# Development of Novel Ceramic Nanofilm-Fiber Integrated Optical Sensors for Rapid Detection of Coal Derived Synthesis Gas

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**Project Duration:** 04/01/2009 – 03/31/2012

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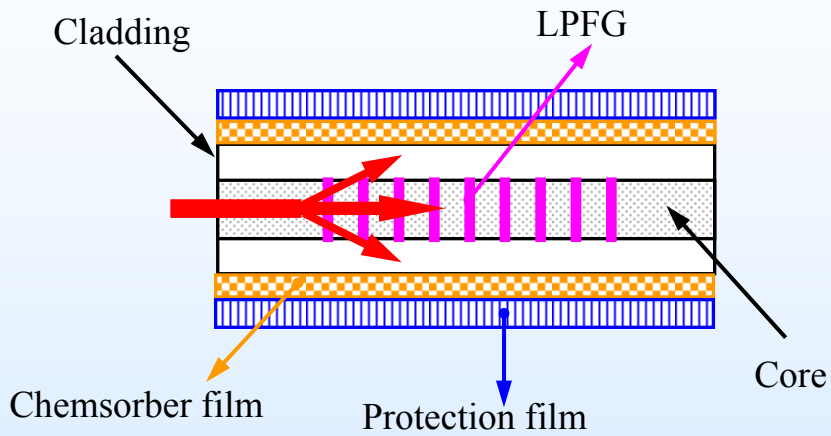
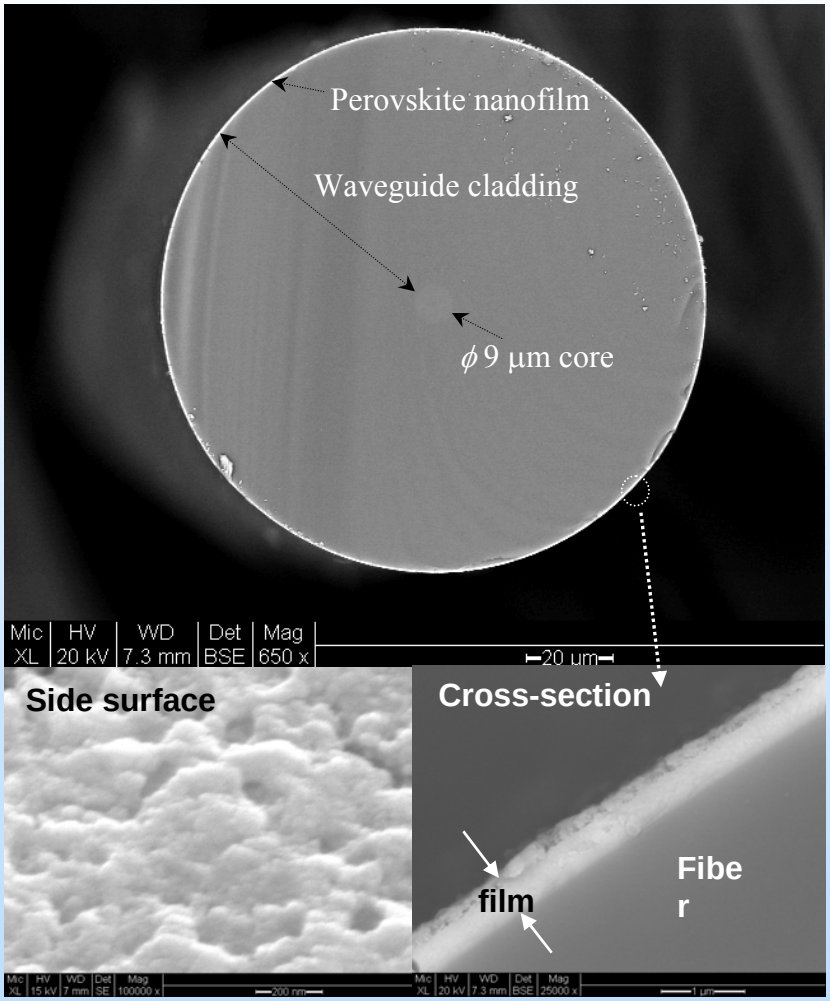
**National Energy Technology Laboratory, U.S. Department of Energy**

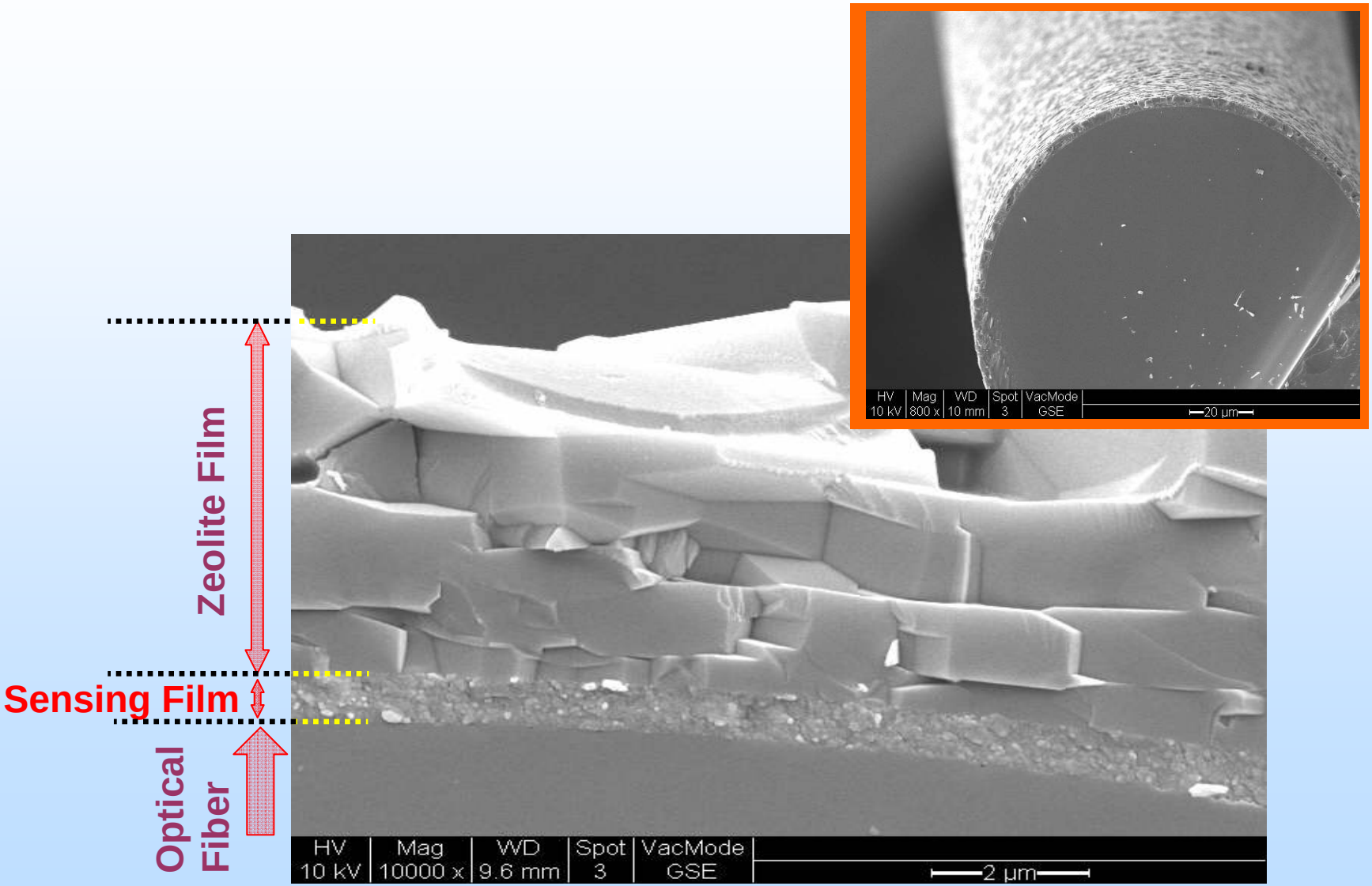
# Ceramic Thin Film Coated High Temperature Fiber Optic Gas Sensors




