

# Novel Modified Optical Fibers for High Temperature In-Situ Miniaturized Gas Sensors in Advanced Fossil Energy Systems

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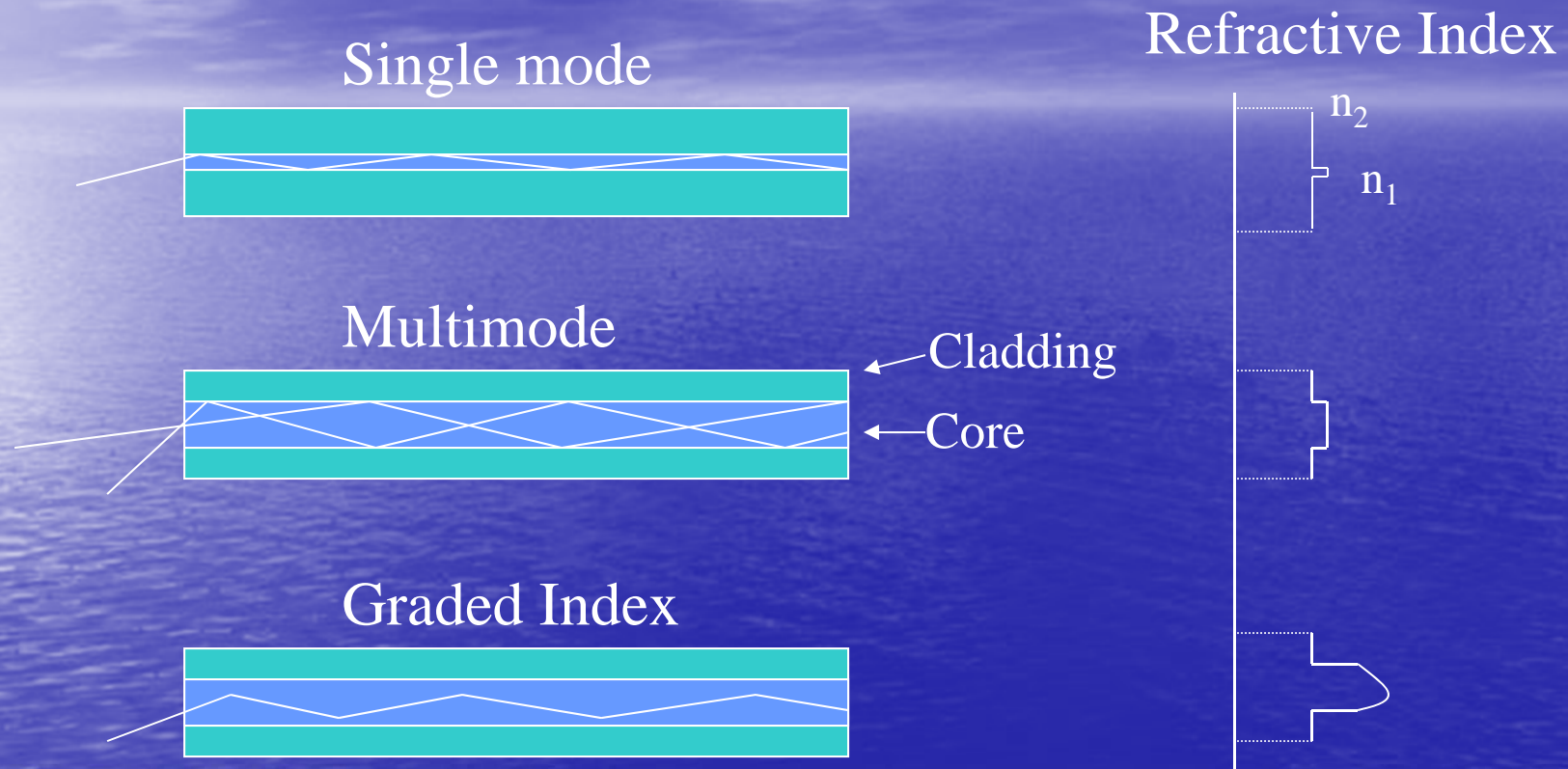
*DOE Award DE-FC26-05NT42441*

*Program Manager: Robie Lewis*

# Project Goal

- To develop high temperature gas sensors for use in advanced power generation systems.
- Two technologies being developed
  - 3-D nanoporous silica optical fibers
  - Sapphire photonic crystal fibers

# Refractive Index Profiles of Some Optical Fiber

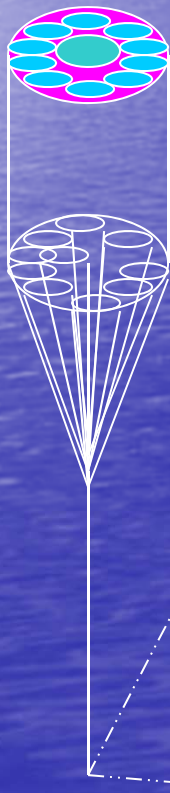


Index difference produced by dopants in either the core or cladding region

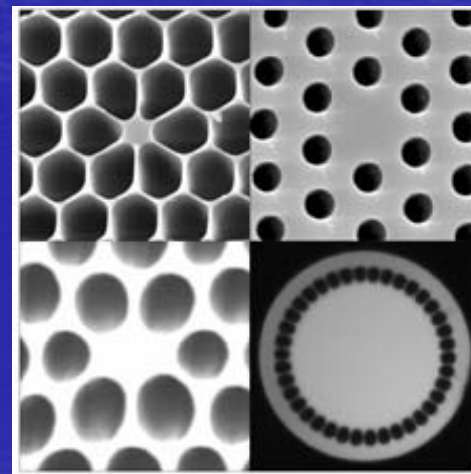
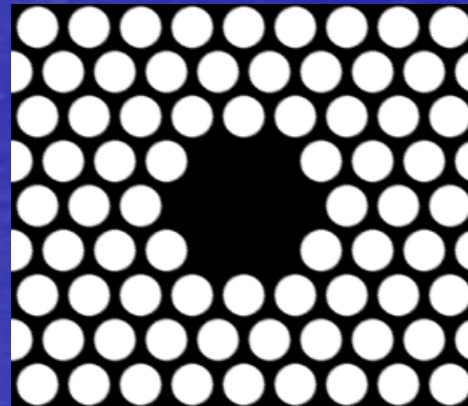
Key Point: all these fibers are solid glass core and solid glass cladding

# Review of Ordered Holey Fiber Structures

Holey fibers are optical fibers which have been fabricated such that the drawn fiber contains a series of air holes. The presence of the air holes confines the light within the fiber.



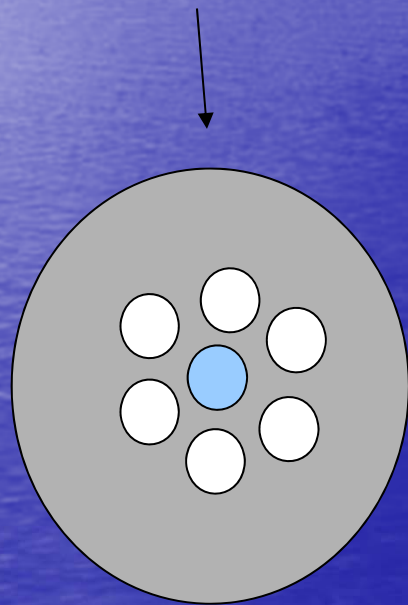
“Tube Stack and Draw” method has been used to produce a variety of ordered hole fibers including photonic band gap fibers and average index fibers.



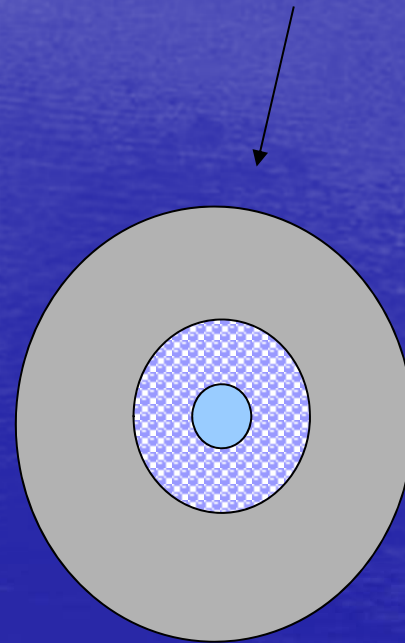
D. Kominsky,  
PhD  
Dissertation,  
Virginia Tech,  
2005

# Previous concept for a new type of Holey Fiber

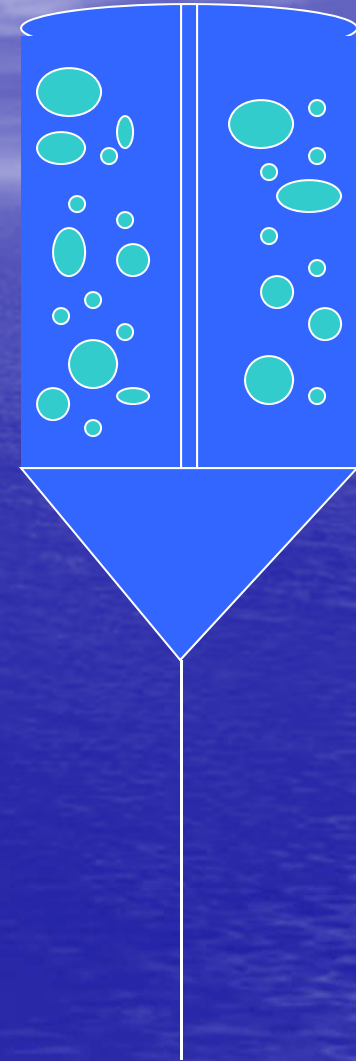
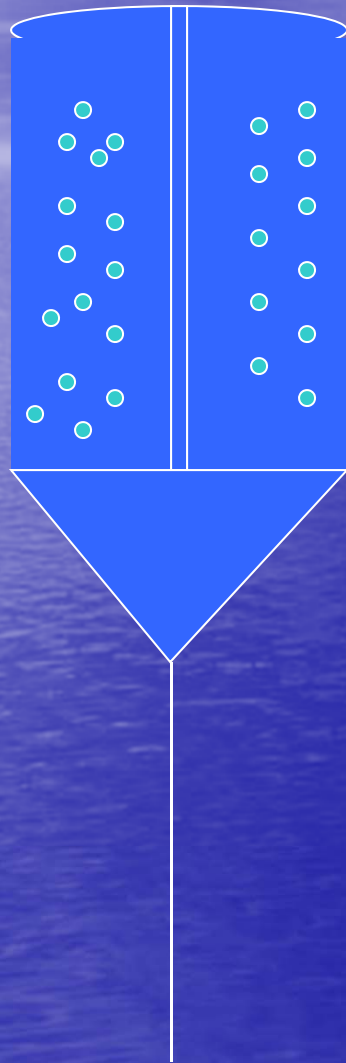
Photonic Crystal Fiber



