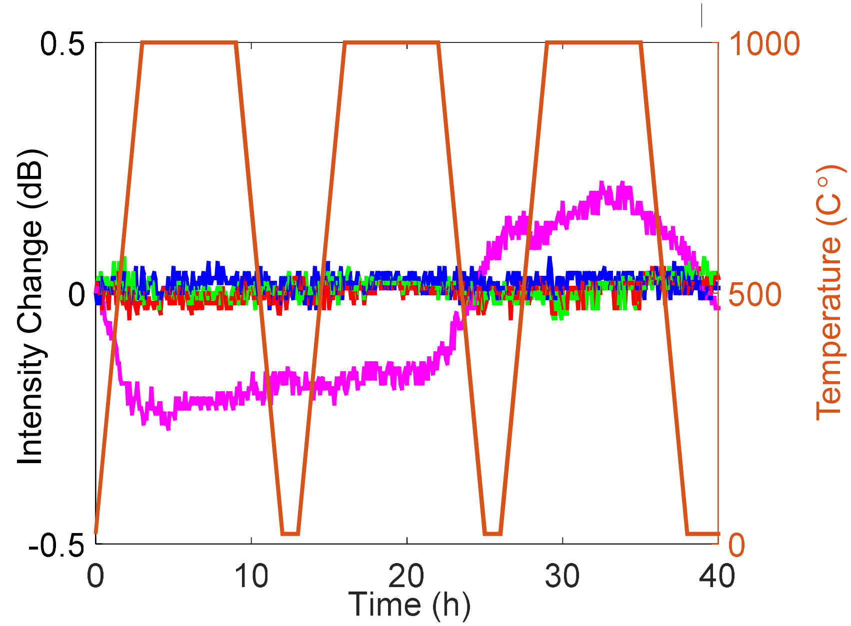
Pure silica and germanium doped core multimode fibers

- Minimal change in attenuation upon thermal cycling between room temperature and 1000ºC (in N_2)
- Limited microbending induced attenuation observed

Pure Silica Core Multimode – Low OH



Germanium Doped Multimode -Low

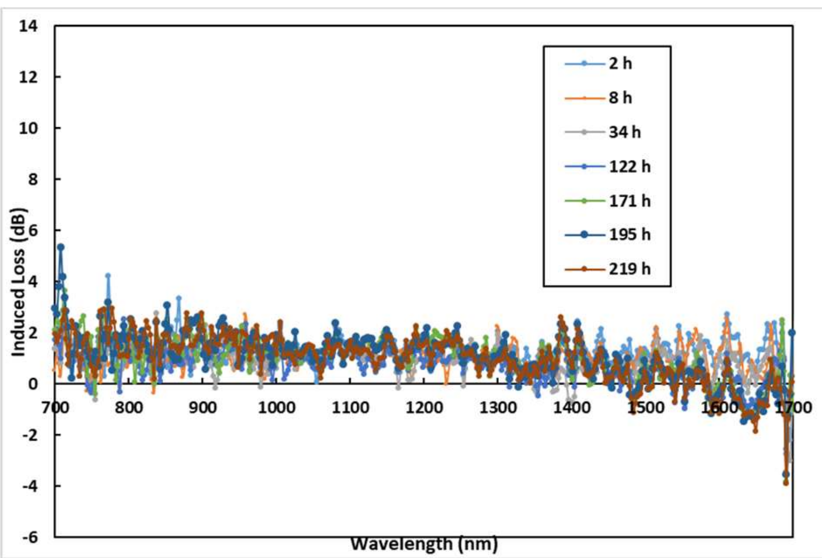


“Long Term” Testing: 1000ºC

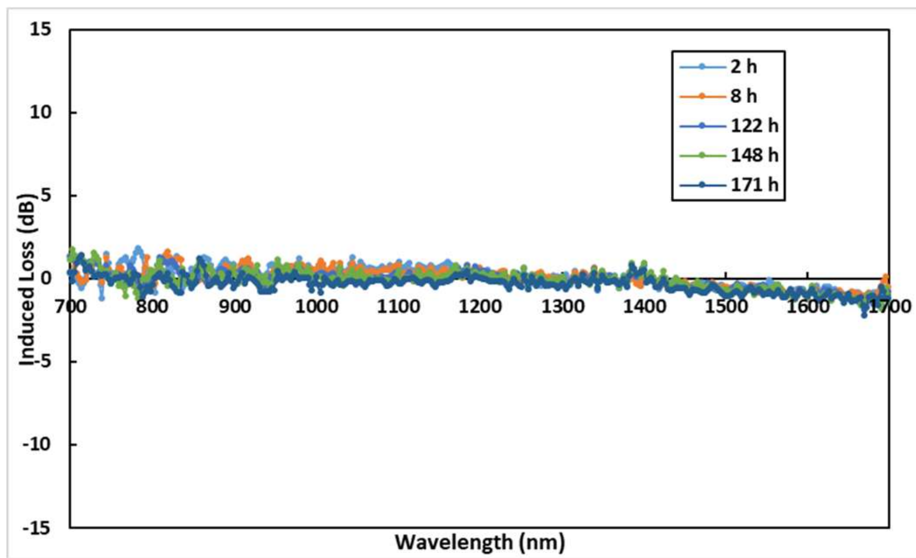
Performance in ambient air

- Germanium doped graded index multimode fiber
  - No observable increase in attenuation over 7 days
- Pure silica core step index multimode fiber
  - No observable increase in attenuation over 9 days

Pure Silica Core Multimode – Low OH



Germanium Doped Single Mode Fiber

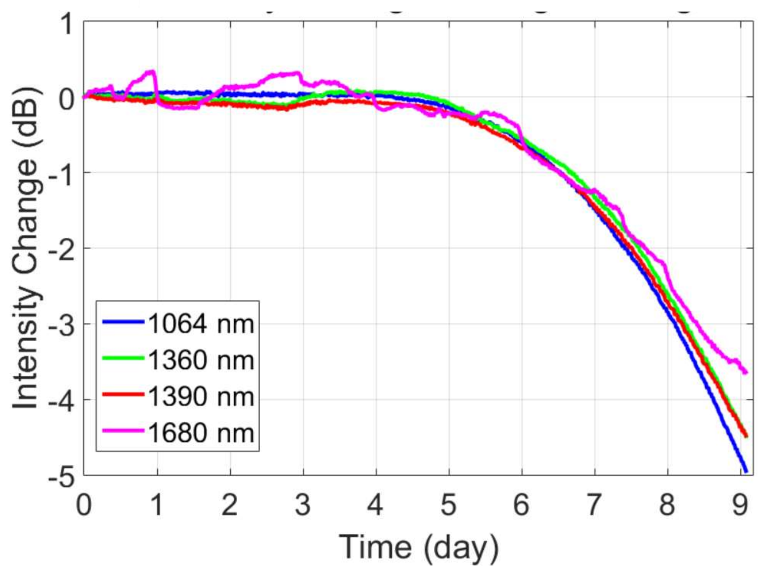


“Long Term” Testing: 1100ºC

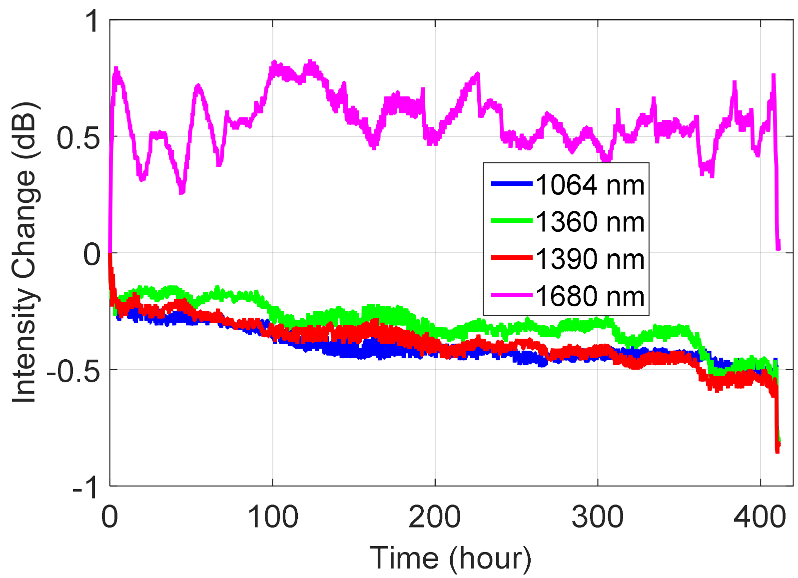
Performance in Nitrogen

- Germanium doped graded index multimode fiber
  - Relatively stable for 2 weeks
- Pure silica core step index multimode fiber
  - Rapid increase in attenuation after 7 days