- **Nanocrystalline doped ceramic coated <u>long period fiber grating</u> (LPFG)**
  - **Device:** resonance wavelength of LPFG is very sensitive to environmental refractive index change
  - **Mechanism:** chemical sorption induced refractive index changes ($\Delta n$) of the coated ceramic thin film
  - **Detection:** Shift in the resonance wavelength ($\Delta\lambda$) of LPFG

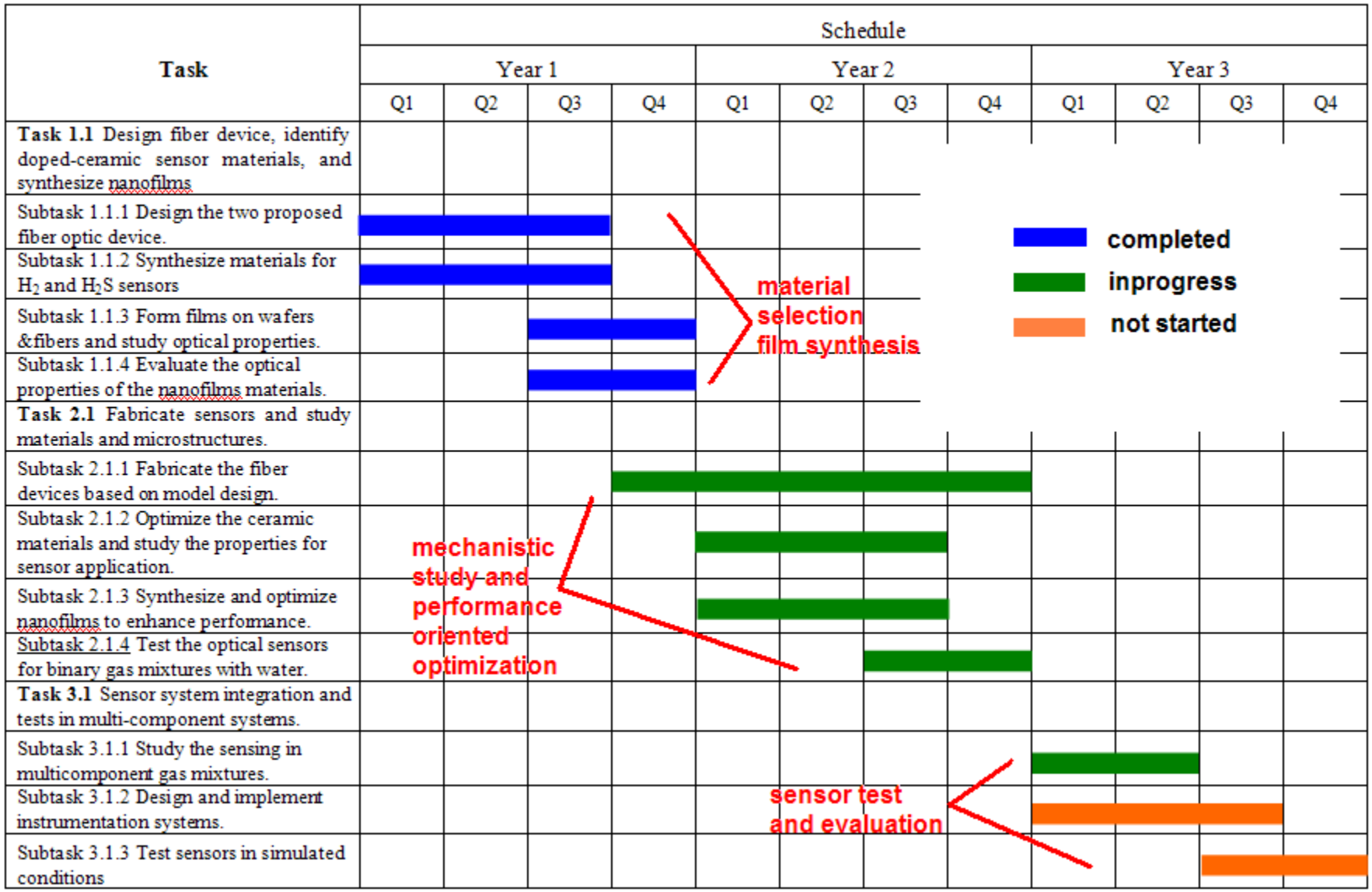
# Architecture of the Silicalite-Protected SCZY-LPFG Hydrogen-Sensor



# Project Objective

- To develop ceramic nanofilm-intergrated fiber optic sensors (FOS) for high temperature (>500 $^{o}$C) monitoring of coal-derived syngas
  - Investigate and demonstrate two new types of nanocrystalline doped-ceramic coated FOS
    - LPFG-coupled self-compensating interferometer sensor
    - second type evanescent tunneling sensor
  - Sensor fabrication and evaluation
    - Proton electron/hole conducting solid oxides for $H_2$ sensing and tin and zinc oxides based materials for $H_2S$
    - Fabrication of sensing material with fiber to construct FOS
    - Demonstrate sensors in binary and multicomponent mixtures (>500 $^{o}$C and up to 250 psi)

# Project Tasks, Timelines, and Status



# Material Identification

- **For $H_2$ sensors**
  - Proton-conducting Perovskite ceramics:
    - Cerate-based $SrCe_{0.95}Tb_{0.05}O_{3-\delta}$ (**SCTb**)
    - Zirconate-based $SrZr_{0.95}Y_{0.05}O_{3-\delta}$ (**SZY**)
    - Cerate-Zirconate solution based $SrCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (**SCZY**)
- **For $H_2S$ sensors**
  - Tin oxide ($SnO_2$)
  - Proton-conducting perovskite (SCTb)
- **For CO sensors**
  - Stabilized zirconia ($Zr_{0.84}Y_{0.16}O_{1.92-\delta}$, YSZ)
  - Cu-doped zirconia ($Zr_{1-x}Cu_xO_{2-x-\delta}$, CDZ)

# Ceramic Thin Film Coating on Fibers

- **Requirements for fabrication process**
  - Density, microstructure, interface for optical function
  - Fabrication temperature < 800°C (fiber stability limit)
  - Fast response – nanocrystalline structure
- **The polymeric precursor route:**

**STEP 1**
Polymeric precursor synthesis: $Sr^{2+}/Zr^{4+}/Ce^{4+}/Y^{3+}$ PEG chelate by acid catalyzed polymerization

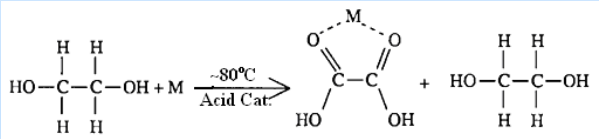
→

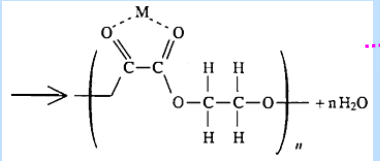
**STEP 2**
Precursor film coating: Brush-coating polymeric precursor film on LPFG surface and drying