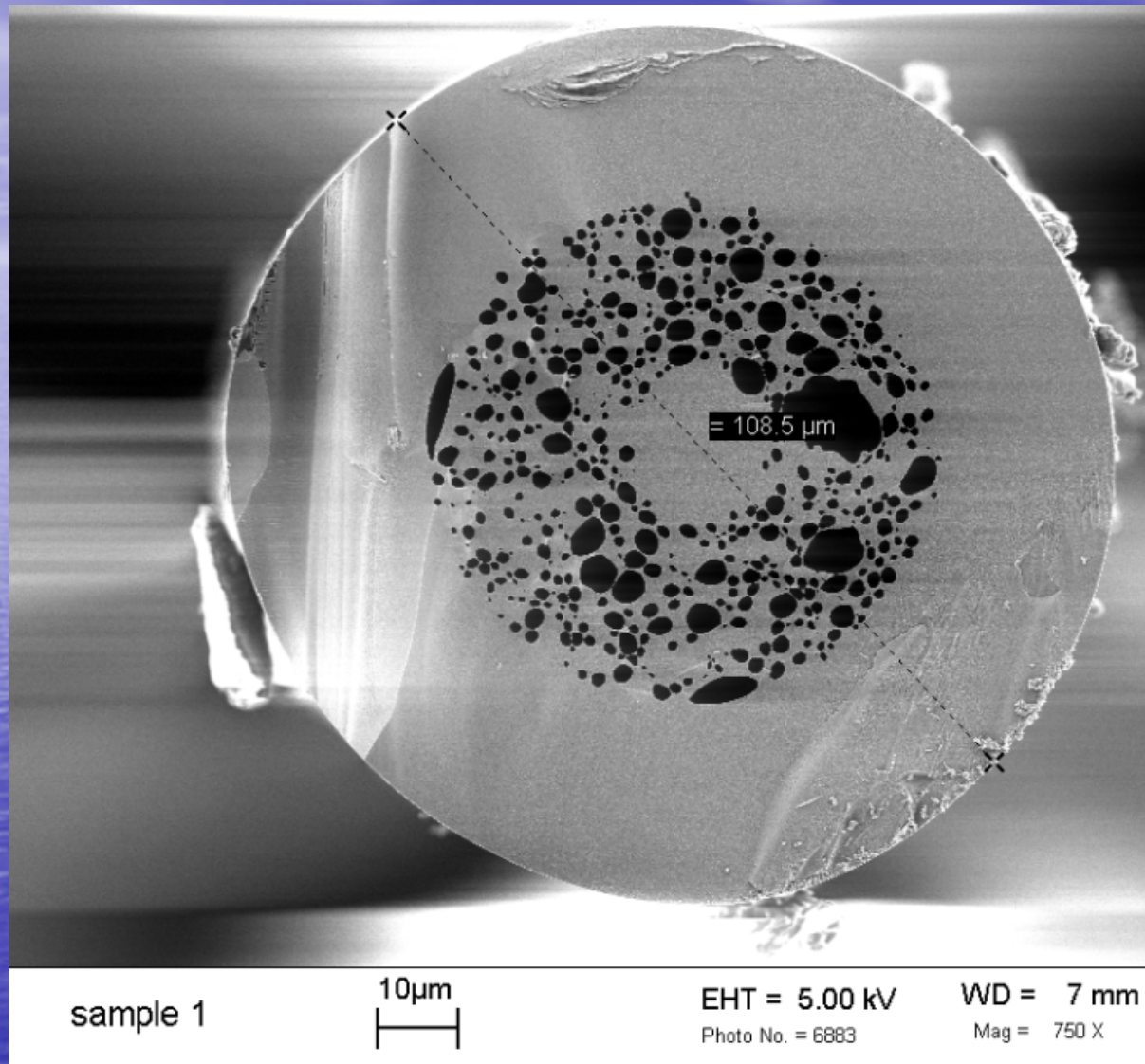
RHOF



# Random Hole Fiber Approach



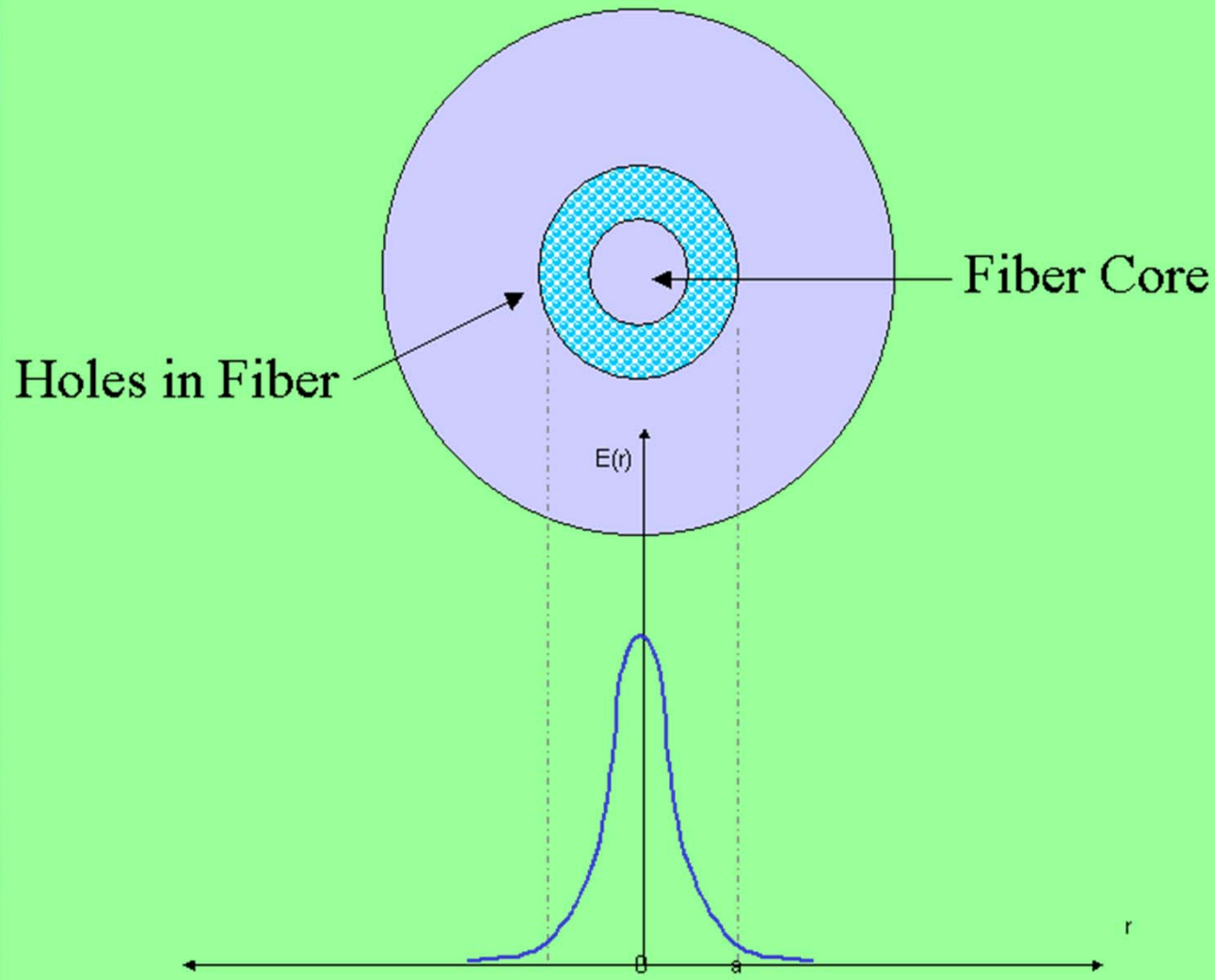
# SEM Micrograph of Optical Fiber from GPP Process



*“Microstructural Analysis of Random Hole Optical Fibers”* Gary Pickrell, Dan Kominsky, Roger Stolen, Fred Ellis, Jeong Kim, Ahmad Saffaai-Jazi, and Anbo Wang, *Photonics Technology Letters*, Vol. 16, No. 2, pg 491-93, 2004

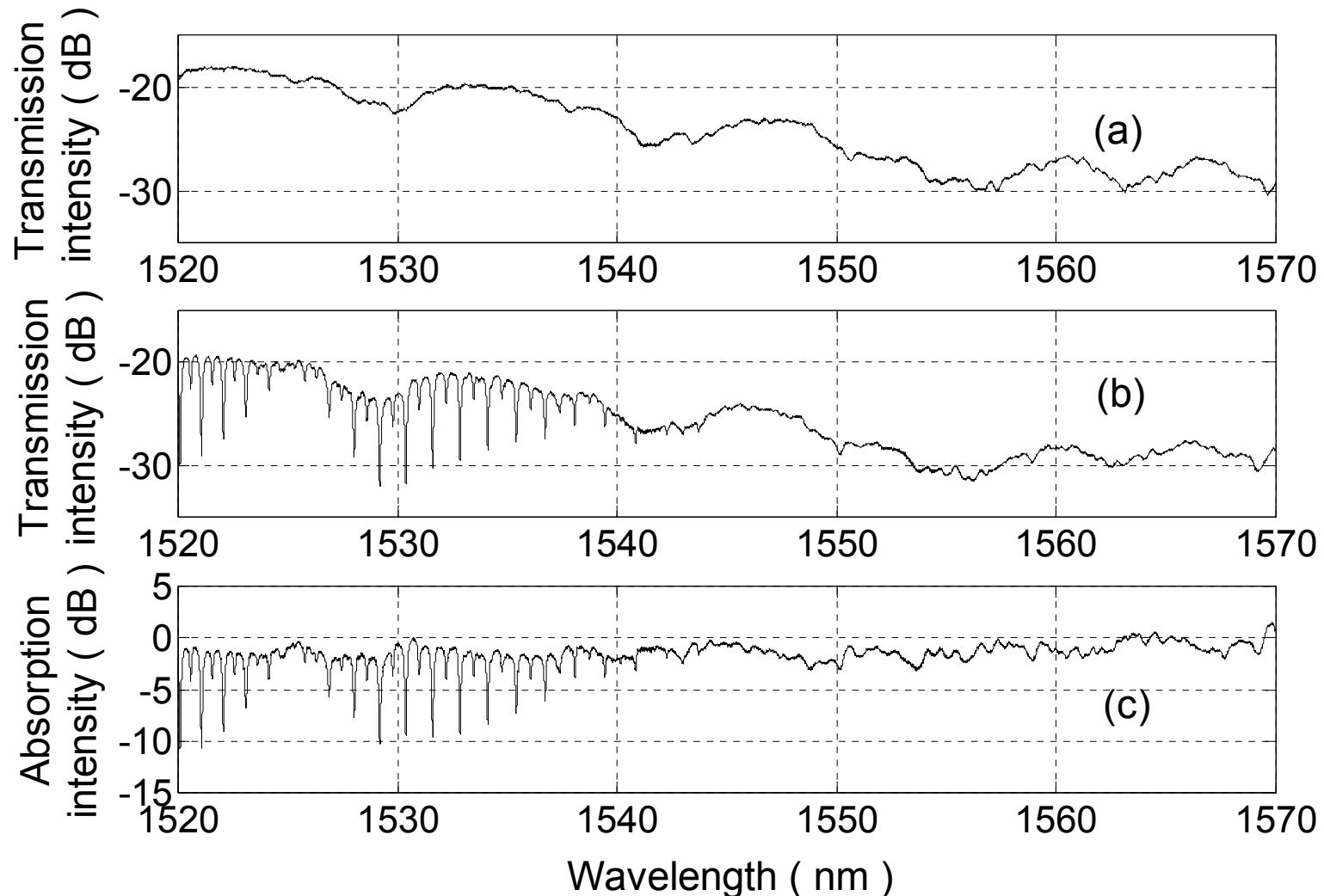
# Chemical Sensing

## Evanescent Wave Sensing of Materials in the Holes



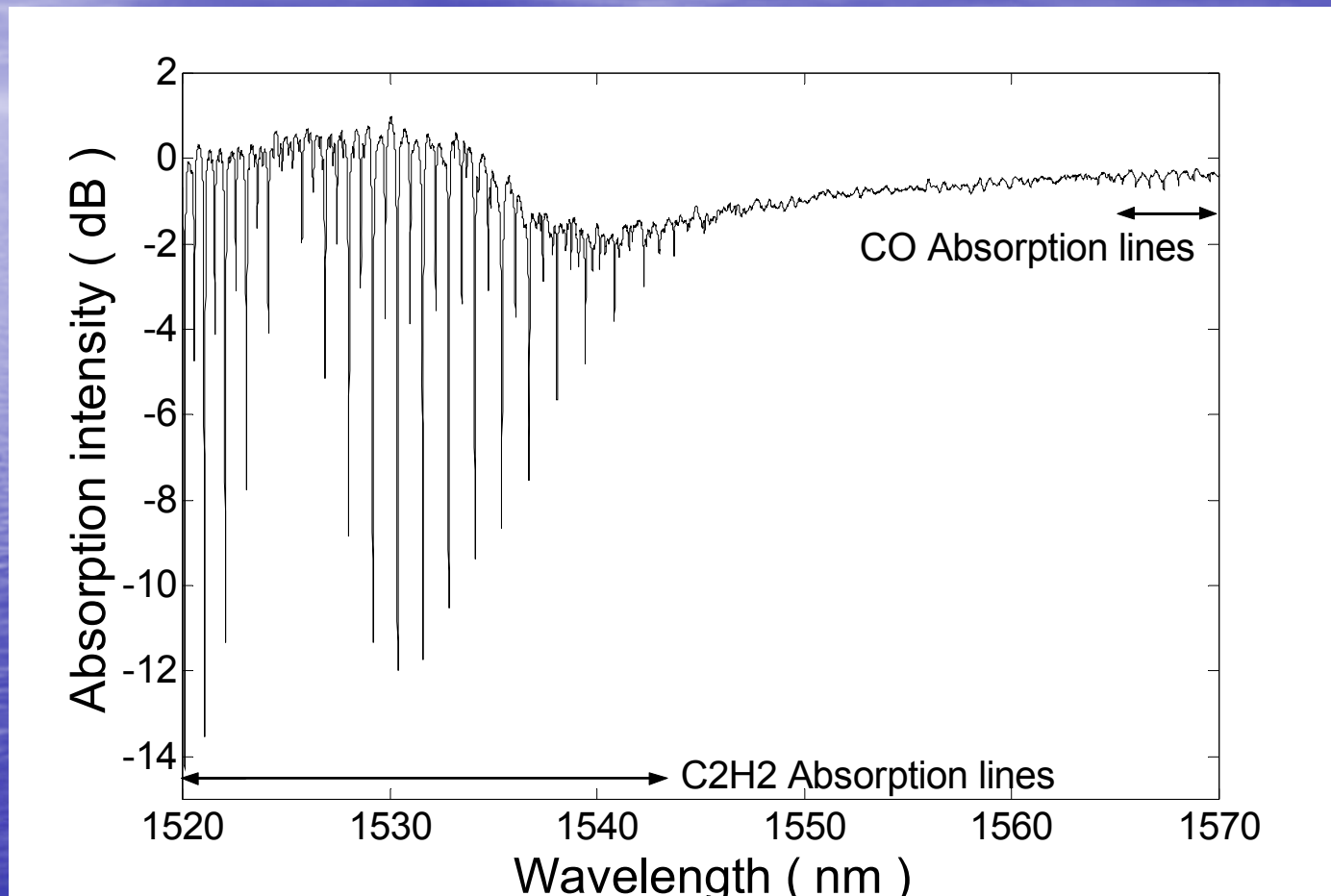


# RHOF Evanescent Wave Gas Sensing - Acetylene



“Random-hole fiber evanescent wave gas sensing”, G. Pickrell, W. Peng and A. Wang, *Optics Letters*, Vol. 29, No. 13, pp 1476-78, July, 2004

# RHOF multiple gas species sensing



Simultaneous  $C_2H_2$  and CO absorption spectrum

W. Peng, G. Pickrell, A. Wang Photonics Technology Letters, 2004

# Improved Response Time for Chemical Sensing

Project Initiated to develop a "holey" optical fiber capable of high temperature gas detection with improved response time.