Pure Silica Core Multimode – Low OH

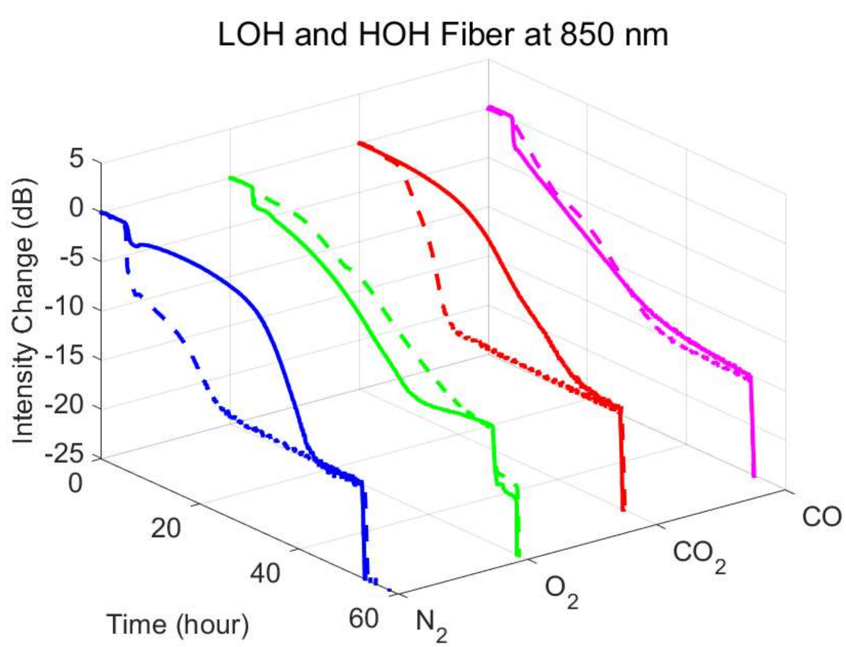


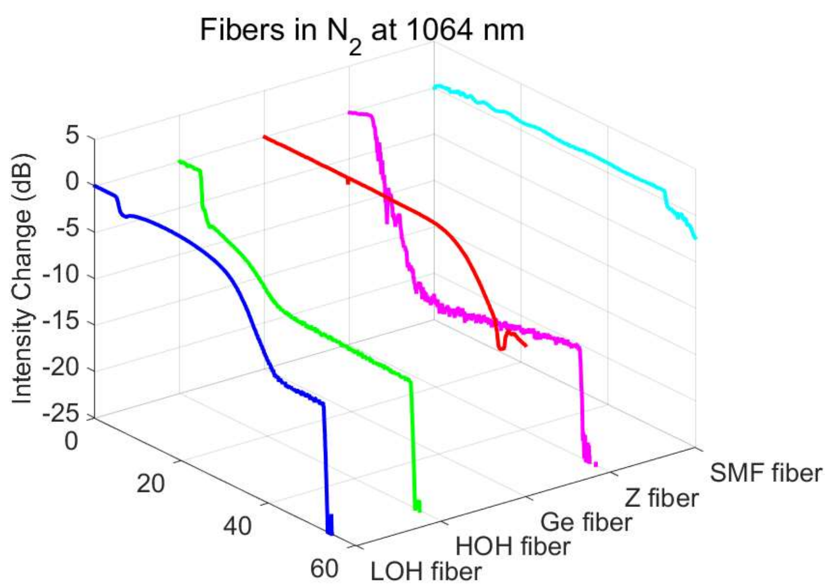
Germanium Doped Multimode –Low OH



Optical Fiber Selection Guide

- Development of a comprehensive guide to aid in the selection of optical fiber type for specific applications





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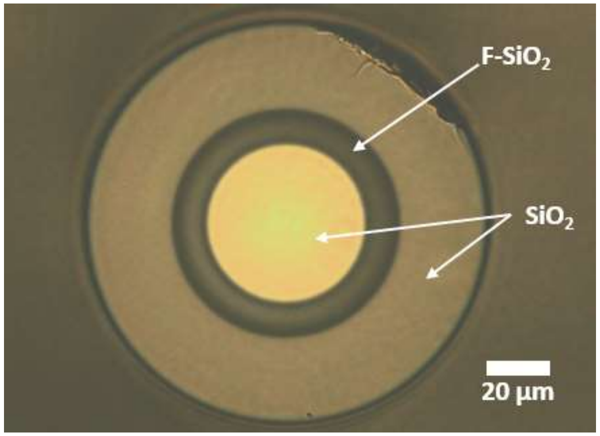
DESIGN STRATEGIES