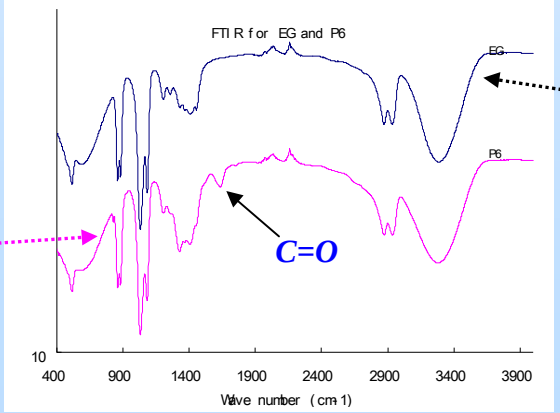
→

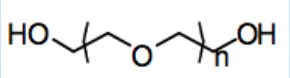
**STEP 3**
CDZ nanocrystalline film: conversion of precursor film to solid oxide film by firing/annealing

**M = Sr, Zr, Ce, Y**



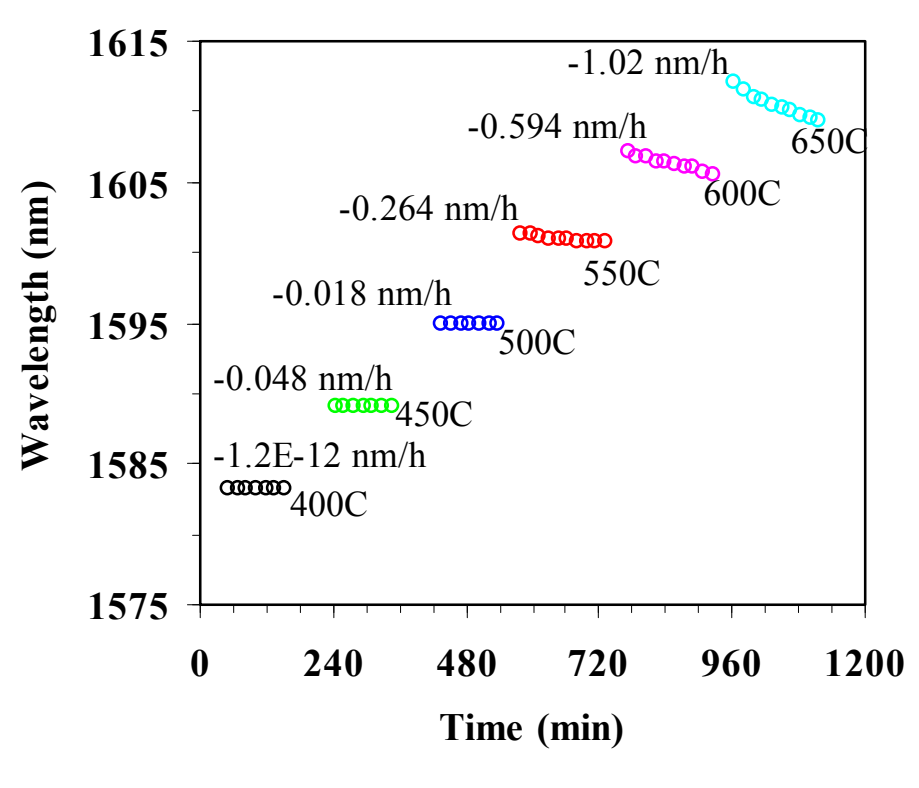



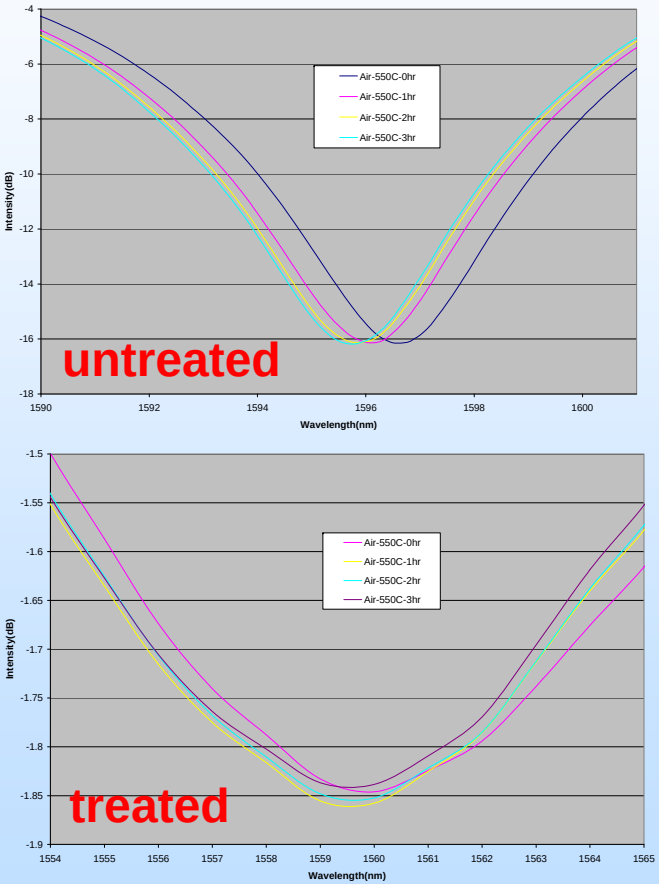



# The Fabrication and Application Temperature

- The $\lambda_R$ thermal drift – minimal at <550°C




- Microstructure stabilization – grains growth inhibition




Thermal drift before and after 30 min treatment at 750°C

# 1. Proton Conducting Perovskite Oxides As $H_2$ sensing Materials

***Switch between $O_2$ and $H_2$***

**In oxygen:** $V_O^{\bullet\bullet} + \frac{1}{2}O_2 \xleftrightarrow{k_1} O_O^X + 2h^\bullet$

**In hydrogen:** $H_2 + 2h^\bullet + O_O^X \xleftrightarrow{k_2} 2OH^\bullet$

$$[h^\bullet] = \sqrt{k_1} P_{O2}^{1/4} [V_O^{\bullet\bullet}]^{1/2} [O_O^X]^{-1/2}$$