Concept was to make the holes in the fiber run perpendicular to the optical axis (instead of parallel to it as in previously demonstrated fibers) to increase the gas sensing response time of the fibers.

# Stochastic Holey Fiber Development

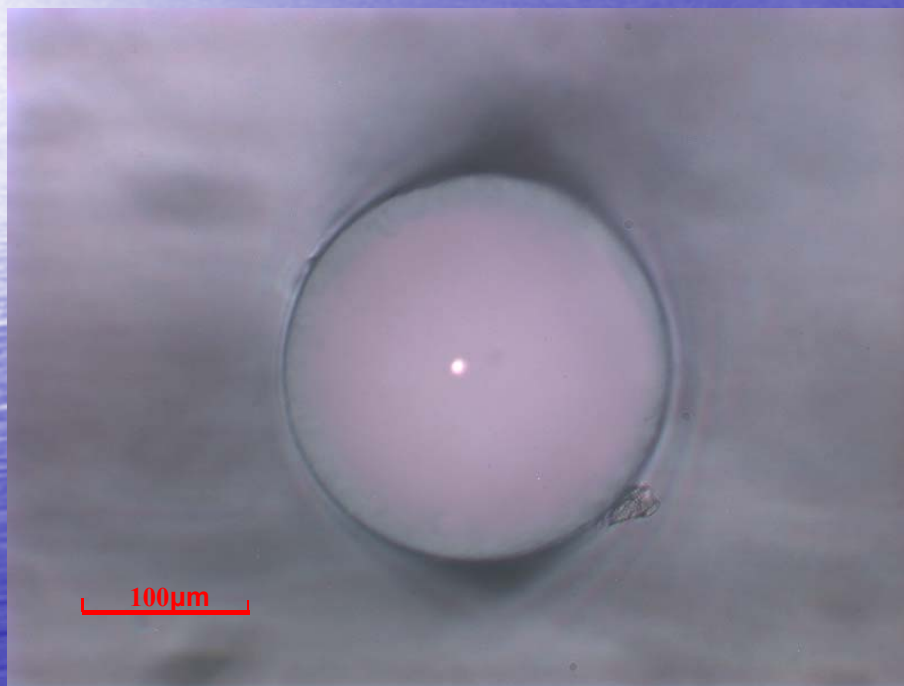
Two types of porous fibers were designed and fabricated:

1. Stochastic porosity cladding/solid core
2. Stochastic porosity ordered hole fiber:

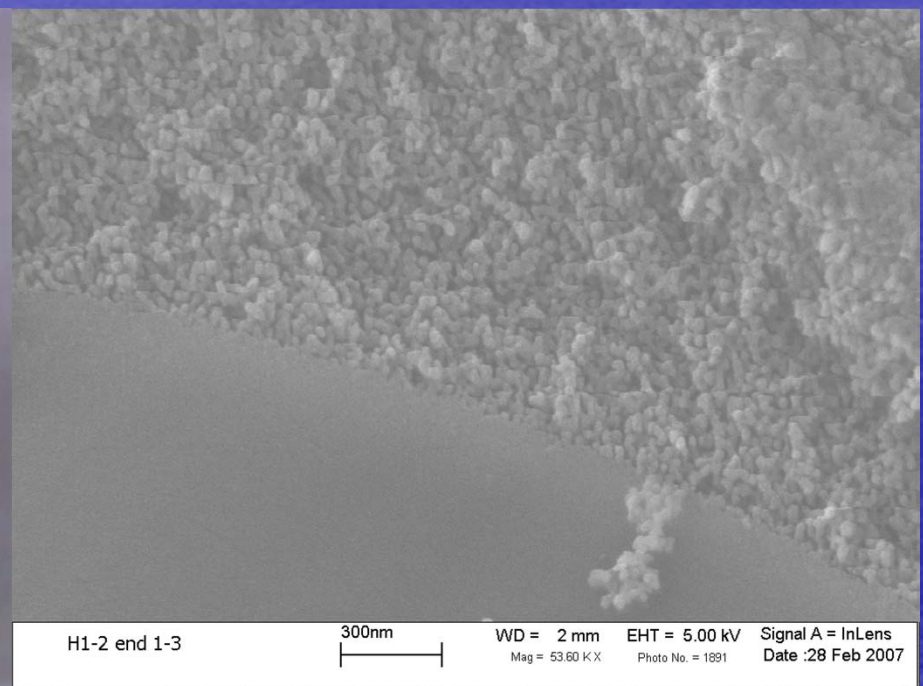
The porous structure is made of nano-scale pores throughout the fiber, pores are randomly oriented and three dimensionally interconnected.

# Fiber Characterization

- Optical and SEM micrograph of the stochastic porosity solid core fiber



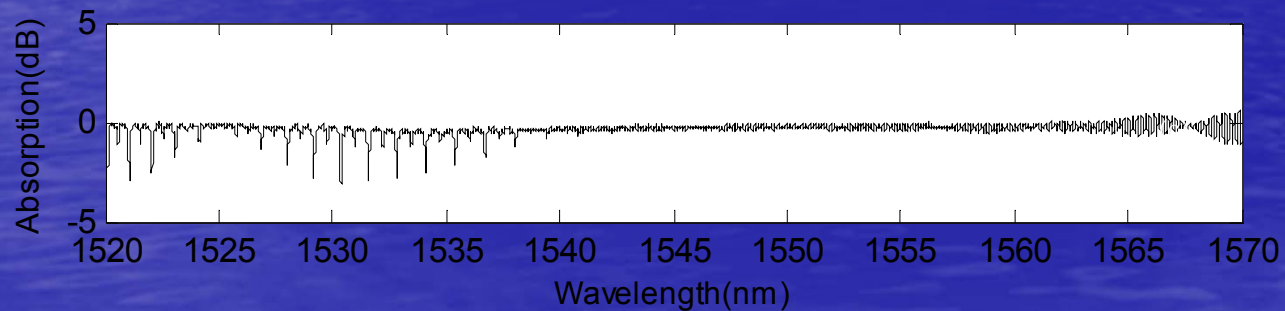
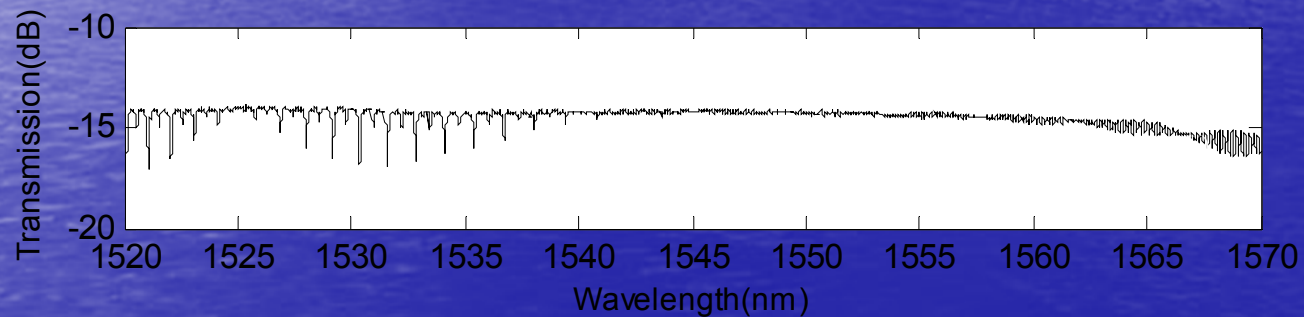
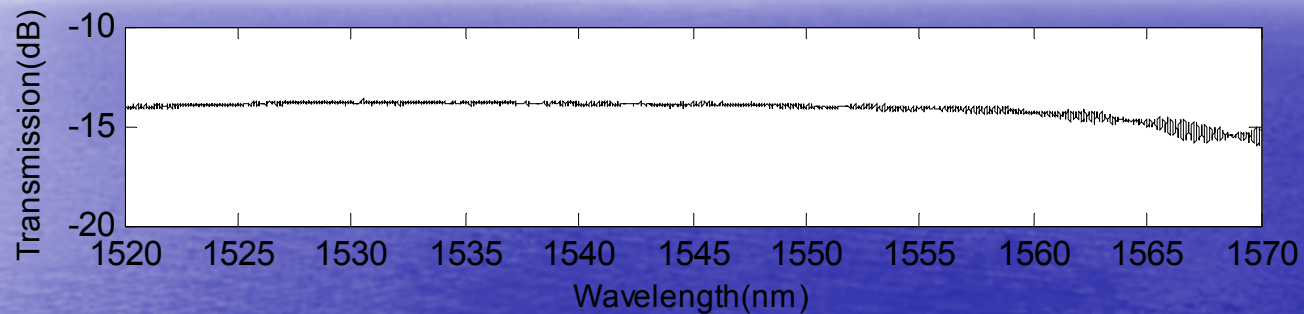
Optical micrograph of the porous clad fiber



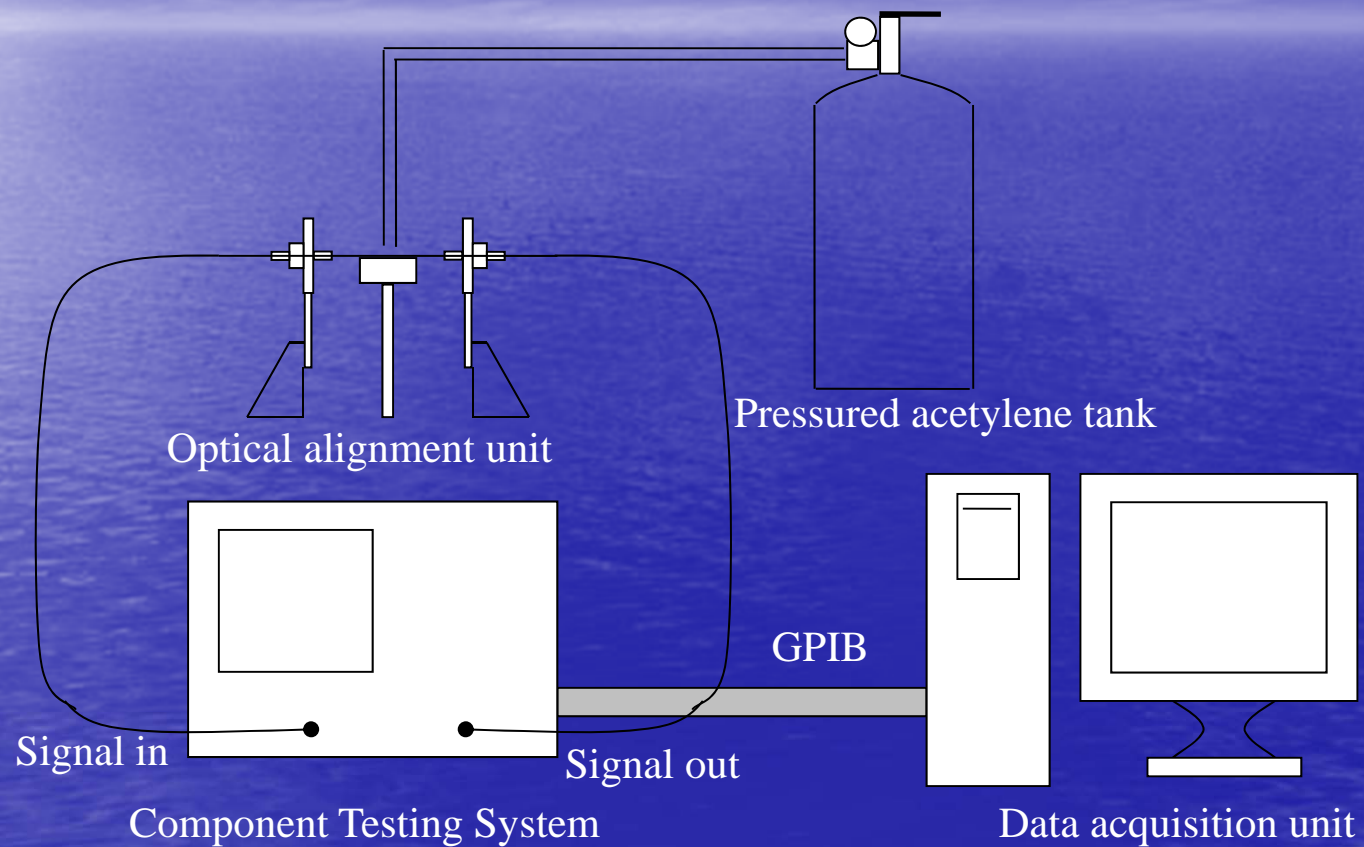
SEM micrograph of typical core-cladding interface of porous clad fiber