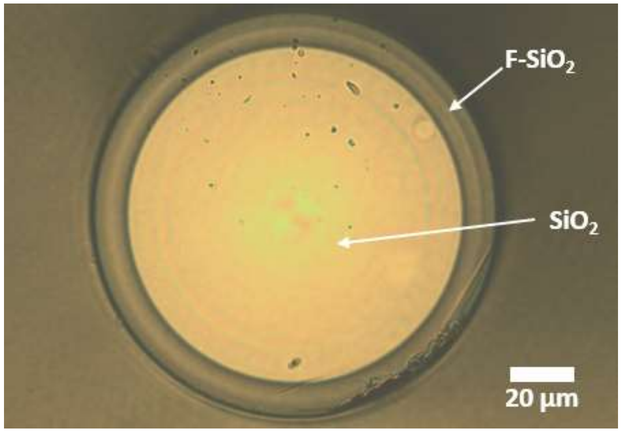
Robust Pure Silica Core Designs

Improvement with fused silica outer cladding

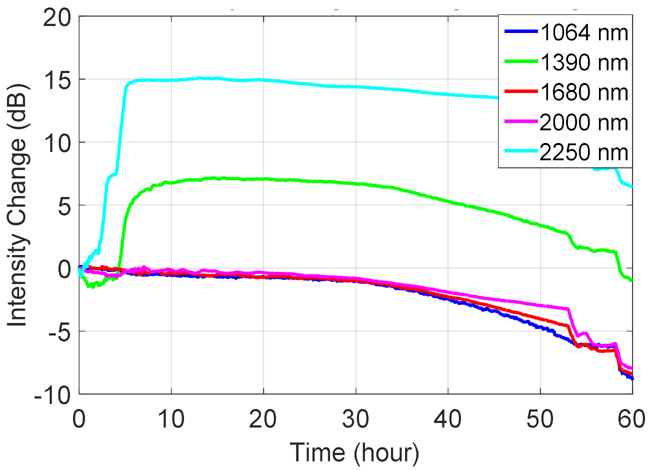
50 µm / 125 µm

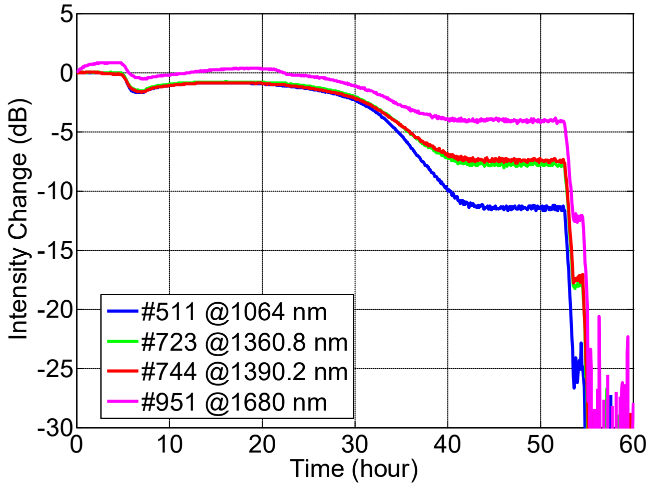


105 µm / 125 µm



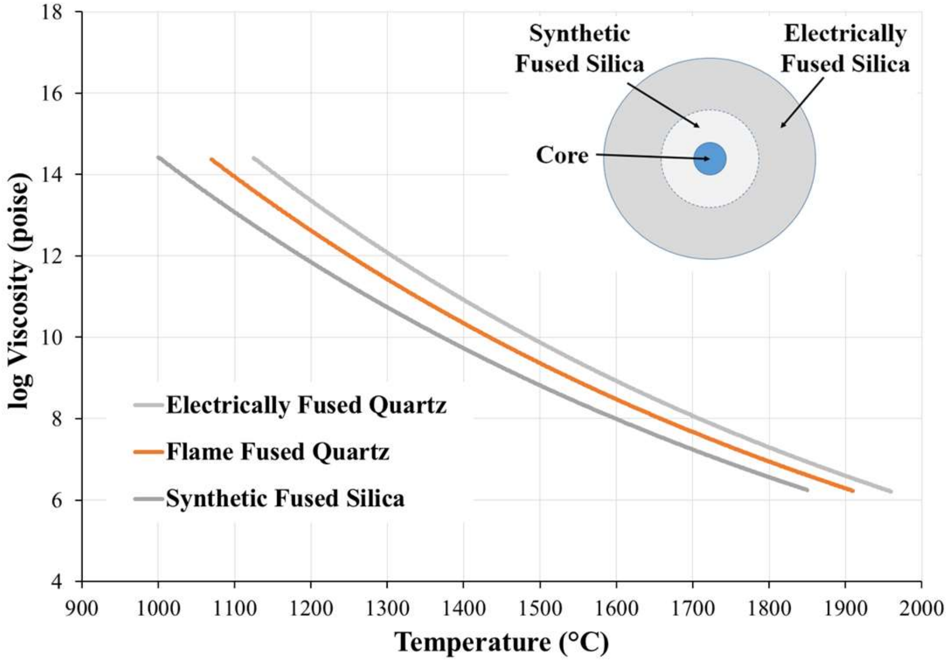
Temperature = 1200ºC (N_2)

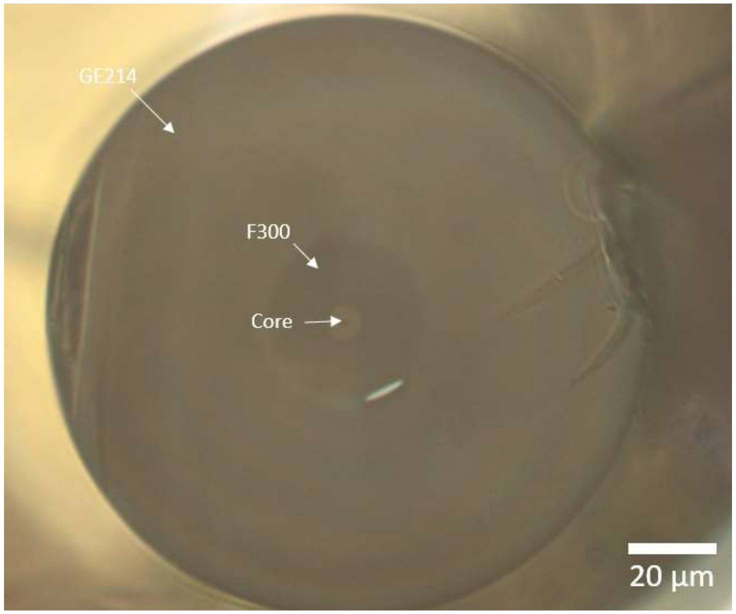




Thermally Tolerant Optical Fibers

Electrically fused quartz dual clad design





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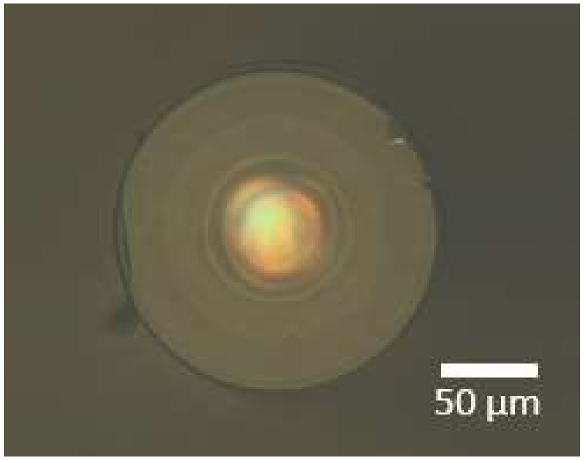
Thermally Tolerant Optical Fibers

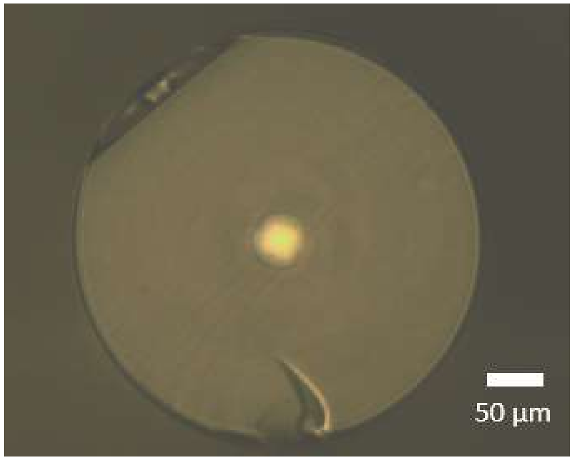
Large diameter design

- Germanium doped graded index multimode core rod
- Stretch and overclad to the desired core/clad ratio
- Draw to desire diameter via the fiber optic draw tower

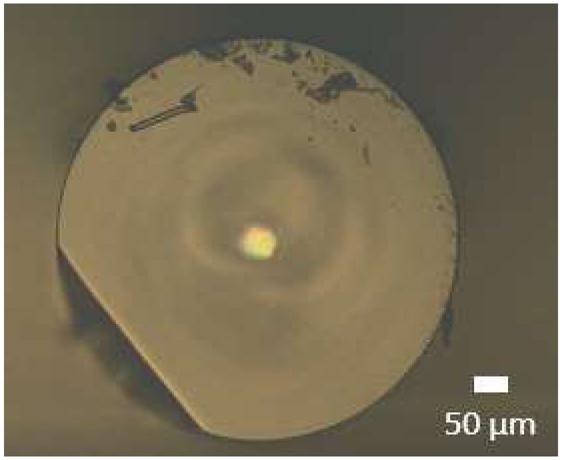
50 µm / 175 µm



50 µm / 300 µm



50 µm / 500 µm



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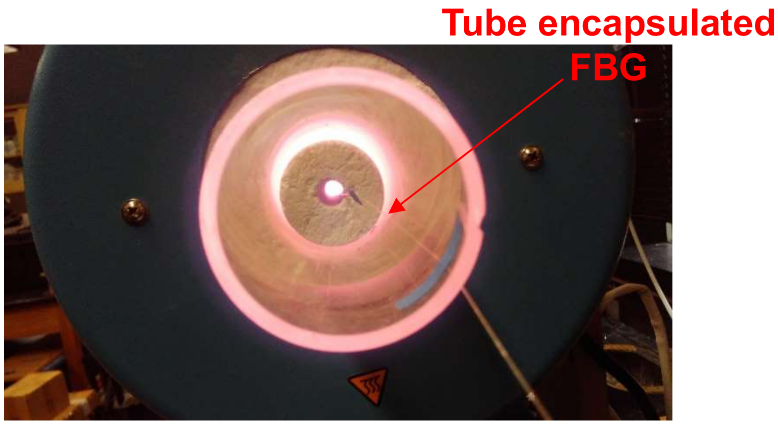
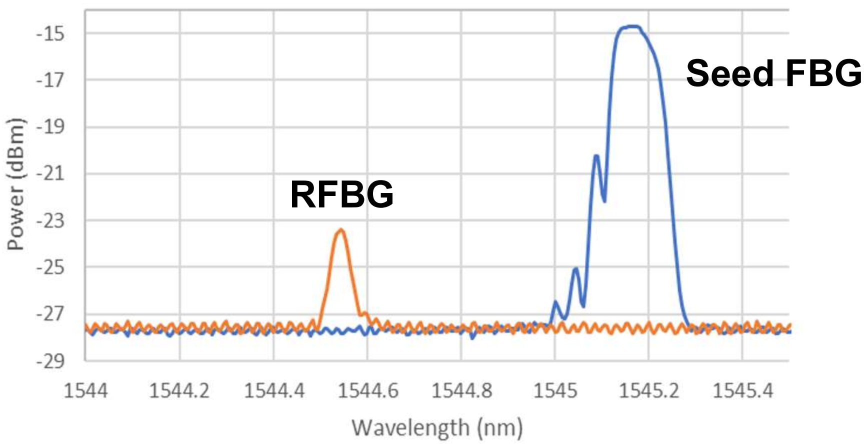
DEMONSTRATION OF HIGH TEMPERATURE FUSED SILICA OPTICAL FIBER SENSOR