***Dependence on $H_2$ partial pressure:***

$$H_2 + 2O_O^X \xleftrightarrow{k_3} 2OH^\bullet + 2e^-$$

$$[OH^\bullet]n = \sqrt{k_3} P_{H2}^{1/2} [O_O^X]$$

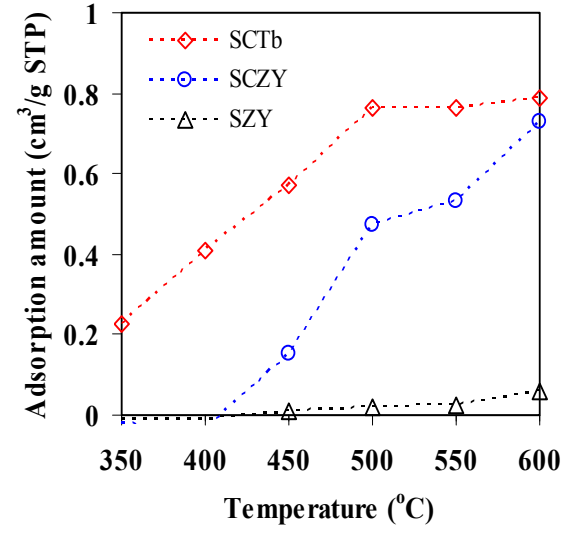
***Interferences:***

**CH4, CO...** $O_O^X \xrightarrow{\text{Red.}} \frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e^-$

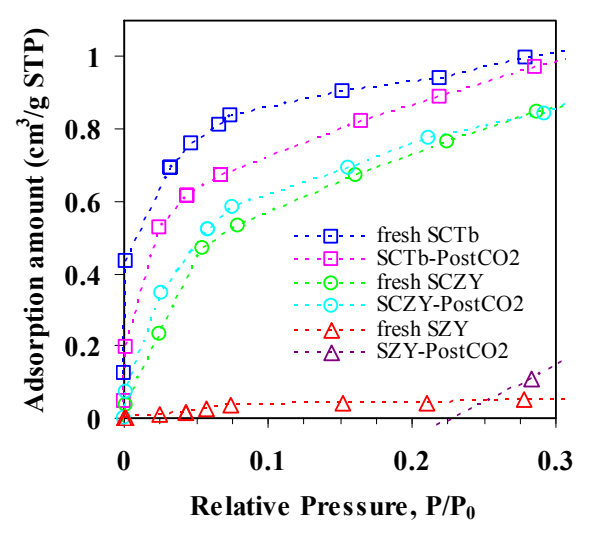
**Water** $H_2O + V_O^{\bullet\bullet} + O_O^X \longleftrightarrow 2OH^\bullet$

**Hydrogen sulfide** $H_2S + V_O^{\bullet\bullet} + 2O_O^X \longleftrightarrow 2OH^\bullet + S_{(S)}$

- **$H_2$ uptake: SCTb > SCZY > SZY**

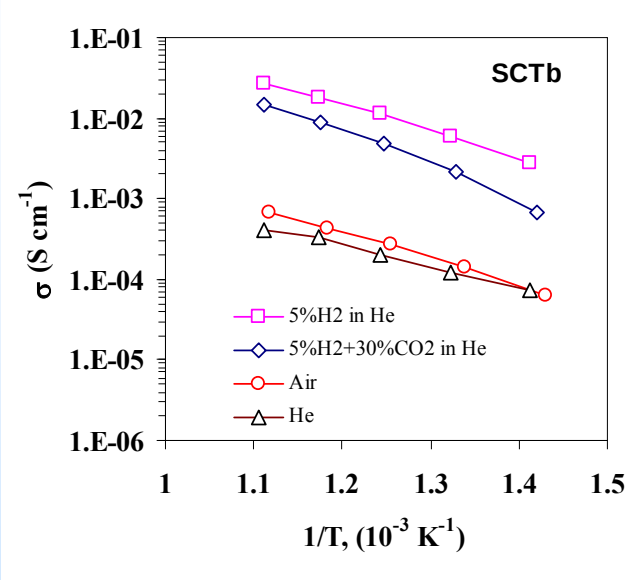


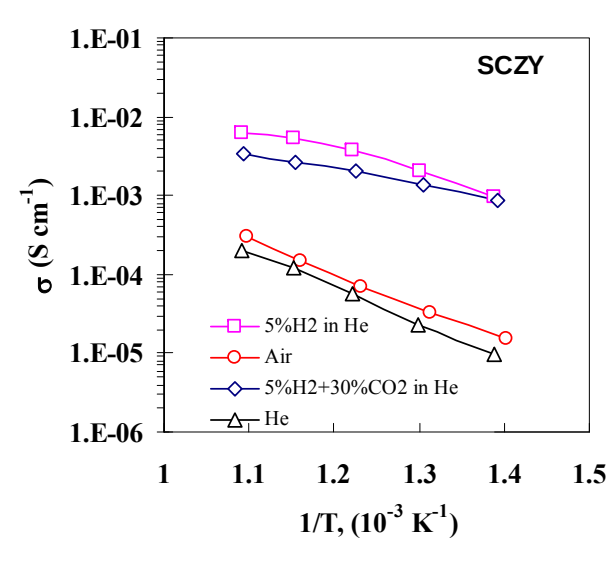

- **$CO_2$ tolerance: SZY > SCZY > SCTb**

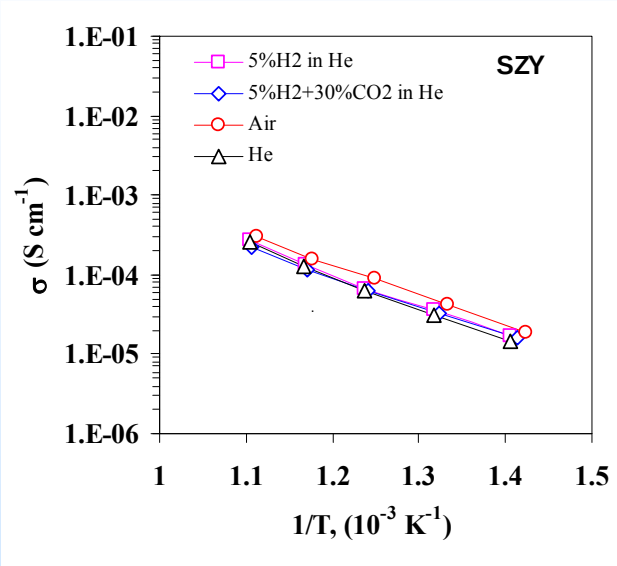


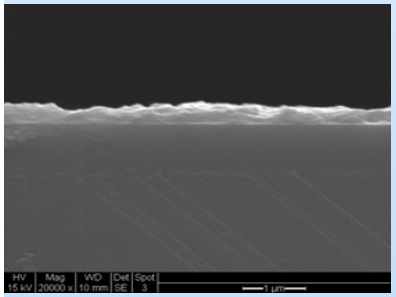
# Proton Conducting Perovskite Oxides As $H_2$ sensing Materials

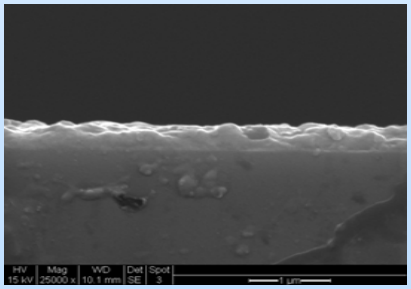
- **Electrical conductivity (sapphire supported films)**