# Gas Sensing

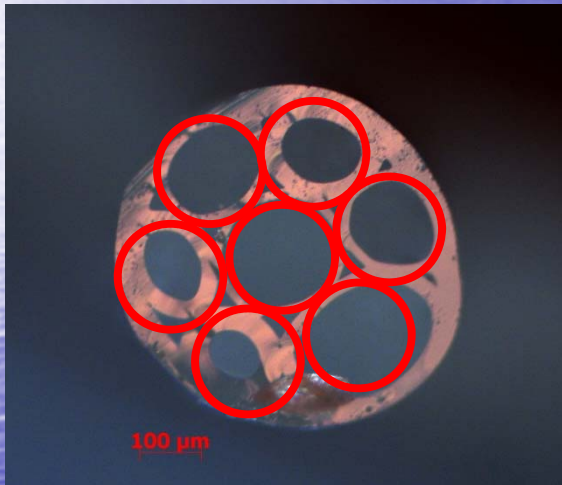
## Stochastic porosity cladding solid core fiber



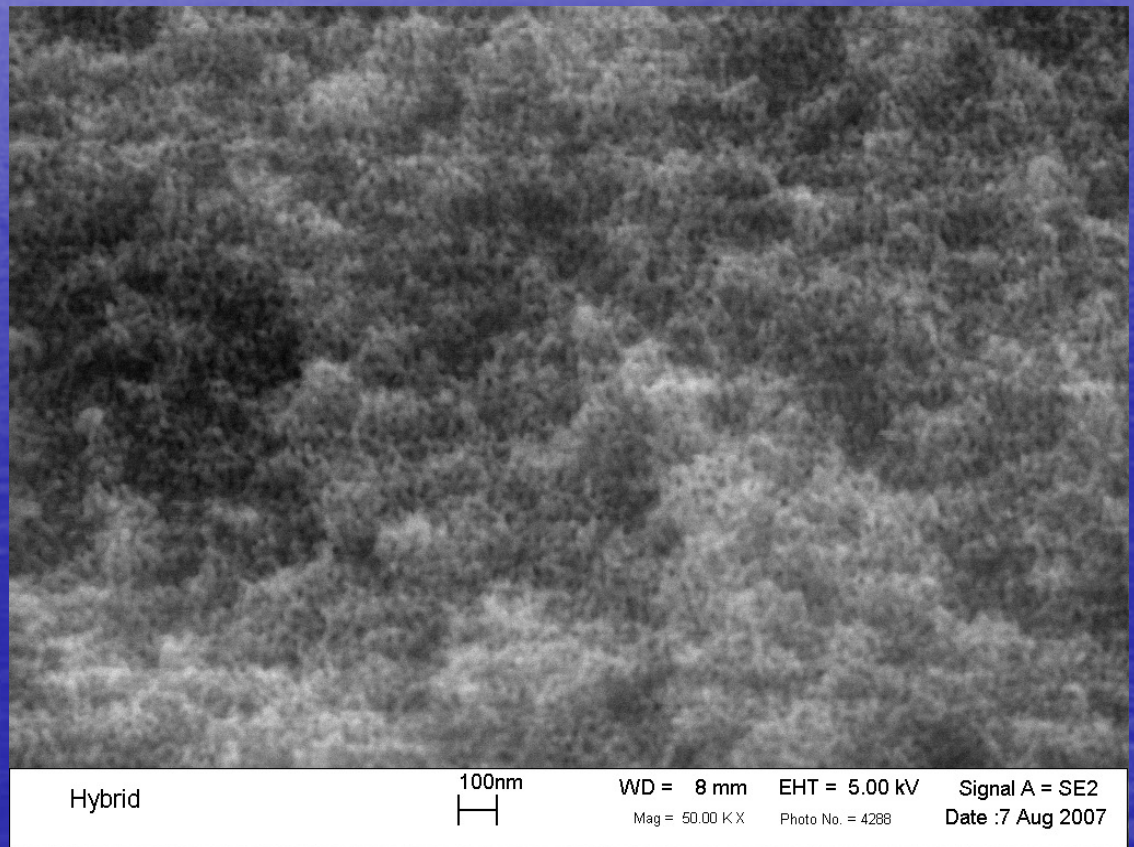
# Schematic of Open Air Gas Sensor Testing System



# Optical and SEM micrograph of the stochastic porosity ordered hole fiber



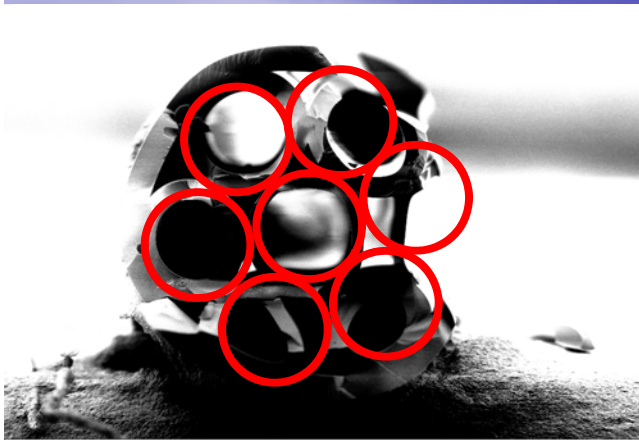
Optical micrograph of the ordered hole fiber



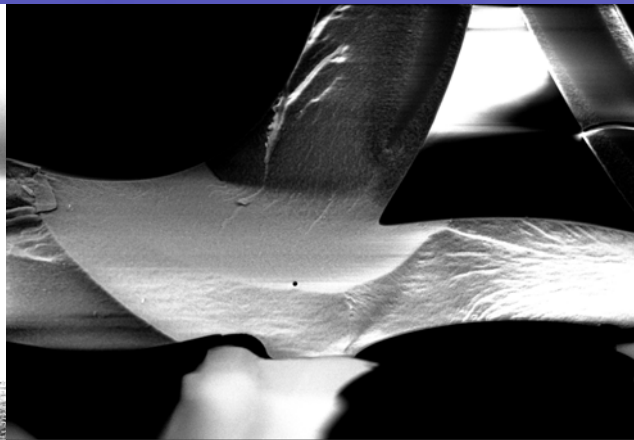
Porosity in ring structure of the stochastic porosity ordered hole fiber



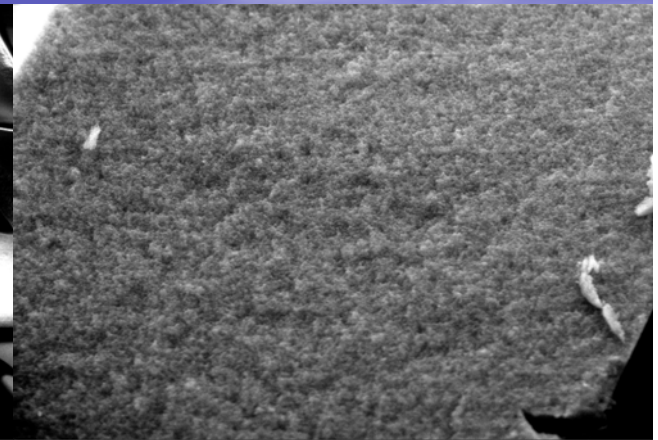
# SEM Analysis of Stochastic Porosity Ordered Hole Fiber



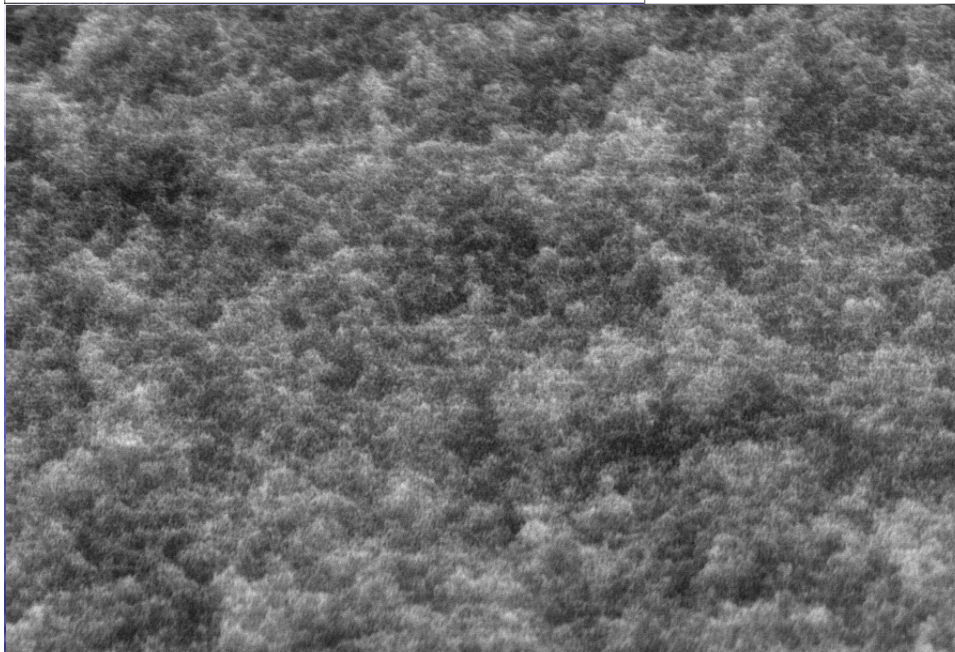
Hybrid 100µm WD = 7 mm EHT = 5.00 kV Signal A = SE2  
Mag = 500 X Photo No. = 4284 Date :7 Aug 2007



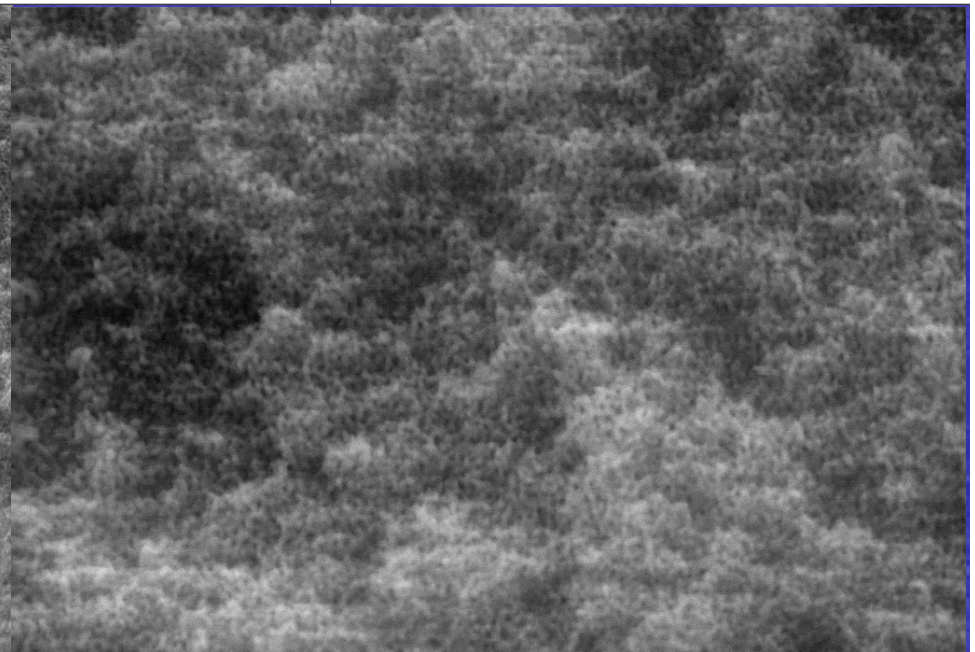
Hybrid 10µm WD = 7 mm EHT = 5.00 kV Signal A = SE2  
Mag = 1.50 K X Photo No. = 4285 Date :7 Aug 2007