Fiber Bragg Grating Sensor

Glass tube encased regenerated FBG

- "Seed" fiber Bragg grating
  - Fiber: SMF28
  - Grating: Type I
  - Vendor: OeLand
- FBG and lead-in fiber length was encapsulated in fused silica capillary tube
  - Unstrained FBG
- Thermal treatment
  - Ramped up (2.5ºC/min) to 1100ºC
  - Held at 1100ºC for 30 minutes
  - Naturally cooled to RT





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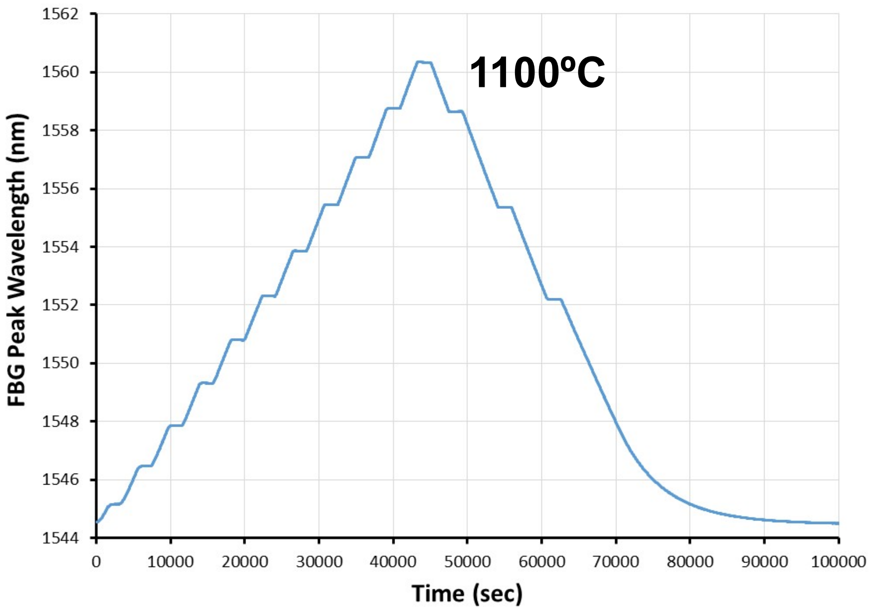
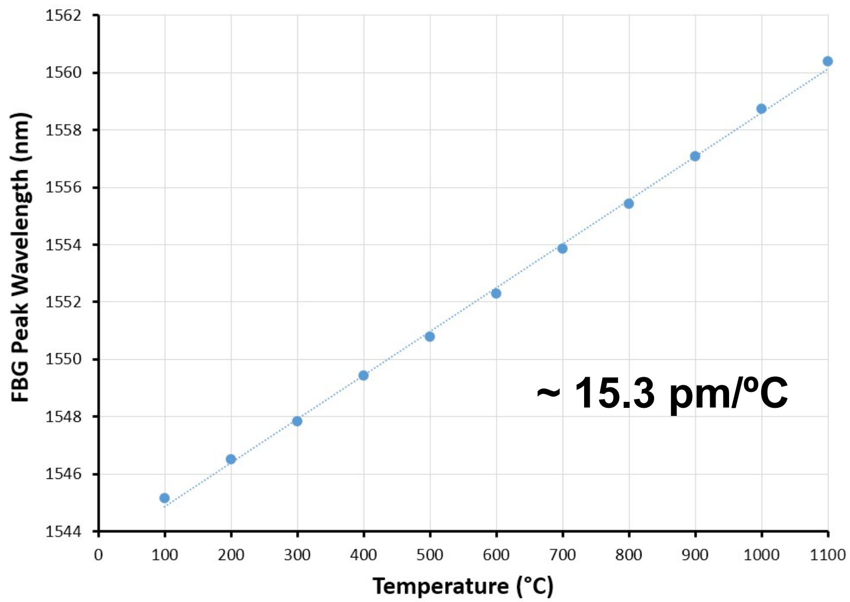
Fiber Bragg Grating Sensor

Sensor testing





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Preliminary Evaluation

- Minor introductions of CO, CO_2, and O_2 to pure nitrogen will not significantly impact optical or mechanical performance up to temperatures of 1000ºC
- Optical fiber with an outer fluorine doped cladding will experience bubbling on the surface due to outgassing in mostly N_2 environments at temperatures > 1100ºC
  - Surface bubbling will not occur in ambient air at temperatures > 1100ºC
- Optical fibers with pure fused silica outer claddings are resistant to outgassing and surface bubbling at temperatures in excess of 1100ºC
  - Fluorine doped fibers with an inner fluorine doped cladding and outer silica cladding do not experience surface bubbling at temperatures > 1100ºC
- Surface devitrification is minimal in mostly N_2 environments up to 1200ºC
- Germanium doped single and multimode optical fibers are recommended for operating temperatures up to 1100ºC in environments that are void of H_2 gas and/or moisture
- Pure silica core outer claddings are recommend for pure silica core fluorine doped cladding fibers up to a temperature of 1200ºC
- Fibers with a lower viscosity (and/or Tf) will be susceptible to short term failure at temperatures in excess of 1100ºC

MILESTONES AND SCHEDULE

Project Milestones

- Technology review
  - Performed literature review
- Performance testing
  - Developed test plan
  - Constructed test facilities
- Novel fiber development
  - Designed andfabricated thermally tolerant fiber designs
- Characterization
  - Optical
    - Conducted 70+ tests on different fiber types, temperature, and environments
  - Mechanical:
    - Optical and scanning electron microscopy
  - Dopant migration
    - Conducted far field measurements and theoretical analyses

Milestone Number	Title/Description	Planned Completion Date	Actual Completion Date
1	Project Management Plan	12/31/2016	12/30/2016
2	Literature and State of the Art Optical Fiber Review	3/31/2017	3/31/2017
3	Optical Fiber Test Plan	3/31/2017	3/31/2017
4	Commission Optical Fiber Test Facilities	6/30/2017	6/30/2017
5	Virginia Tech Optical Fiber Fabrication	9/30/2017	9/30/2017
6	Fiber Mechanical and Dopant Stability Report	3/31/2018	3/31/2018
7	Final Report	9/30/2018	50%

Milestones met on time and on budget

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Milestone Success Criteria

- High temperature fiber test facilities
  - Design and construct fiber testing facilities
- Fused silica fiber fabrication and testing
  - Fabricate two different optical fibers design for high temperature operation
  - Demonstrated adequate lengths and tensile strength
- Testing of commercial optical fibers
  - Evaluated the performance of commercial optical fibers
  - Developed comprehensive understanding of fundamental mechanisms

ID	Title	Description	Result	M.S.	Planned Completion	Actual Completion
SC1	High Temperature Fiber Test Facilities	1. Maximum Temperature = 900°C 2. Minimum Fiber Length > 0.5 m 3. Minimum two gases: H_2, O_2, N_2, CO, CO_2	1. Maximum Temperature = 1200°C 2. Minimum Fiber Length > 0.5 m 3. Minimum two gases: H_2, O_2, N_2, CO, CO_2	M4	6/30/2017	3/31/2017
SC2	Fused Silica Fiber Fabrication and Testing	1. Minimum Length of 1 m 2. Minimum Tensile Strength of 100 kpsi	1. Length > 1 m 2. Minimum Tensile Strength > 100 kpsi	M5	9/30/2017	9/30/2017
SC3	Testing of Commercial Fibers	1. Sensing length of 2 m 2. Resolution < 20 cm	----------------------	M7	9/31/2018	------