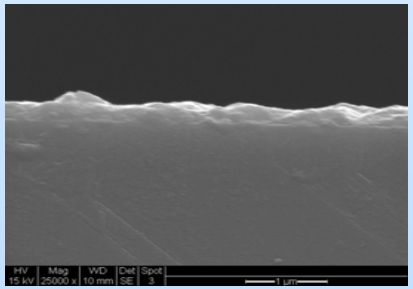


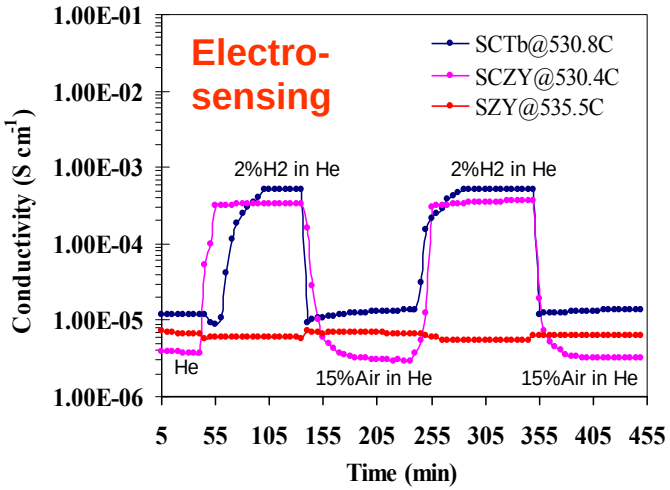





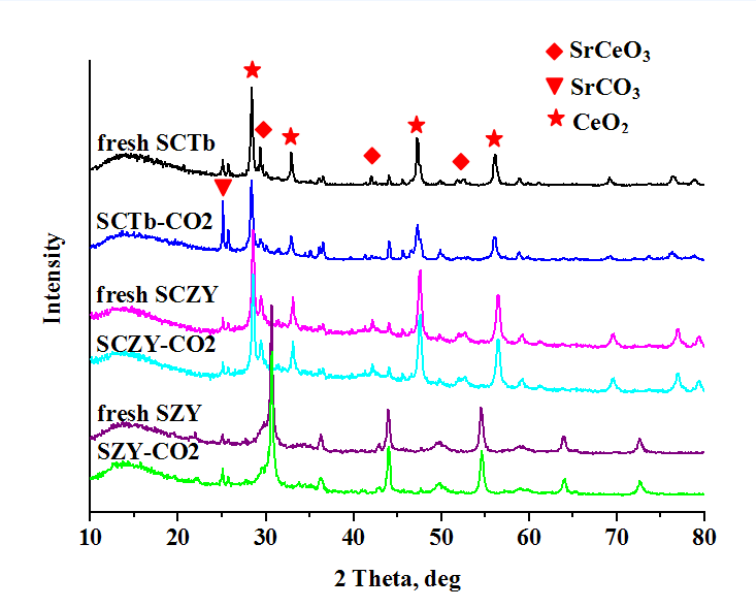




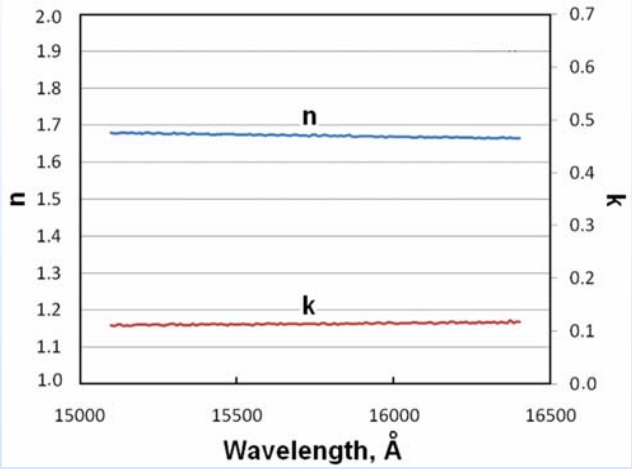

- **$CO_2$ tolerance: SZY > SCZY > SCTb**
- **Conductivity: SCTb > SCZY > SZY**

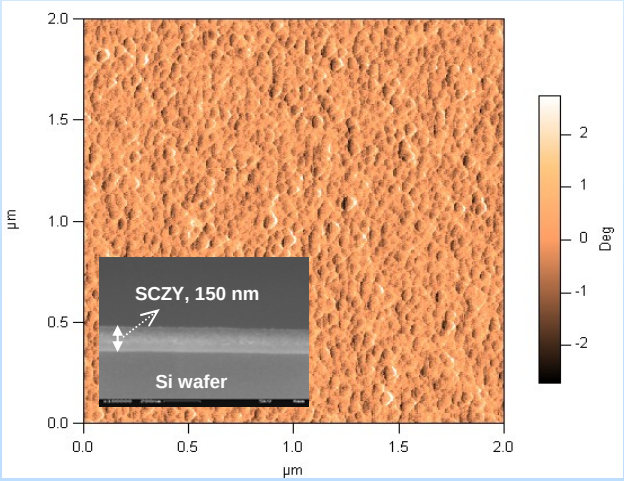
# Cause of Instability in $CO_2$

- **Formation of carbonate (3 h in 1:1 $CO_2/N_2$)**



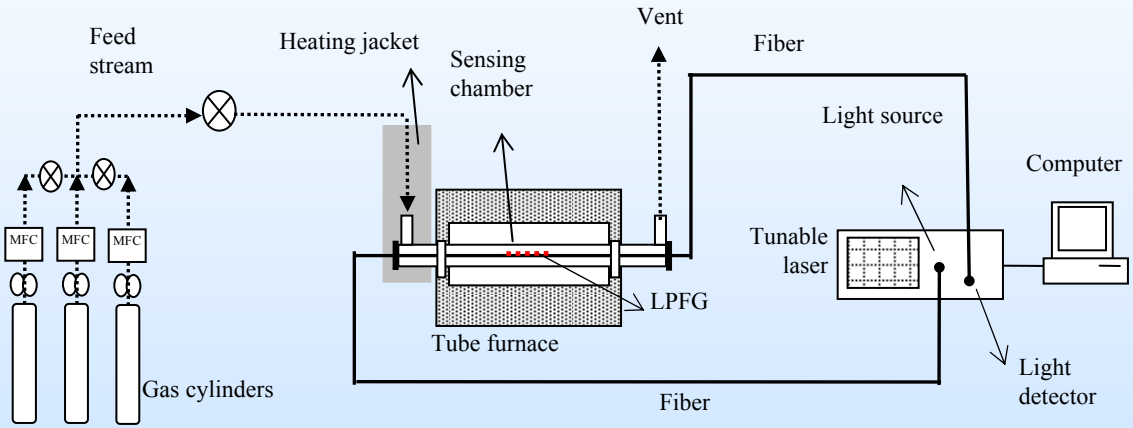

- **Film refractive index (e.g. SCZY)**

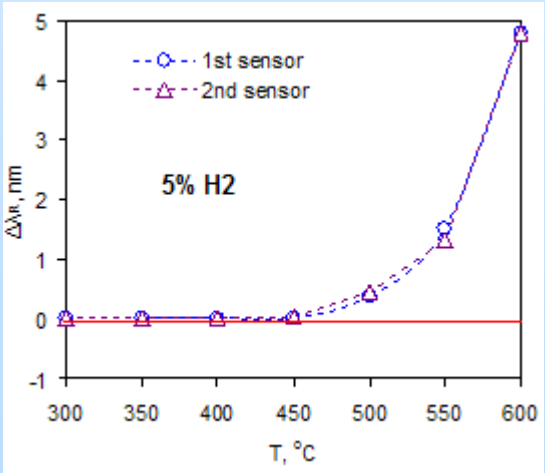


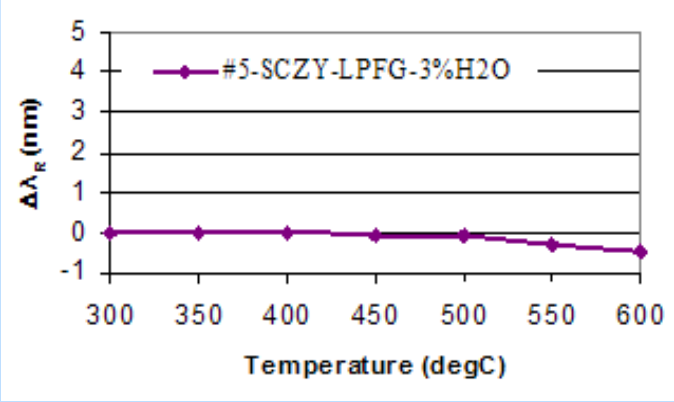



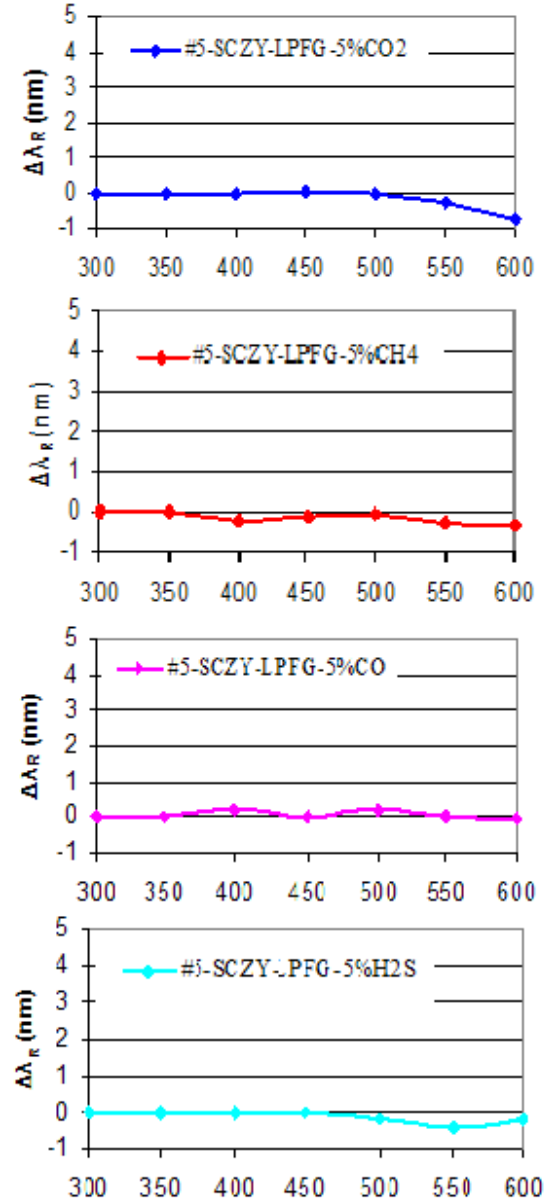
# Selectivity/Sensitivity vs. Temperature