Hybrid 1µm WD = 8 mm EHT = 5.00 kV Signal A = SE2  
Mag = 5.00 K X Photo No. = 4286 Date :7 Aug 2007



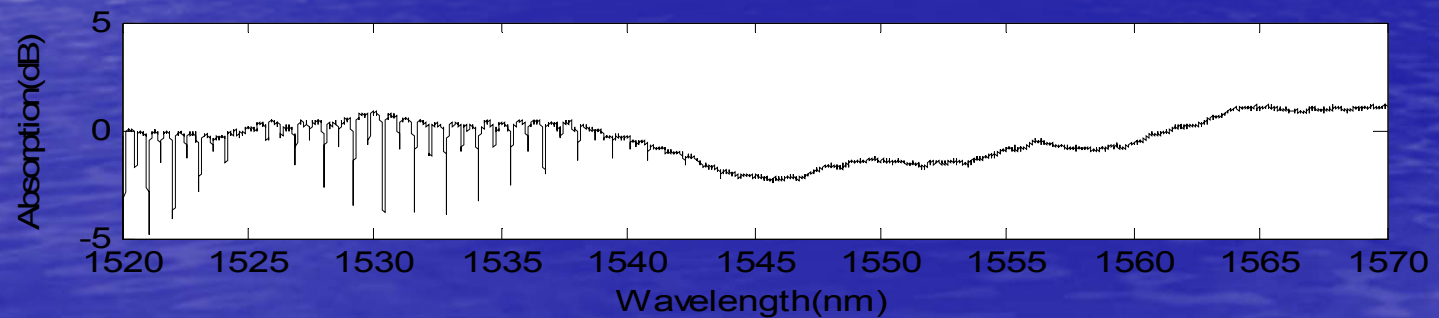
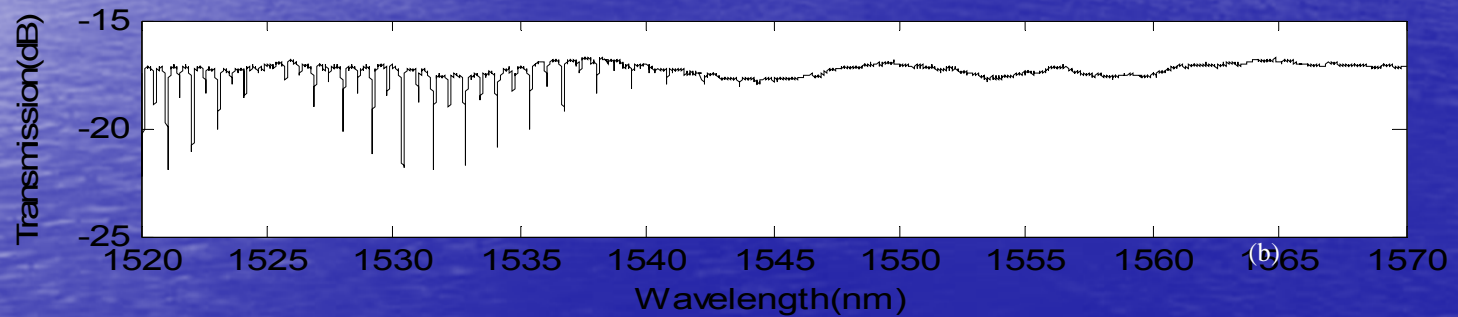
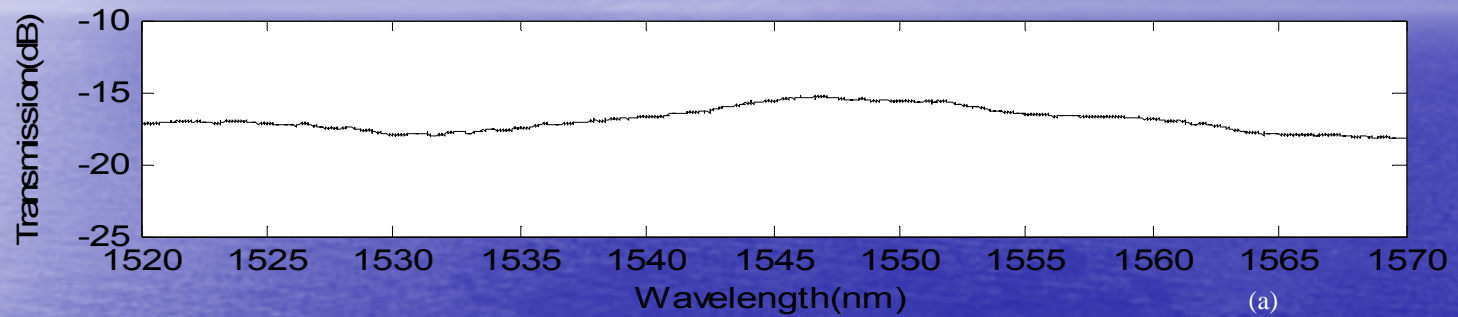
Hybrid 1µm WD = 8 mm EHT = 5.00 kV Signal A = SE2  
Mag = 20.00 K X Photo No. = 4287 Date :7 Aug 2007



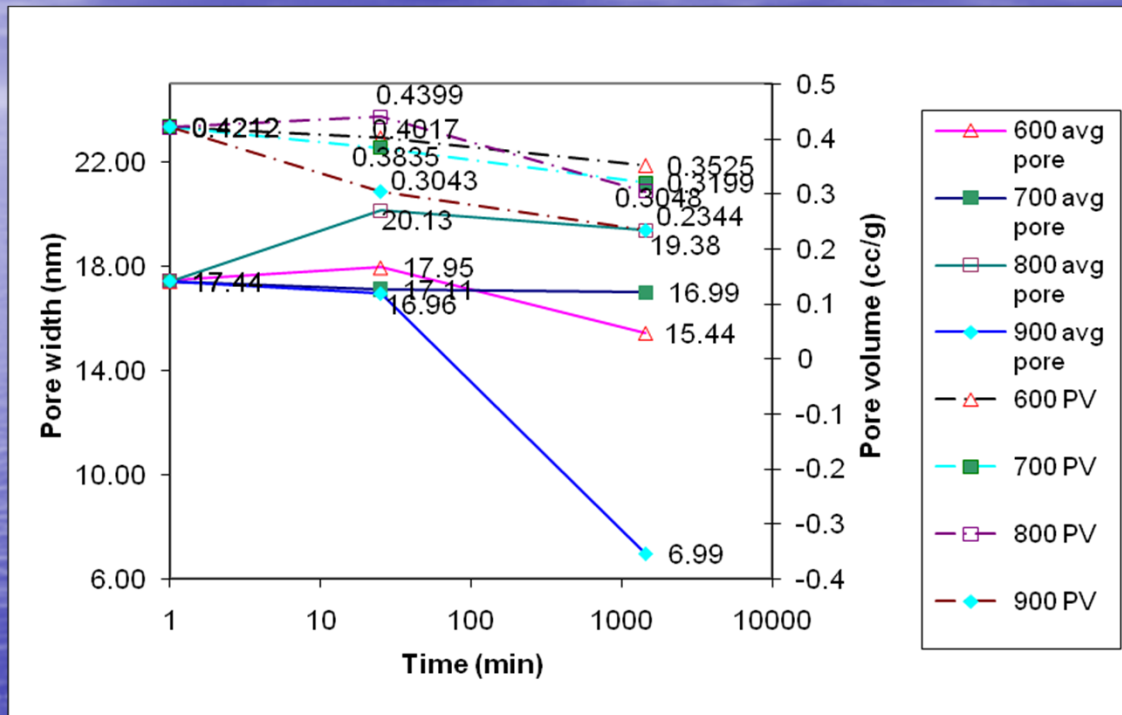
Hybrid 100nm WD = 8 mm EHT = 5.00 kV Signal A = SE2  
Mag = 50.00 K X Photo No. = 4288 Date :7 Aug 2007

# Results

## Ordered hole fiber sensor data

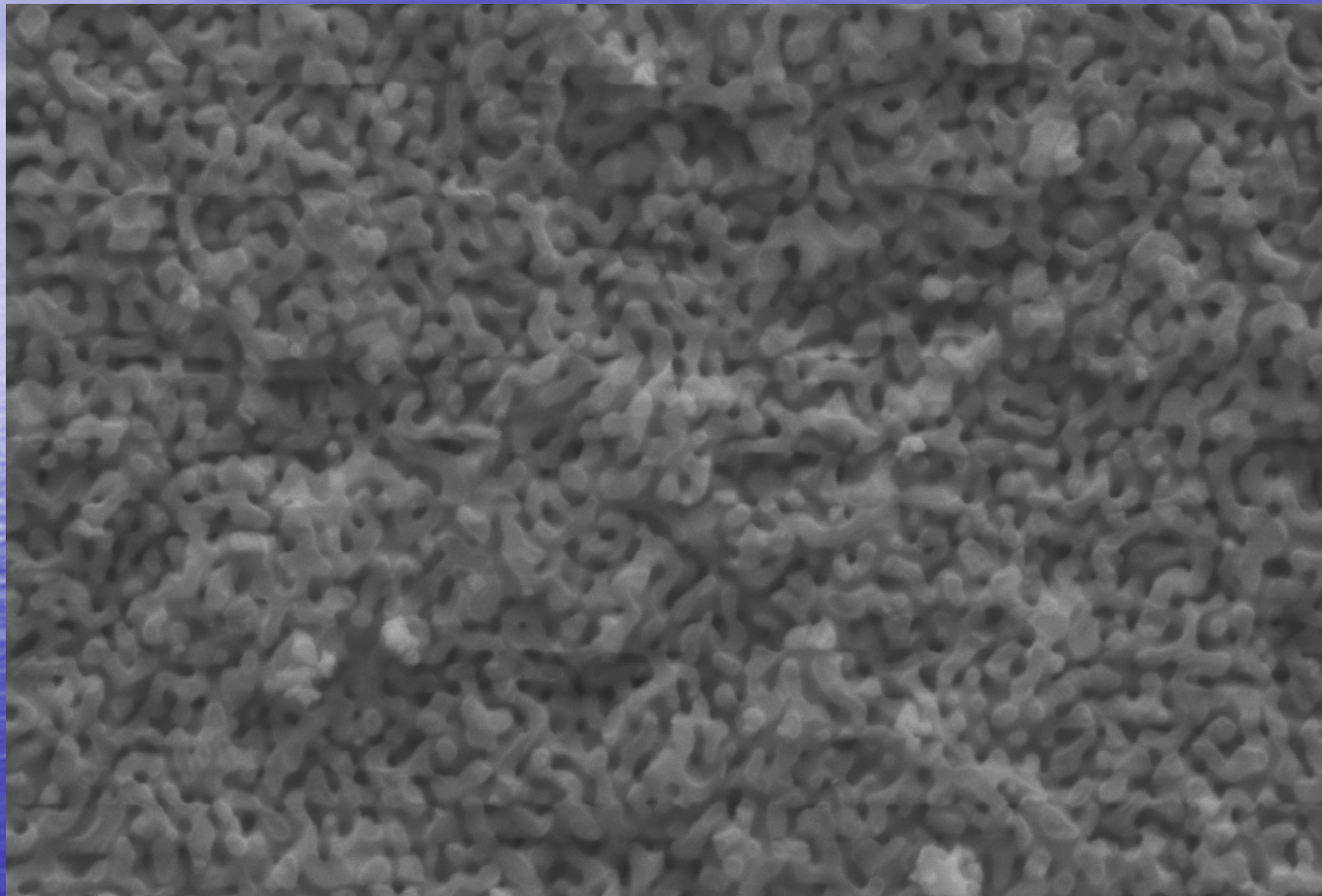


# Pore Morphology Changes as a Function of Temperature



Determination of the gas sensing capability at high temperatures is ongoing.

# Increased Pore Size through Special Processing Conditions



3-D Solid  
Phase

With

3-D Porous  
Phase

CVD 4

200nm  
┌───┐  
└───┘

WD = 11 mm  
Mag = 30.00 K X

EHT = 5.00 kV  
Photo No. = 1105

Signal A = SE2  
Date :8 Mar 2007

# Response Time Improvement

The response time of the fiber on the order of a second. This is an improvement of approximately 1000-10,000 times when compared to random hole or ordered hole fibers published data.