Success Criteria met on time and on budget

Project Schedule

GANTT CHART		Project Year 1				Project Year 2				Key Dates	
Task #	Task Name	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Start Date	End Date
1	Project Management and Planning									10/1/2016	12/30/2016
M1	**MILESTONE 1**									**12/31/2016**	
2	Literature and State of the Art Optical Fiber Market Review									10/15/2016	3/30/2017
2.1	Perform Literature Review									10/15/2016	3/15/2017
2.2	Perform Commercial Optical Fiber Market Review									10/15/2016	3/15/2017
2.2	Generate Literature Review and Market Report									1/1/2016	3/30/2017
M2	**MILESTONE 2**									**2/28/2016**	
3	Develop Test Plan									11/15/2016	3/30/2017
M3	**MILESTONE 3**									**3/30/2017**	
4	Prepare for Optical Fiber Stability Testing									12/15/2016	3/30/2017
4.1	Acquire Materials and Supplies									12/15/2016	4/15/2017
4.2	Construct and Commission the Environmental Test Facilities									4/1/2017	6/30/2017
M4	**MILESTONE 4**									**6/30/2017**	
5	Evaluate the Mechanically Stability of Commercial Optical Fibers and Drawn Fibers									4/1/2017	3/30/2018
5.1	Draw Fused Silica Fibers on Virginia Tech Draw Tower									4/1/2017	9/15/2017
M5	**MILESTONE 5**									**9/30/2017**	
5.2	Conduct Environmental Testing									6/15/2017	11/15/2017
5.3	Perform Data Analyses and Interpretation									9/16/2017	12/30/2017
5.4	Generate Mechanical Stability Report									12/1/2017	12/30/2017
6	Evaluate the Dopant Stability of Commercial Optical Fibers									10/1/2017	2/15/2018
6.1	Conduct Environmental Testing									10/15/2017	1/15/2018
6.2	Perform Material Characterization									11/1/2017	2/15/2018
6.3	Perform Data Analyses and Interpretation									2/1/2018	3/15/2018
6.4	Generate Dopant Diffusion Test Report									3/1/2018	3/30/2018
M6	**MILESTONE 6**									**3/30/2018**	
7	Evaluate the Optical Stability of Commercial Fibers									7/15/2017	8/1/2018
7.1	Conduct Environmental Testing									7/16/2017	5/15/2018
7.2	Perform Data Analyses and Interpretation									4/1/2018	8/15/2018
7.3	Generate Optical Stability Test Report									8/15/2018	9/15/2018
8	Prepare and Submit Final Report									9/1/2018	9/30/2018
M7	**MILESTONE 7**									**9/30/2018**	

Next Steps

- Refine mechanical reliability lifetime calculations
- Refine dopant migration lifetime calculations
- Conduct optical stability lifetime calculations
- Fully characterize thermally tolerant optical fibers
- Generate final report