**SCZY: reasonable $H_2$ sensitivity with negligible interferences from other gases at 500°C**



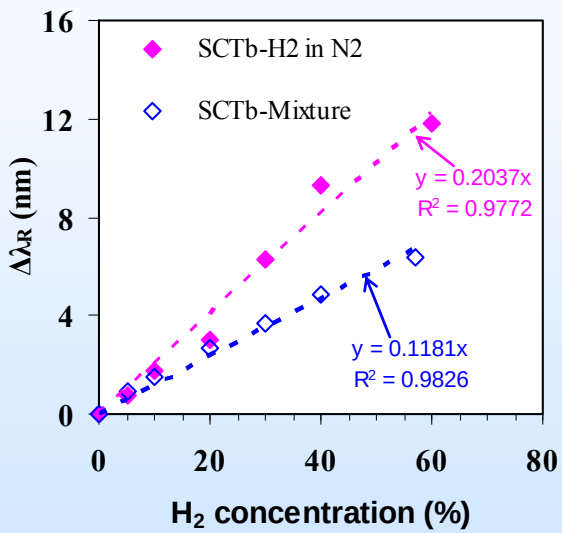



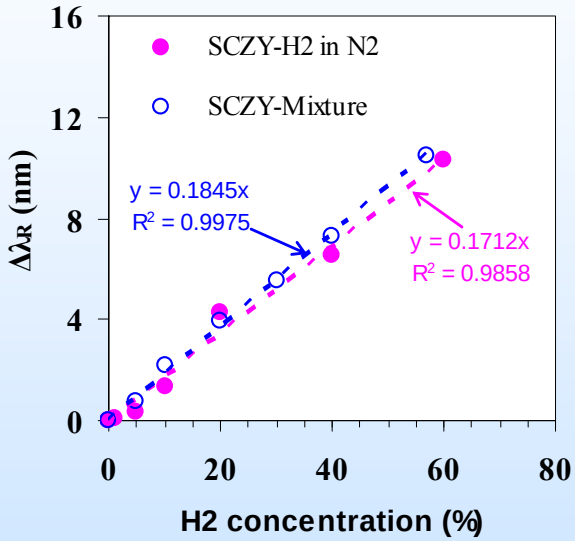



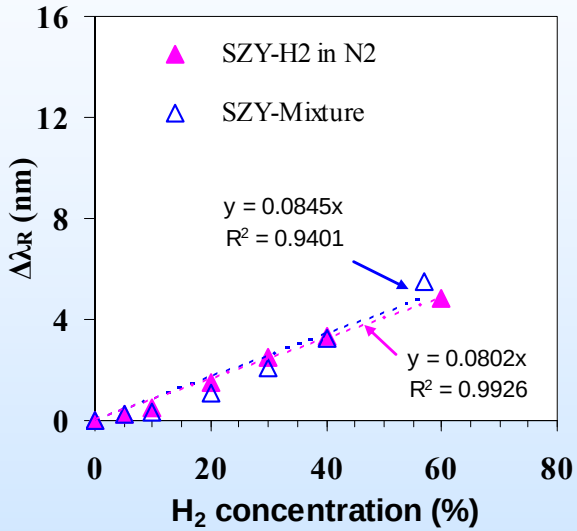



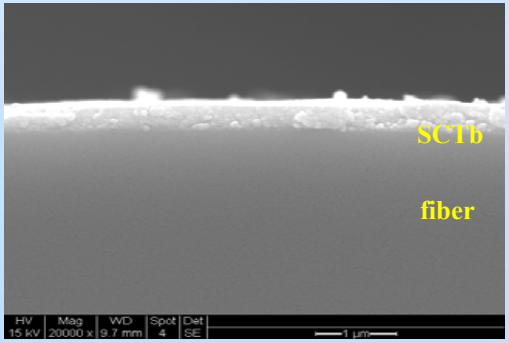
# Proton Conducting Ceramic Coated-LPFG

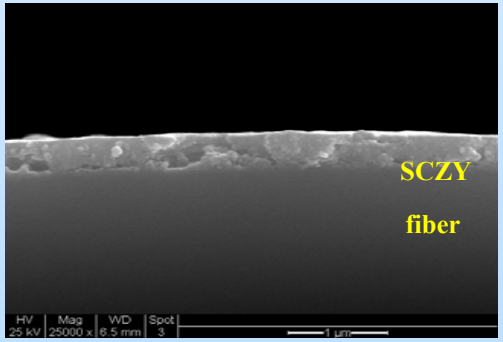
- **Sensitivity and selectivity**

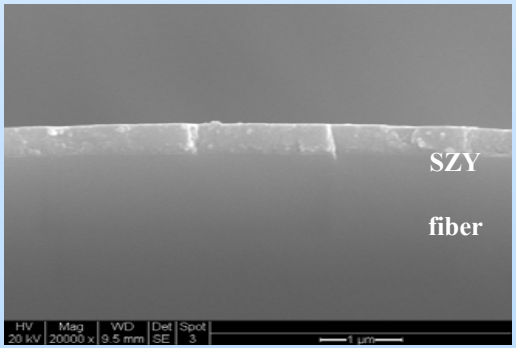


# 2. Cu-doped zirconia (CDZ)

- **Chemical mechanism**

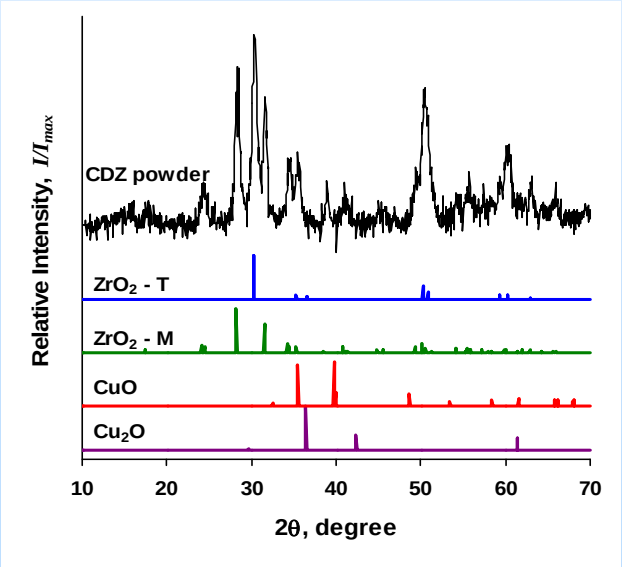
**Cu-doping:** $$CuO \xrightarrow{ZrO_2} Cu''_{Zr} + V_O^{\bullet\bullet} + O_O^X$$

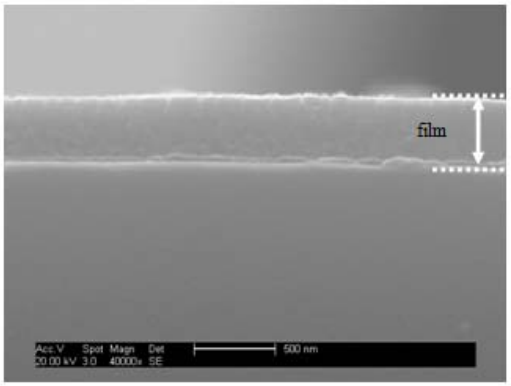
**Reaction:**

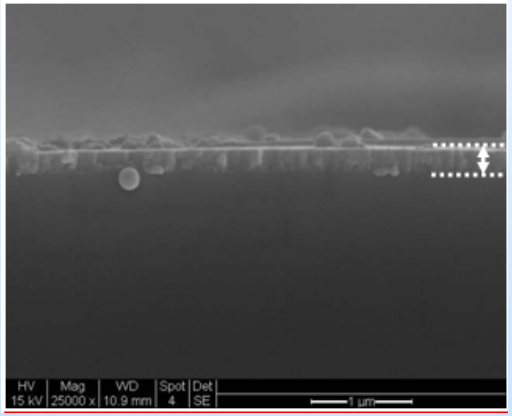