# Current Project

- Project Authorization Number issued January, 2012
- Two main thrust areas
  - 3-D Nanoporous Silica Fiber
  - Sapphire Photonic Crystal Fiber

Subtask	Work Schedule											
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
4.1 Sapphire Photonic Crystal Fiber Fabrication	_____											
<b>M1: Fabrication of SPCF</b>	_____ Δ											
4.2 Modeling of the Sapphire Photonic Crystal Fiber Optical Properties	_____											
4.3 Fabrication of the Optimized Sapphire Photonic Crystal Fiber Structures	_____											
4.4 Development of Long Wavelength Fiber Interrogation Instrumentation	_____											
<b>M3: Long Wavelength Instrumentation Development</b>	_____ Δ											
4.5 Optical Property Testing and Characterization of the Sapphire Photonic Crystal Fibers	_____											
4.6 Testing of the Sapphire Photonic Crystal Fiber Gas Sensing Capabilities	_____											
<b>M5: SPFC gas sensing test</b>	_____ Δ											
5.5. Development of suitable joining technologies between the sensor and the standard lead-in/lead-out fibers	_____											
<b>M2: Development of porous glass fiber joining technologies</b>	_____ Δ											
5.6 Sensor system sensitivity improvement	_____											
5.7 Signal processing improvement	_____											
5.8 Investigation of pore size and fiber geometry on the observed optical properties	_____											
<b>M4: Characterization of Pore structure/optical property relationship</b>	_____ Δ											
5.9.1 Development of optical fiber sensor packaging methods	_____											
5.9.2 Prototype fabrication for laboratory testing	_____											
<b>M6: Prototype porous glass fiber sensor fabrication</b>	_____ Δ											
Final Report Preparation	_____											
Technical Progress Report	Q	Q	Q	A	Q	Q	Q	A	Q	Q	Q	F

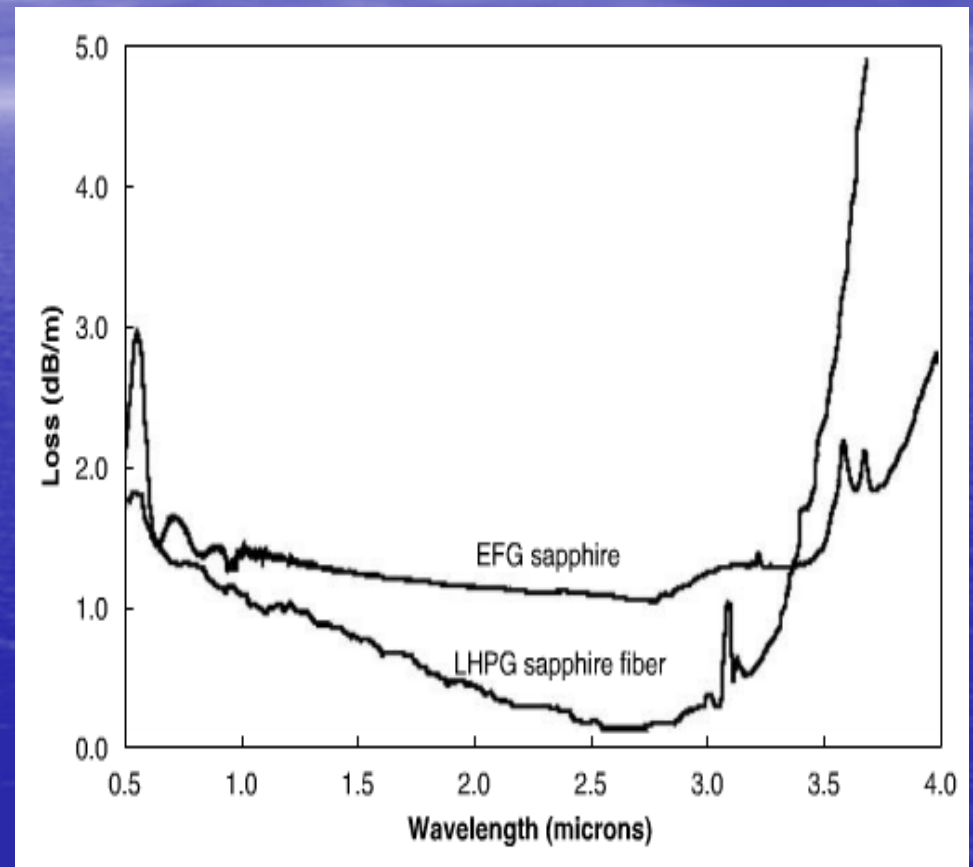
# Sapphire Photonic Crystal Fiber Development

- Currently working on development of sapphire photonic crystal fibers
  - Fabrication
  - Modeling
  - Testing



# Background

- Single Crystal Sapphire ( $\alpha\text{-Al}_2\text{O}_3$ )
  - Continuous crystal lattice
    - Hexagonal structure
    - No grain boundaries
    - Grown on c-axis
  - Refractive index
    - 1.744 at  $1.693\mu\text{m}$  with a operation range from  $1.75 - 3.2\mu\text{m}$
  - Broad transmission window ( $0.19\mu\text{m}$  to  $5.2\mu\text{m}$ )
    - Loss minimum of  $0.13\text{dB/m}$  at  $2.94\mu\text{m}$
  - Resists corrosion in harsh, high-temperature environments
  - Can transmit at infrared wavelengths

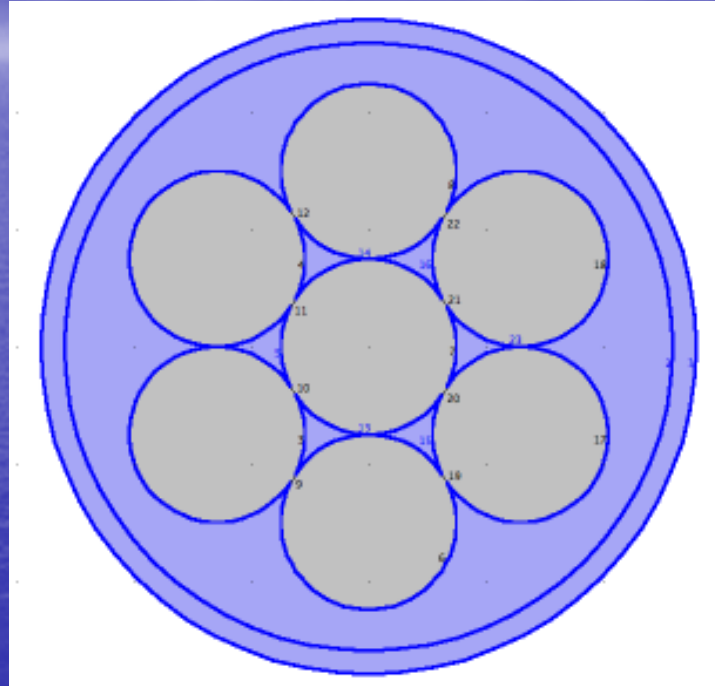


*Loss transmission of EFG vs. LHPG growth methods for single crystal sapphire from J. J. Fitzgibbon, H. E. Bates, A. P. Pryshlak, and J. R. Dugan, "Sapphire optical fibers for the delivery of Erbium:YAG laser energy," in Biomedical Optoelectronic Instrumentation, A. Katzir, J. A. Harrington, and D. M. Harris, eds., SPIE 2396, 60-70 (1995).*

# Currently no commercially available high temperature cladding for sapphire

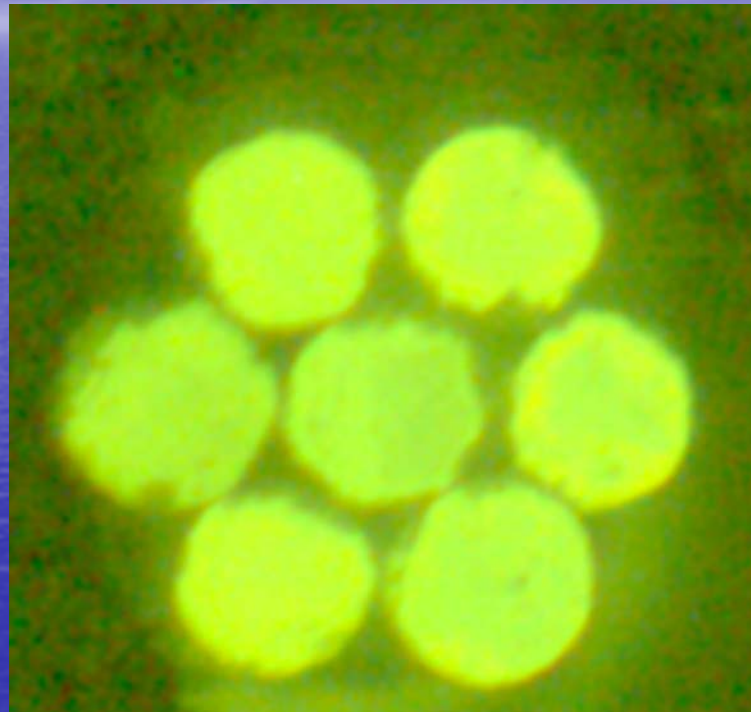
- Fiber Protection
  - Harsh environments
  - Mechanical stability
- Limit attenuation
  - Surface contamination
- Decrease effective refractive index difference
  - Reduction of modes in MMF
- Cladding for single mode operation
  - Sapphire high refractive index (1.744 at 1.693 $\mu\text{m}$ )

# Sapphire photonic crystal – wanted to make this structure



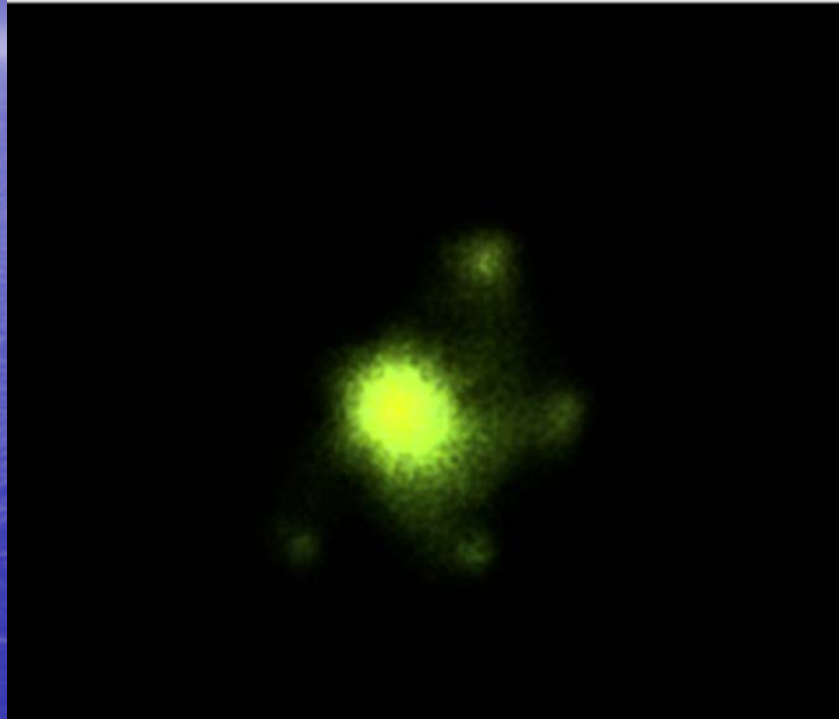
- 7-rod structure surrounding a single rod of single crystal sapphire. The air (blue) region is set to  $n = 1.0$  and sapphire (grey) ( $\alpha\text{-Al}_2\text{O}_3$ ) is set to  $n = 1.74618$
- First sapphire photonic crystal fiber produced
  - 70 $\mu\text{m}$  diameter single crystal sapphire rods that were 15cm in length (z-direction)