Acknowledgements

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Nevada Davis

Department of Energy

National Energy Technology Laboratory

Project Manager: Barbara Carney

Paul Ohodnicki

Michael Buric

Benjamin Chorpening

Bo Lui

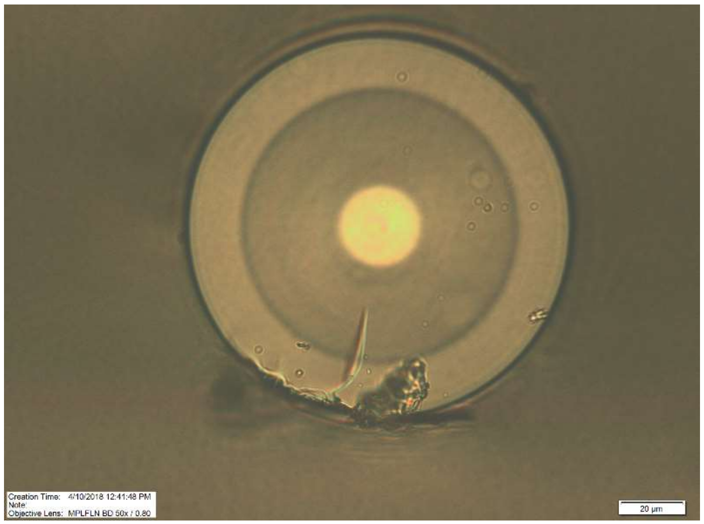
Sydni Credle

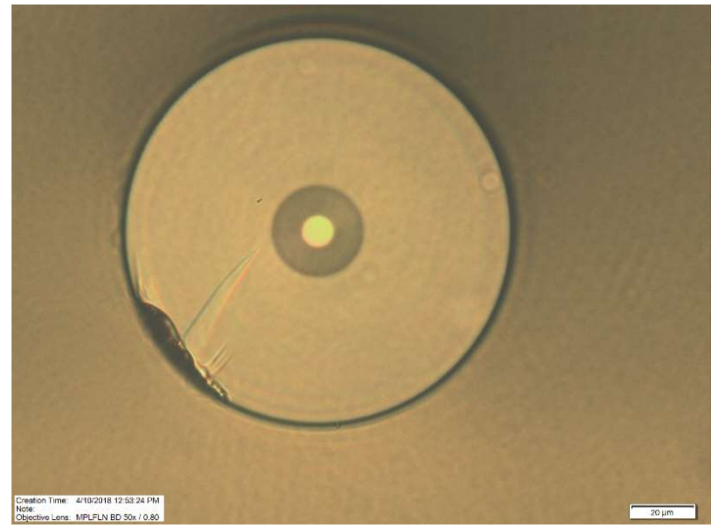
THANK YOU FOR YOUR TIME

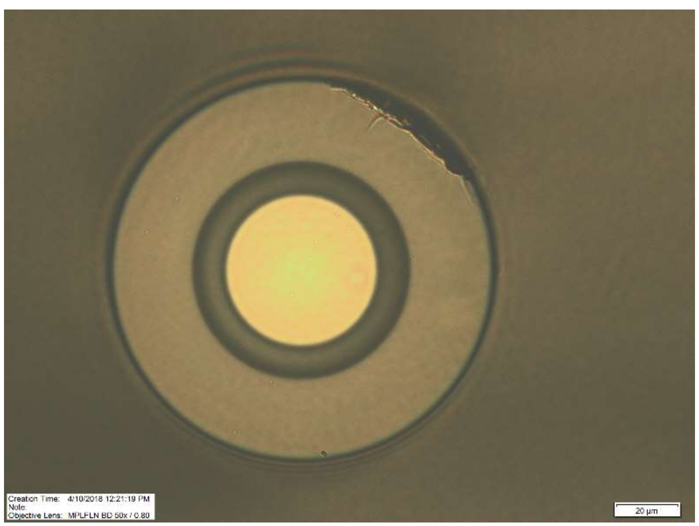
SUPPLEMENTAL INFORMATION

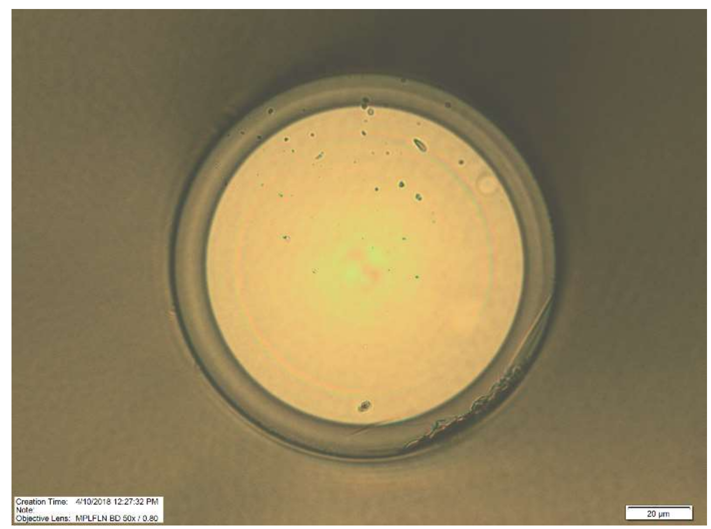
Step Index Multimode Optical Fibers

Pure silica core / Fluorine doped cladding

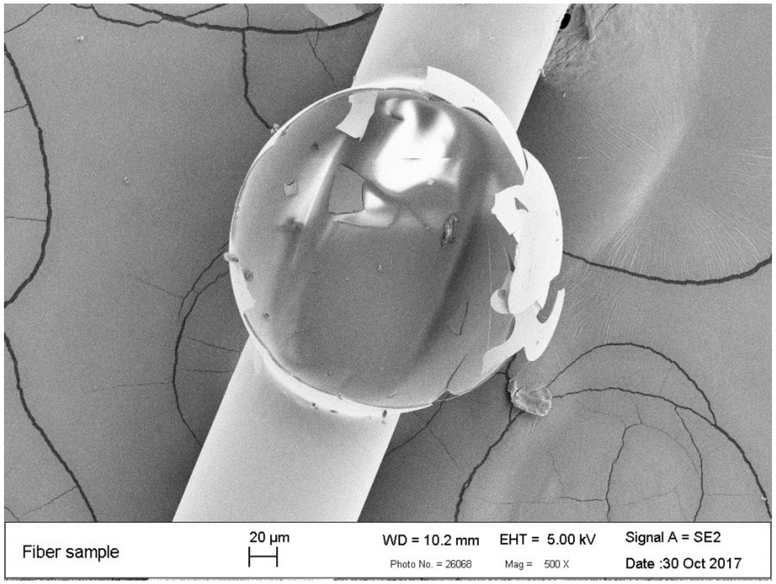


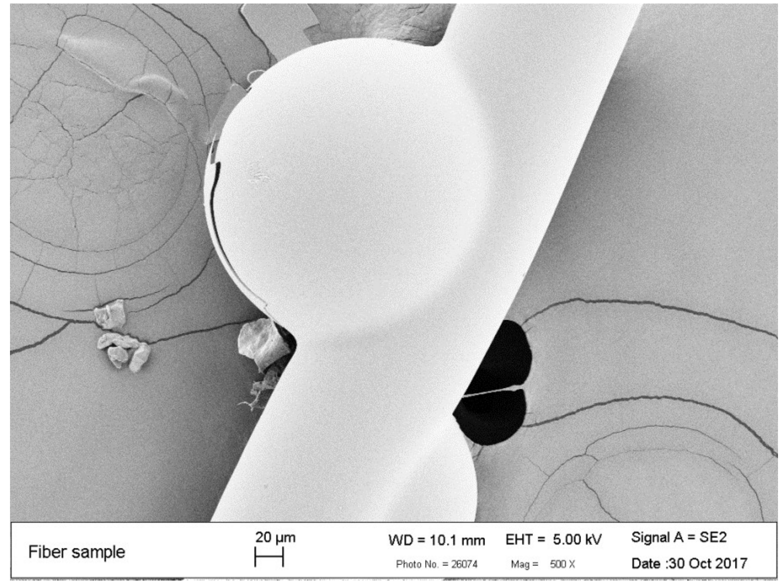


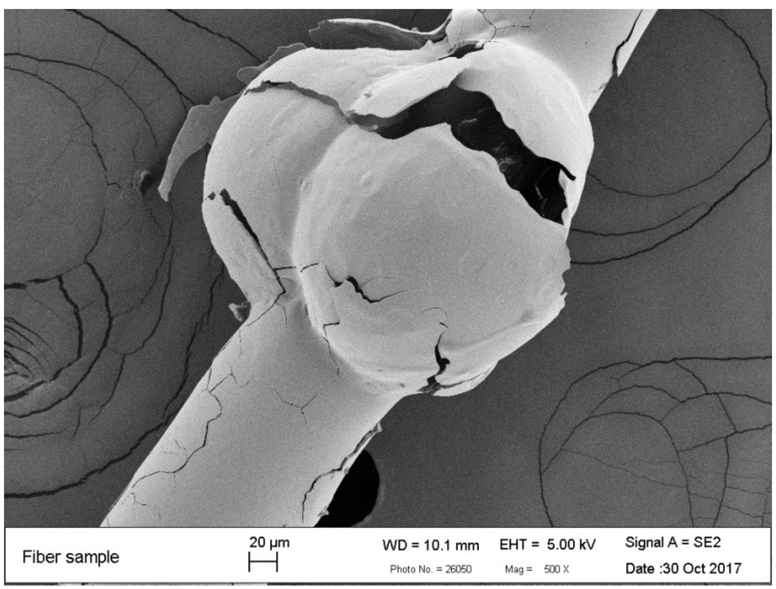


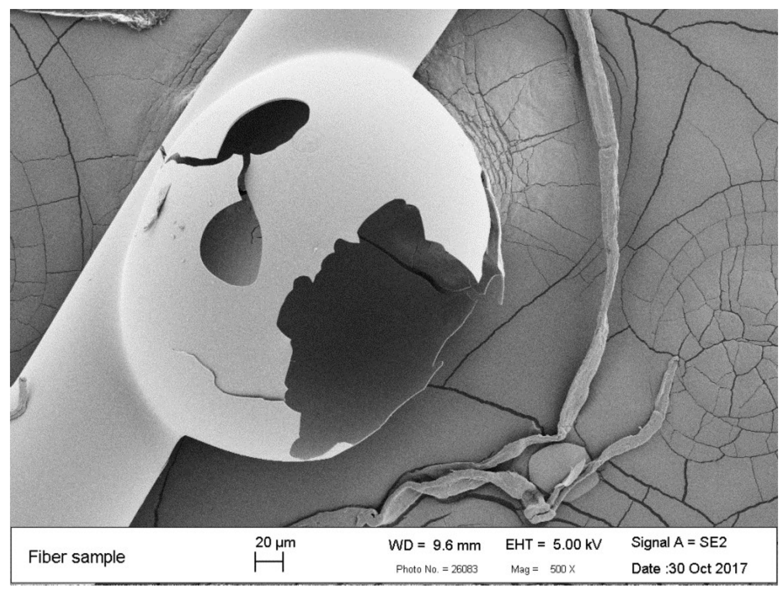


Surface Bubbling : 105/125 SIMMF



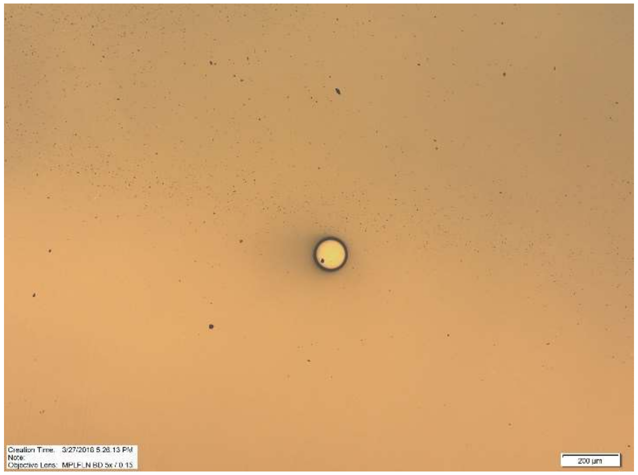


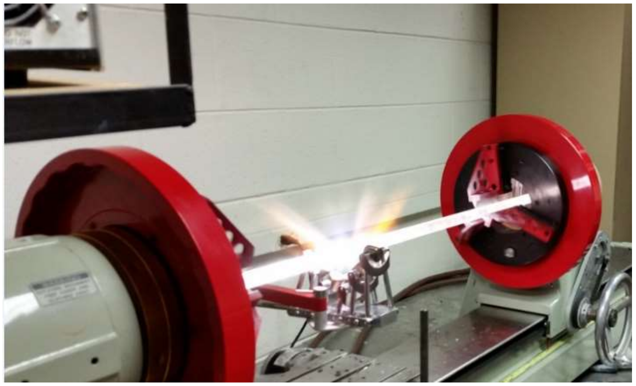




Overcladding Optical Fibers

- General fabrication process
  - Remove acrylate coating via sulfuric acid soak
  - Insertion of bare fiber in overclad tube
  - Pull vacuum and collapse overclad tube on fiber
- Larger fibers (d=1-5 mm) allow for easier handling
  - Optical and scanning microscopy, beam profile measurements
  - Devitrification and dopant diffusion studies