$$CO + 2Cu''_{Zr}(Cu^{2+}) + O_O^X \rightarrow 2Cu'''_{Zr}(Cu^{+}) + V_O^{\bullet\bullet} + CO_2$$

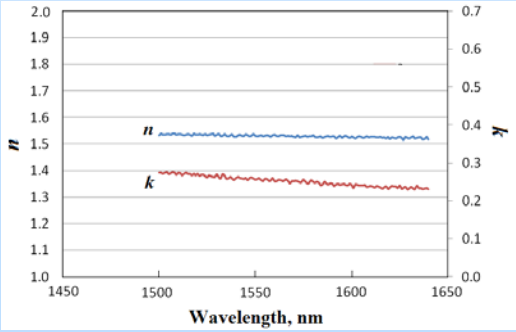
$$\tfrac{1}{2}O_2 + 2Cu'''_{Zr}(Cu^{+}) + V_O^{\bullet\bullet} \rightarrow 2Cu''_{Zr}(Cu^{2+}) + O_O^X$$

$$\tfrac{1}{2}O_2 + V_O^{\bullet\bullet} \rightarrow O_O^X + 2h^{\bullet}$$



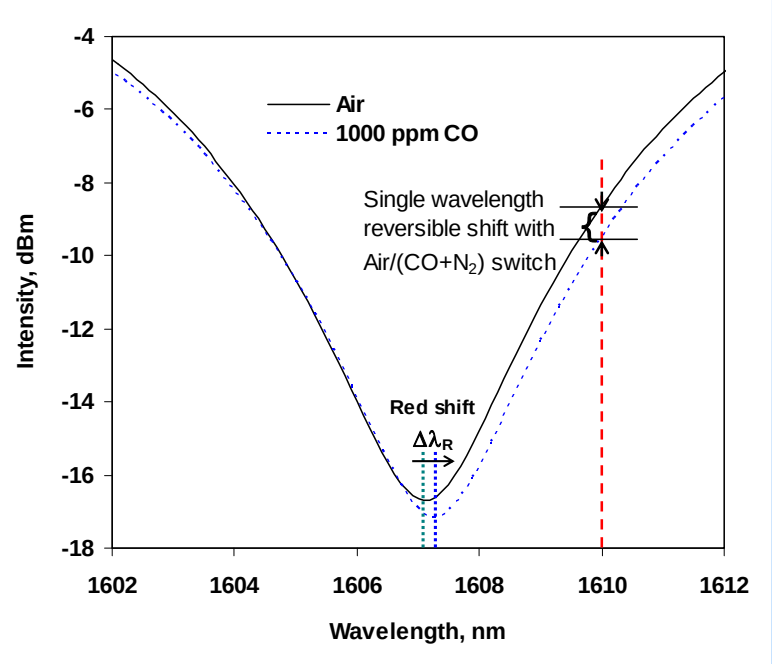



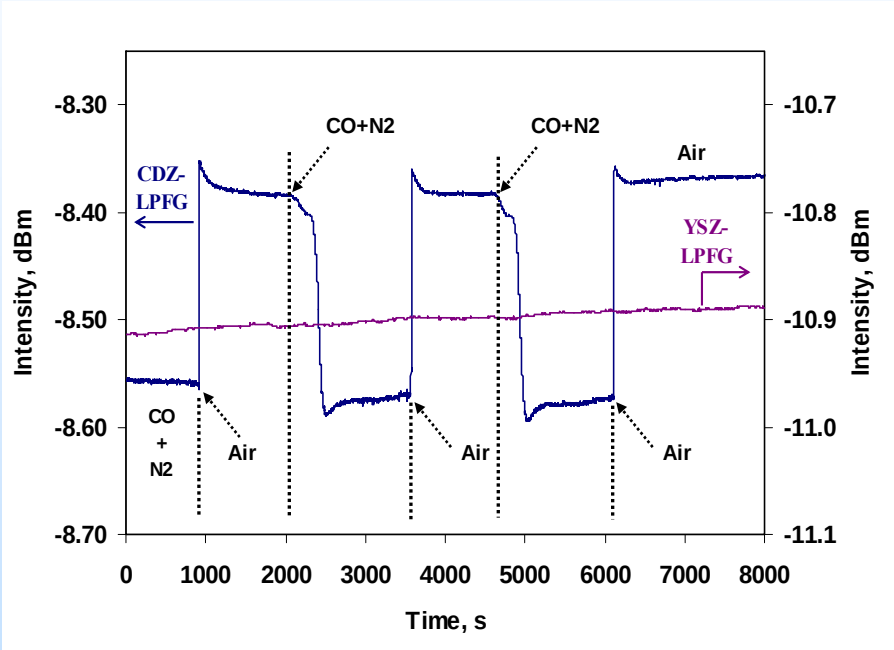



# Single-wavelength response to CO at 550$^{o}$C

- **Low concentration CO (<1,000 ppmv)**
- **No detectable response on YSZ-LPFG**




The CDZ-LPFG response to switching between air and 1,000 ppmv CO in N2 at 550$^{o}$C: (a) transmission spectra in the two gases and (b) the single wavelength (l = 1610 nm) temporal responses to gas switching (arrows indicating gas switching points).