# Sapphire Photonic Crystal Fiber – after firing at 1600°C



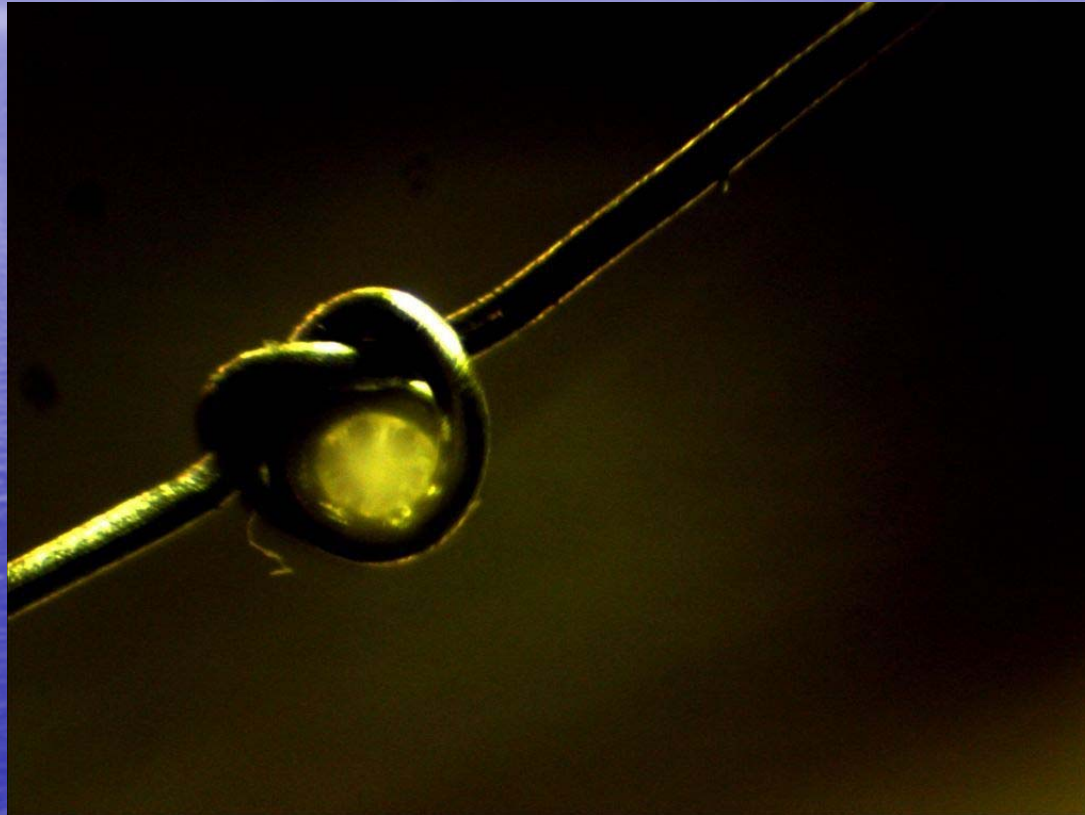
First Sapphire Photonic  
Crystal Fiber Produced

# Sapphire photonic crystal



Micrograph of transmitted light in the sapphire photonic crystal fiber structure under white light illumination from the backside of the fiber.

# Sapphire photonic crystal development



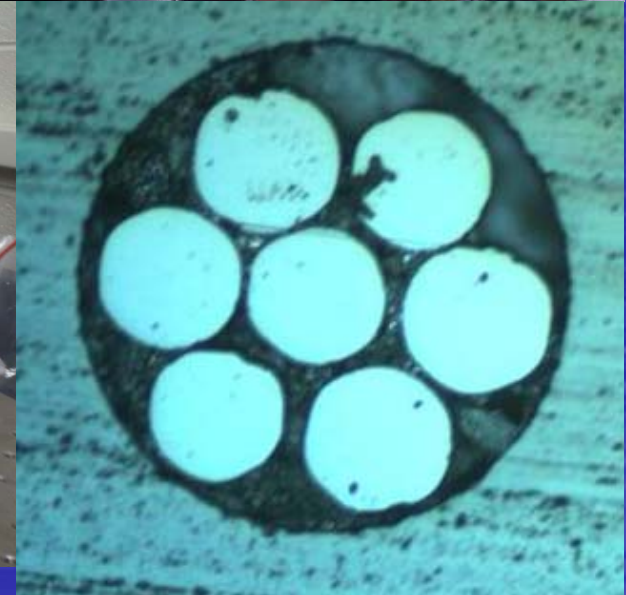
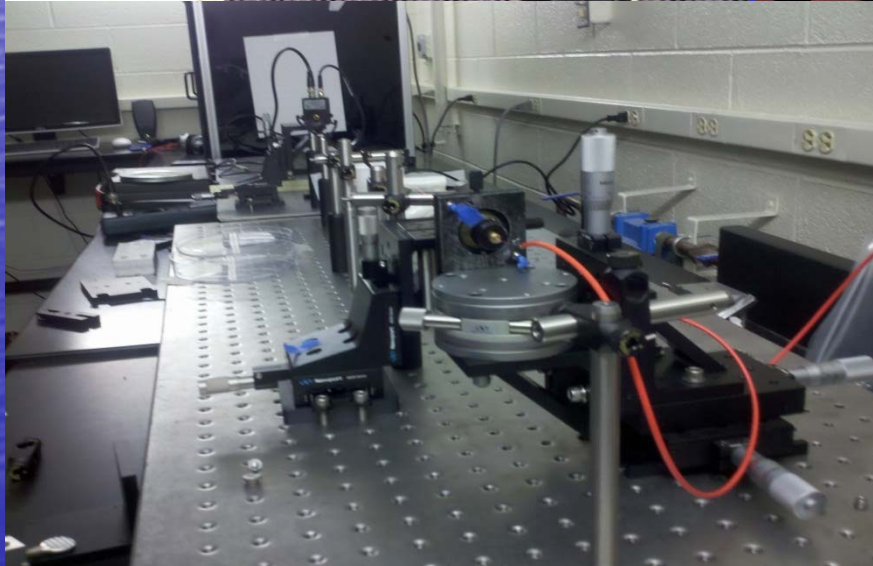
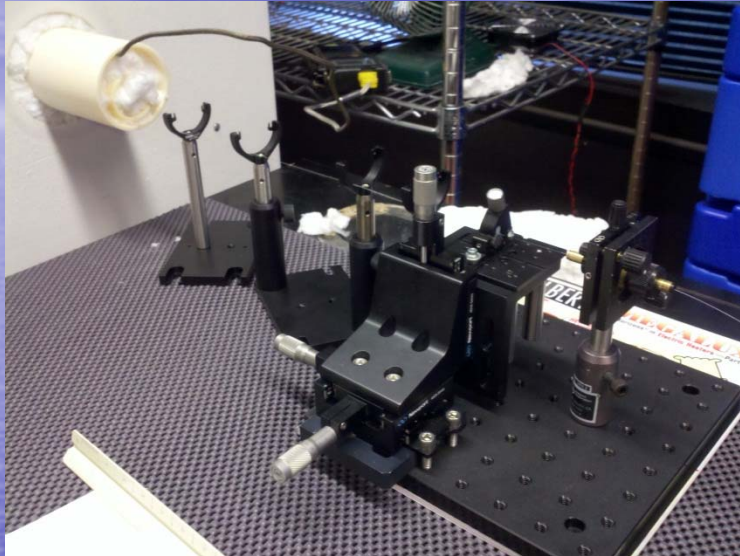
Sapphire Photonic Crystal Fiber tied by platinum wire.

# Sapphire Photonic Crystal Fiber Fabrication

- One of the newer sapphire photonic crystal fibers being polished

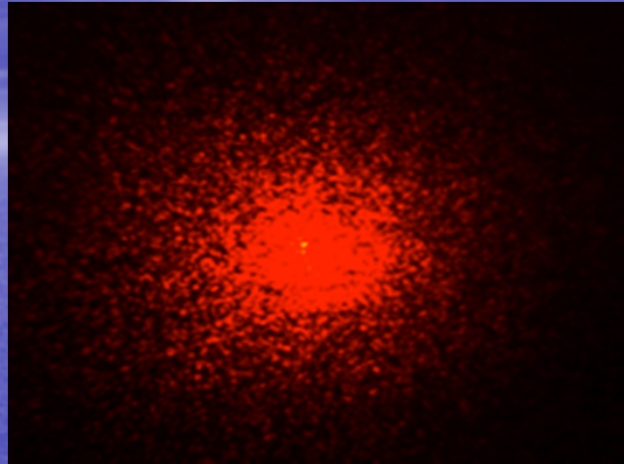


# Sapphire Photonic Crystal Fiber Testing

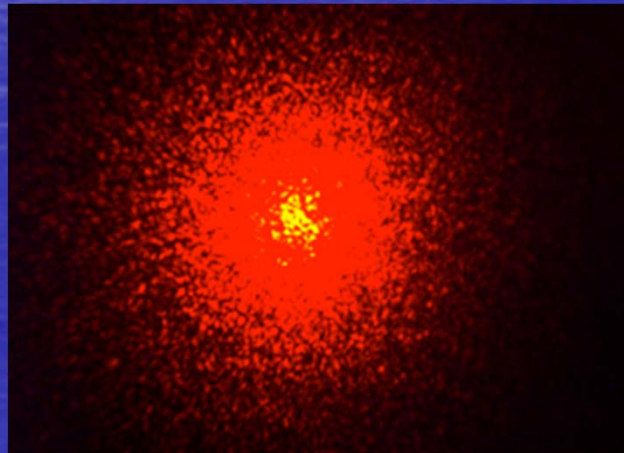




# Far Field Pattern Measurements



Far-field pattern for a single rod of single crystal sapphire.



Far-field pattern for the sapphire photonic crystal fiber.

# COMSOL Modeling

- Modeling of the modes in these fibers has begun with COMSOL Multiphysics 4.0a modeling software
- Modeling steps include:
  - Select materials
  - Physical Settings in RF Module
  - Meshing
  - Solving
  - Post-processing

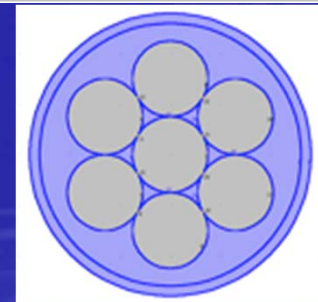
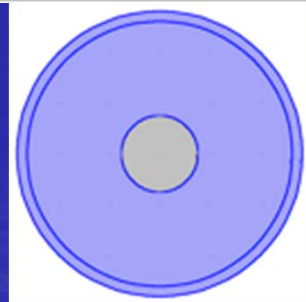
# COMSOL Modeling

- Air (blue region)  
n=1.0
- Sapphire ( $\alpha\text{-Al}_2\text{O}_3$  in grey region)  
n=1.74618
- All listed values with a free space wavelength =  $1.55\mu\text{m}$

Property	Name	Value	Unit	Property group
✓ Electric conductivity	sigma	0	S/m	Basic
✓ Relative permittivity	epsilon <sub>nr</sub>	1.000	1	Basic
✓ Relative permeability	mu <sub>r</sub>	1.000	1	Basic
nu <sub>0</sub>	nu <sub>0</sub>	nu <sub>0</sub> (T)		Basic
Density	rho	rho(pA,T)	kg/m <sup>3</sup>	Basic
Heat capacity at constant pressure	Cp	Cp(T)	J/(kg*K)	Basic
Speed of sound	c	cs(T)	m/s	Basic
Ratio of specific heats	gamma	1.4	1	Basic
Thermal conductivity	k	k(T)	W/(m*K)	Basic
Dynamic viscosity	mu	eta(T)	Pa*s	Basic
Refractive index	n	1.0	1	Refractive index
Refractive index, imaginary part	ki	0		Refractive index