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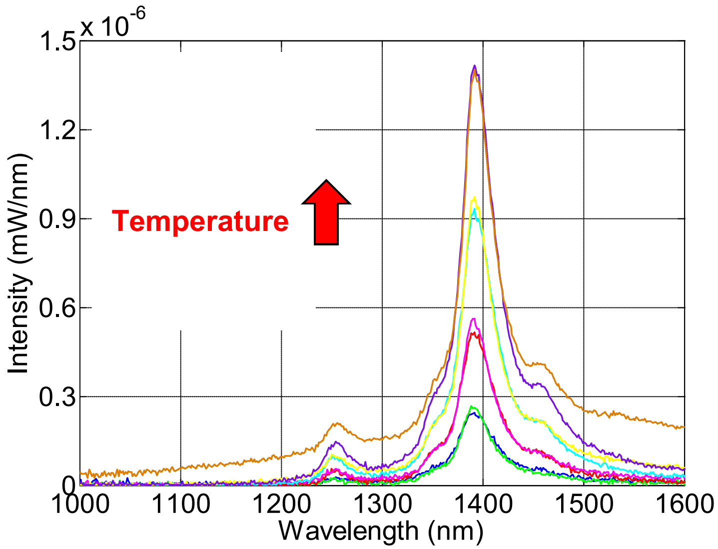
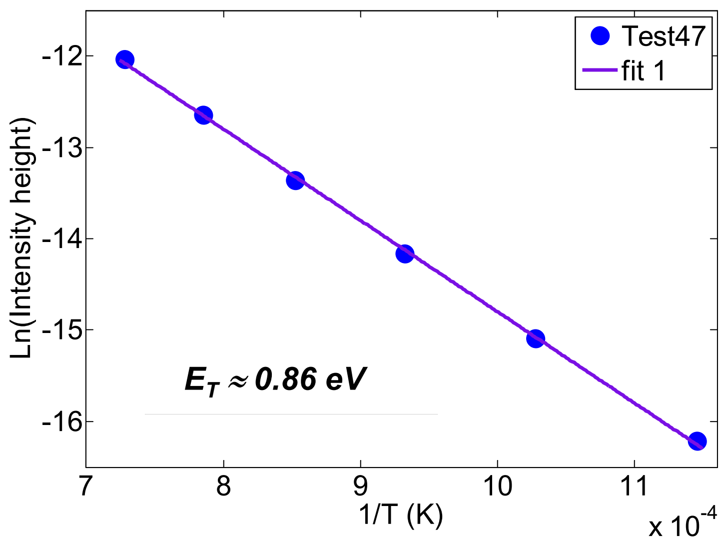
"OH Thermal Emission"





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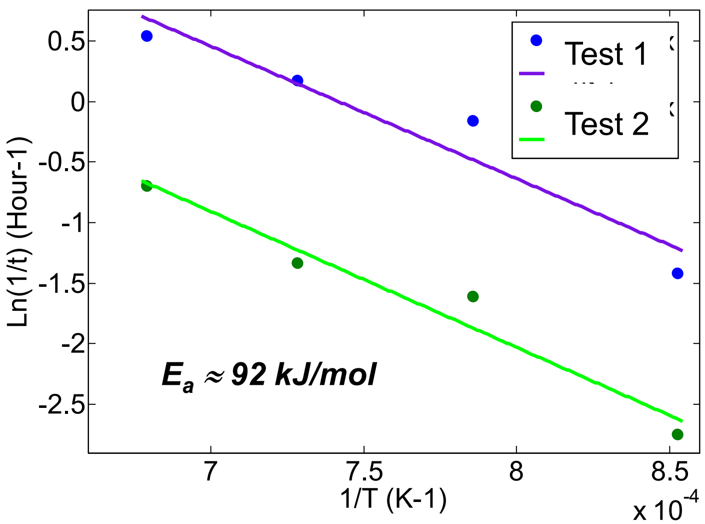
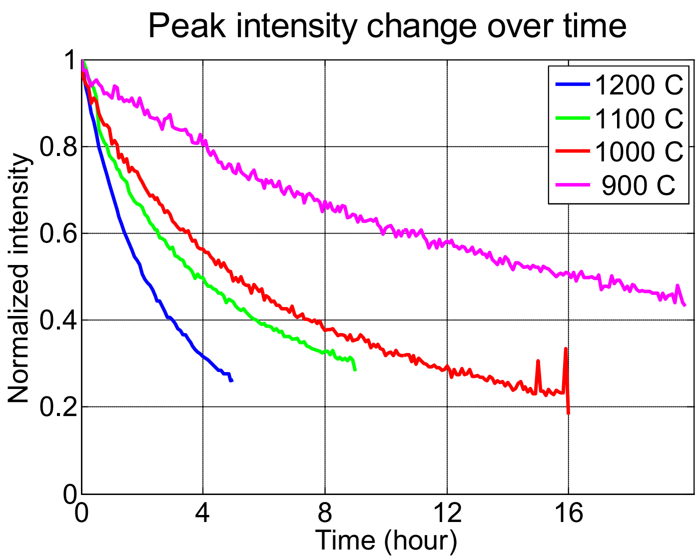
"OH Thermal Emission"

Hydroxyl out-diffusion





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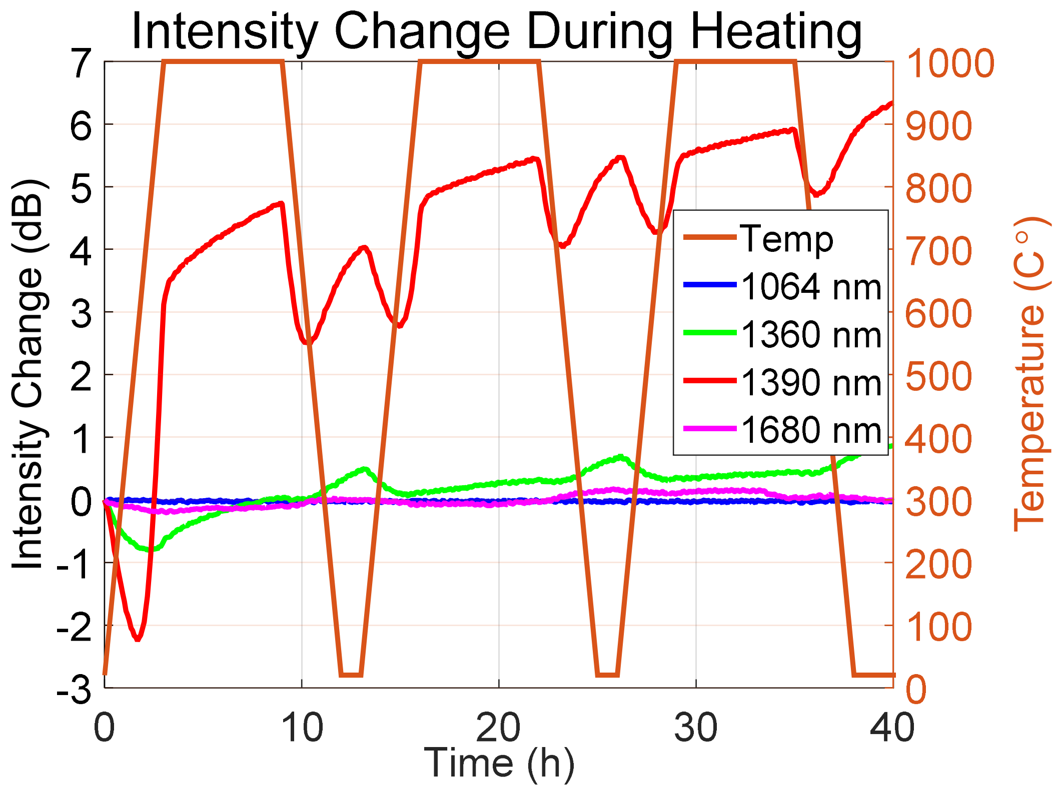
Thermal Cycling