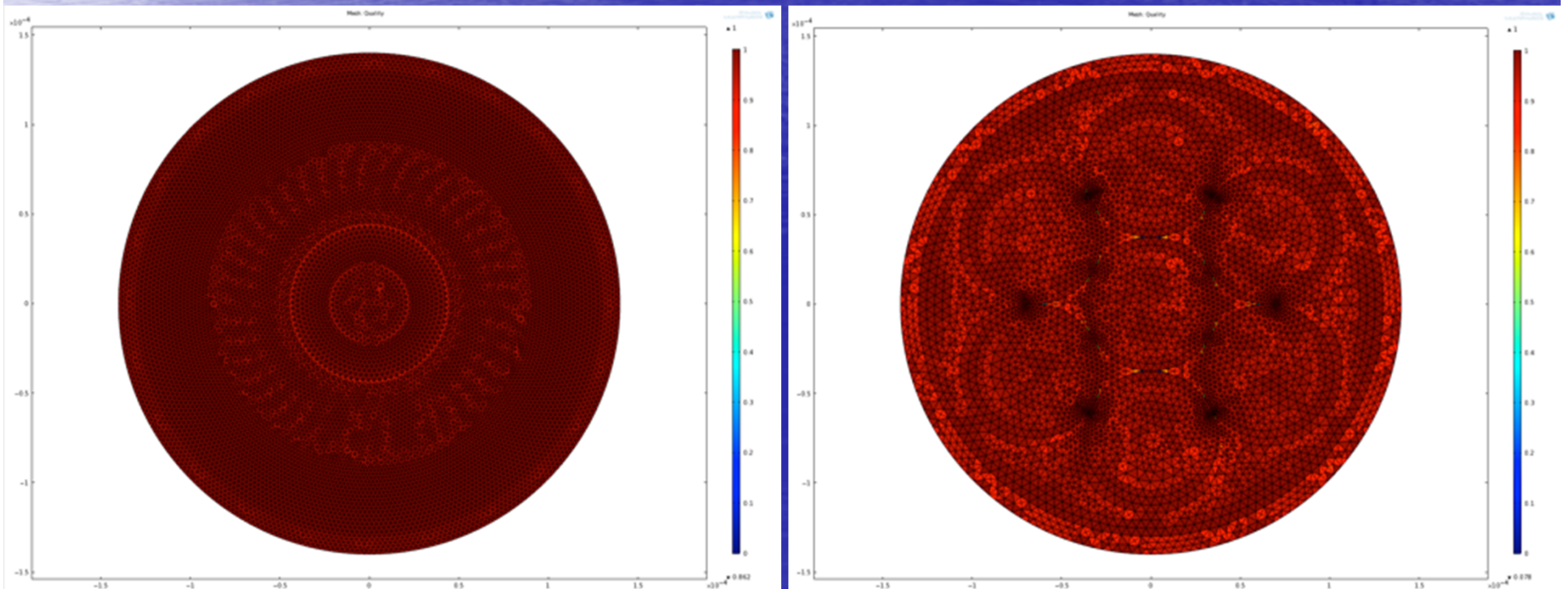
Property	Name	Value	Unit	Property group
Density	rho	3965	kg/m <sup>3</sup>	Basic
Coefficient of thermal expansion	alpha	6.5e-6	1/K	Basic
Heat capacity at constant pressure	Cp	730	J/(kg*K)	Basic
Relative permittivity	epsilon <sub>nr</sub>	5.7	1	Basic
Electric conductivity	sigma	0	S/m	Basic
Thermal conductivity	k	35	W/(m*K)	Basic
Young's modulus	E	400e9	Pa	Young's modulus and Poisson's ratio
Poisson's ratio	nu	0.22	1	Young's modulus and Poisson's ratio
Refractive index	n	1.74618	1	Refractive index
Refractive index, imaginary part	ki	0		Refractive index



# Preliminary Work

## Comsol modeling

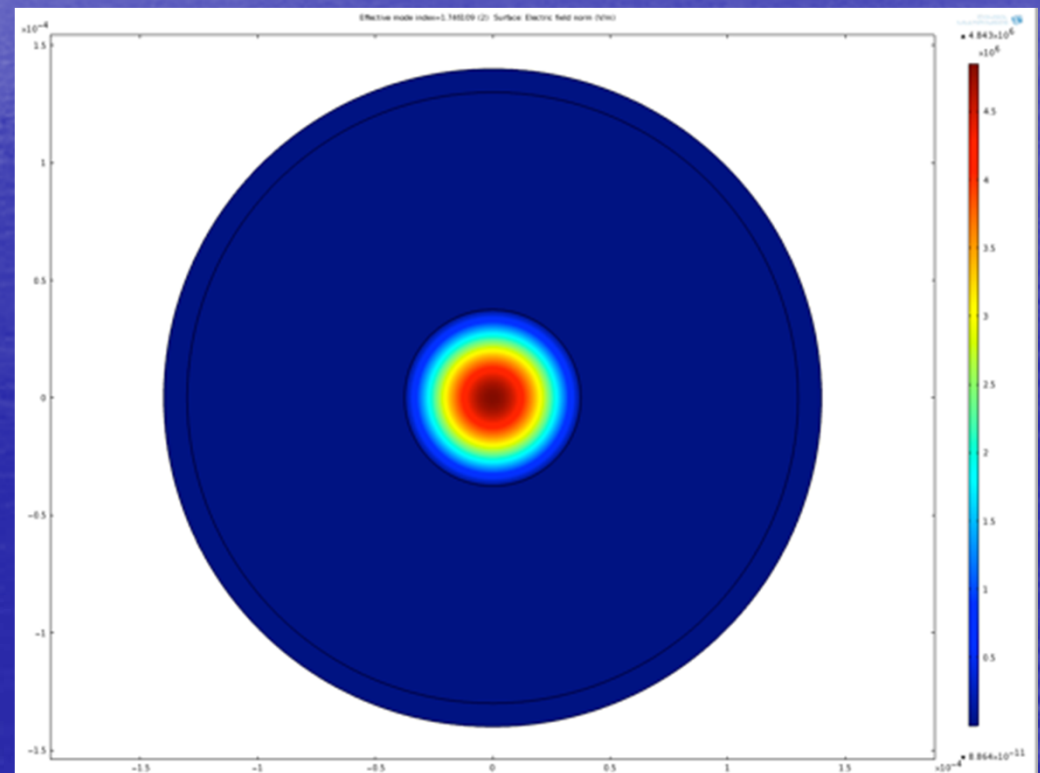
- Precision related to refinement of the mesh
- Limitation of the mesh is the memory of the computer that will be solving the boundary equations



# Preliminary Work

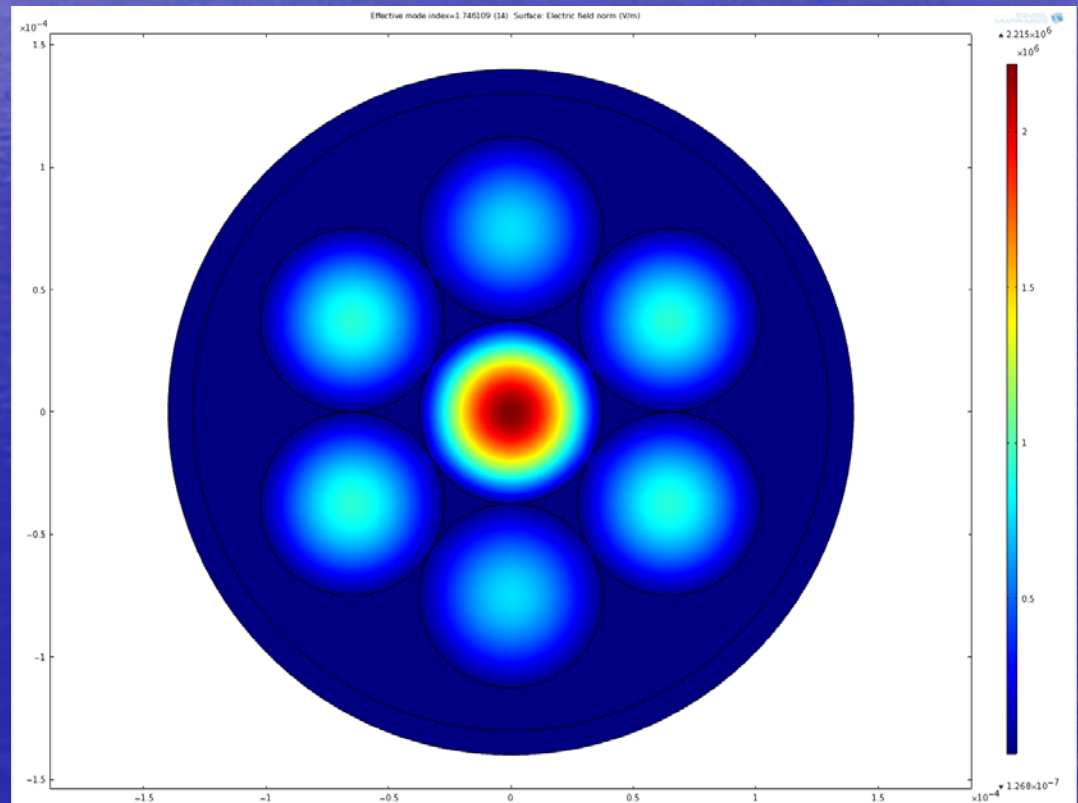
## Comsol modeling

- Single rod Sapphire Photonic Crystal Fiber
- Highly multimode
- The resultant lowest order fundamental hybrid linearly polarized mode ( $LP_{01}$ ) is shown at right at 1550nm with an effective mode index = 1.746109
- Confinement Loss  $L_c = 2.0166e-8$  dB/km



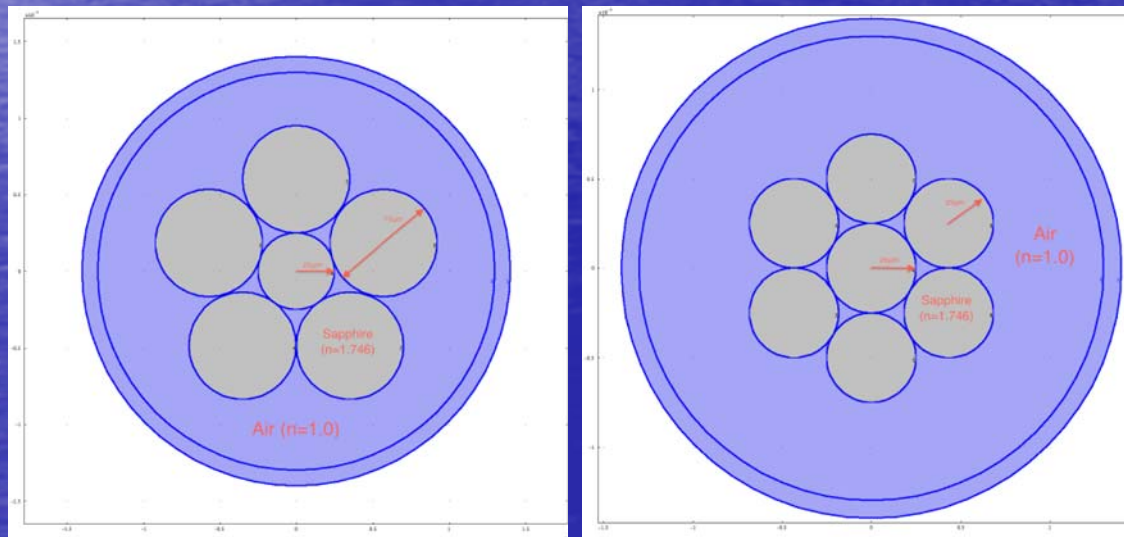
# Preliminary Work Comsol modeling

- Six ring Sapphire Photonic Crystal Fiber
- Highly multimode
- The resultant lowest order fundamental hybrid linearly polarized mode ( $LP_{01}$ ) is shown at right at 1550nm with an effective mode index = 1.746109
- Confinement Loss  $L_c = 1.3933e-6$  dB/km



# COMSOL Modeling

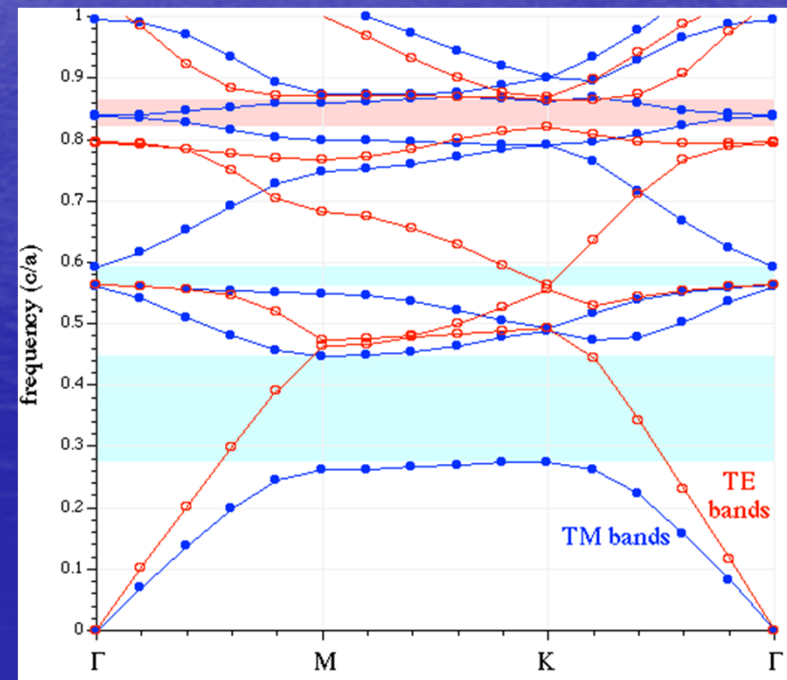
- Investigating additional methods for increased modal reduction
  - 1. 50 $\mu\text{m}$  core surrounded by 5 70 $\mu\text{m}$  rods of single crystal sapphire fiber (left).
  - 2. 50 $\mu\text{m}$  core rod of single crystal sapphire surrounded by 6 50 $\mu\text{m}$  diameter single crystal fibers bundled in a hexagonal arrangement (right).



# MPB Modeling

## MIT Photonic Bands Program

- Compute the eigenvalues of Maxwell's equations for plane waves in the frequency domain
- Predict the feasibility of creating a photonic band gap within the holey single crystal sapphire fiber







Thanks for Listening