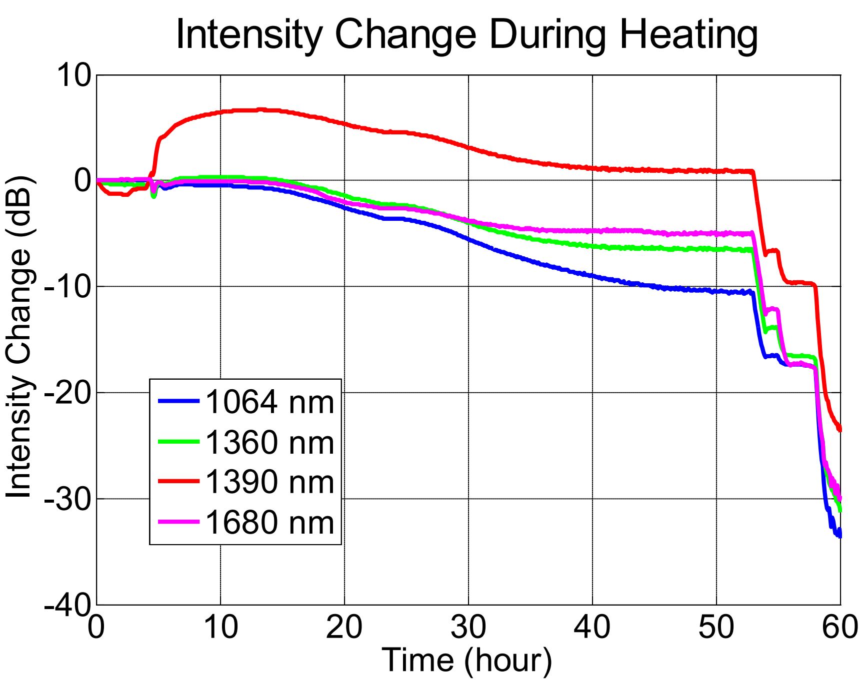
High OH Pure Silica Core Multimode Fiber

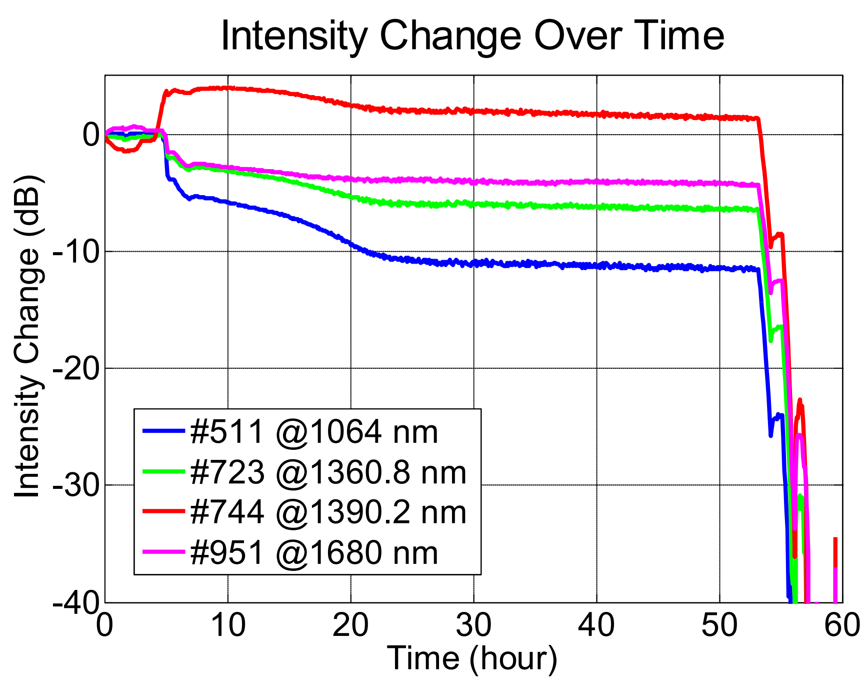


Oxygen Exposure Test

5% O_2 in N_2

- No observable difference between exposure to 5% O_2 (left) and N_2 (right) regarding overall loss increase





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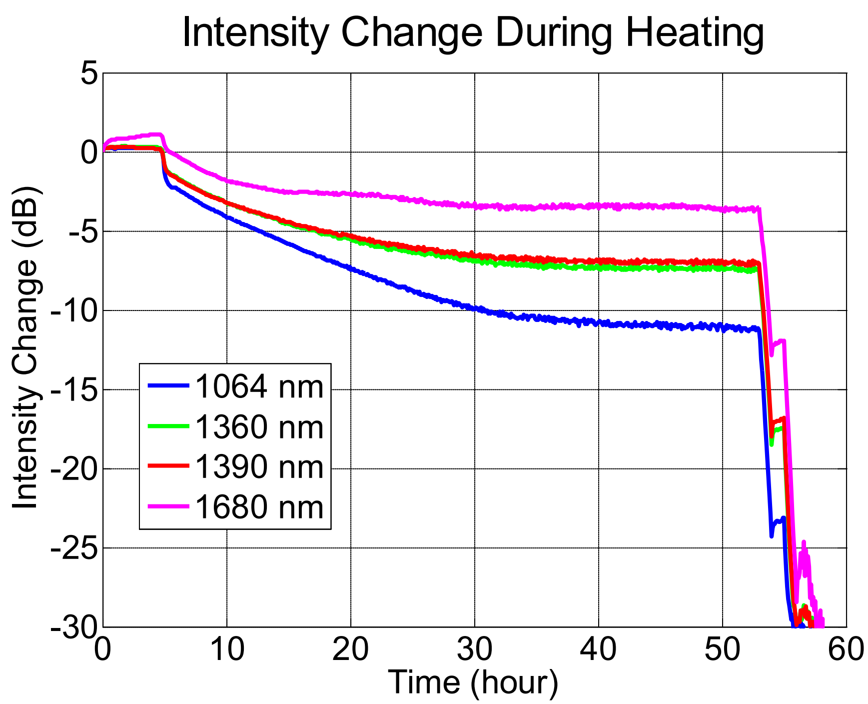
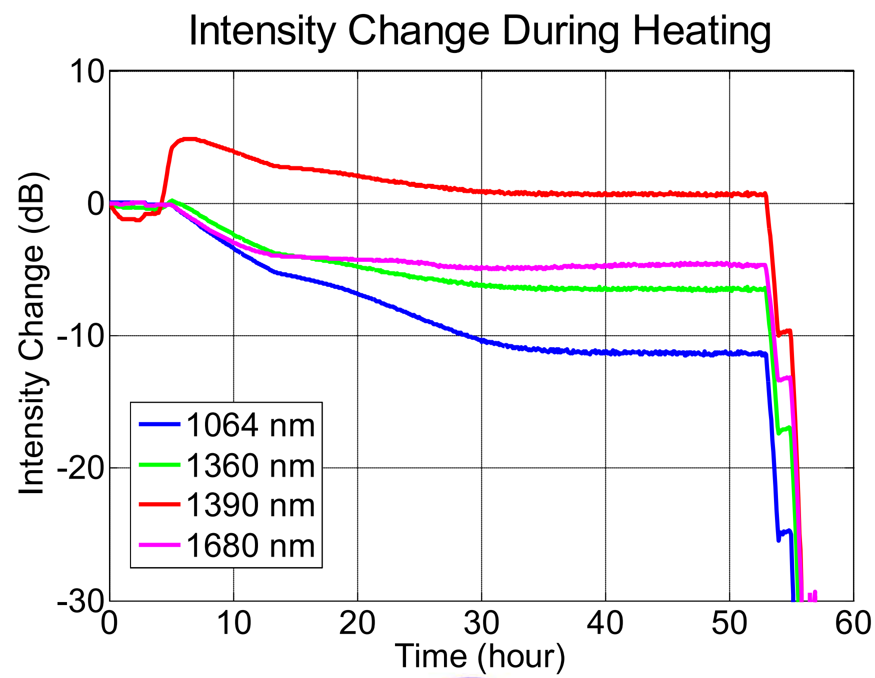
CO Exposure Test

1000 ppm CO in N_2

- No observable difference between exposure to1000 ppm CO and N_2 for either fibers (left: LOH and right: HOH)





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