# Single-wavelength response to CO at 550$^{o}$C

- **High concentration CO >1 vol%) – anomalous response**

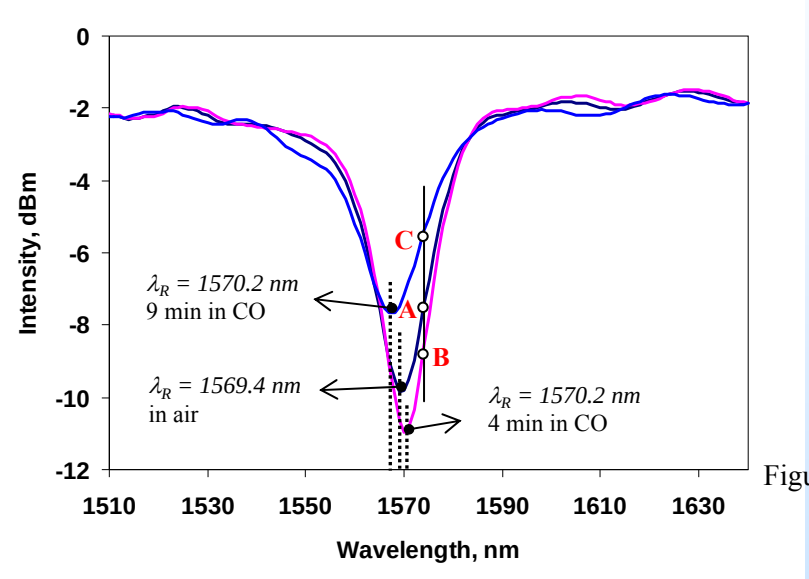
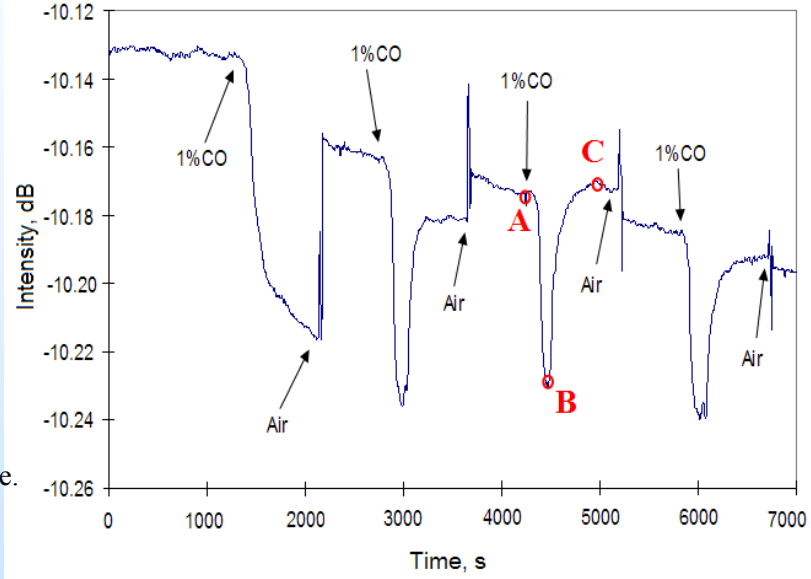
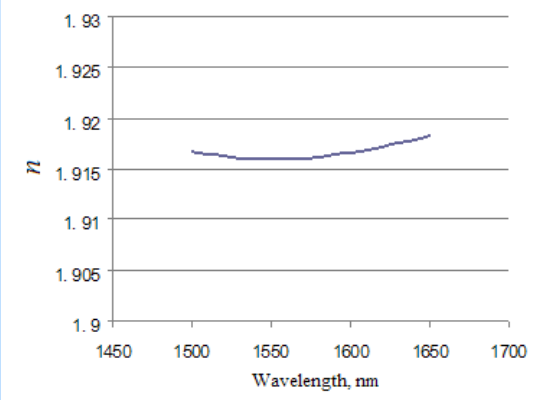



Figure.




$n_{CDZ}$

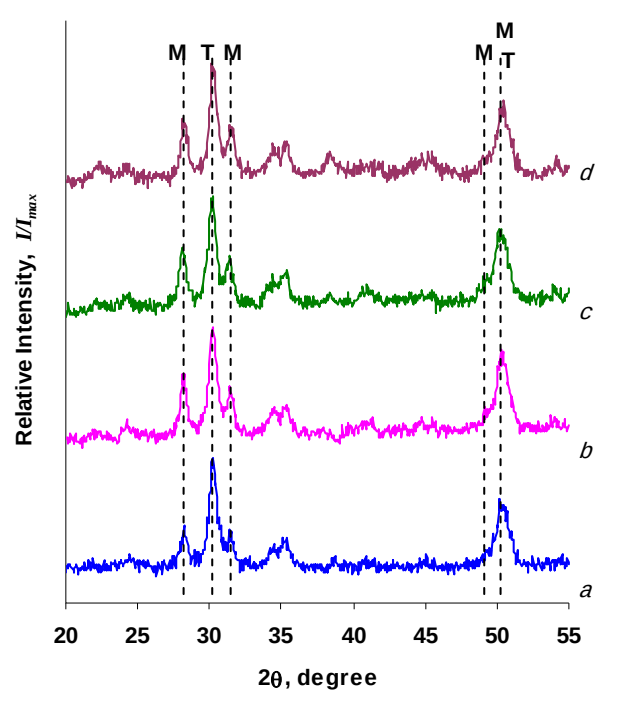
(a) The CDZ-LPFG single wavelength (l = 1576 nm) response to switch between air and 1vol% CO in N2 at 550$^{o}$C (arrows indicating points of gas switch) and (b) the transmission spectra at different times in contact with 1vol% CO




RI after treated in high concentration CO gas at 550$^{o}$C.

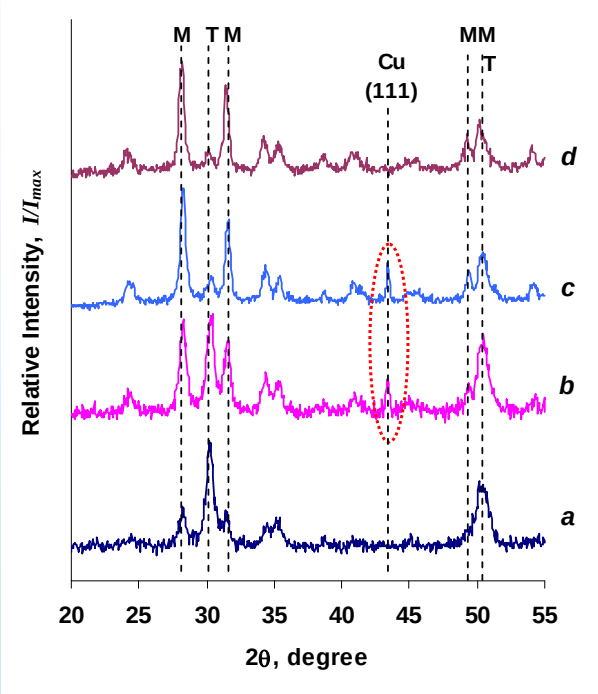
# Causes of CDZ instability in high Concentration CO

- **Stable in ppm-level CO**



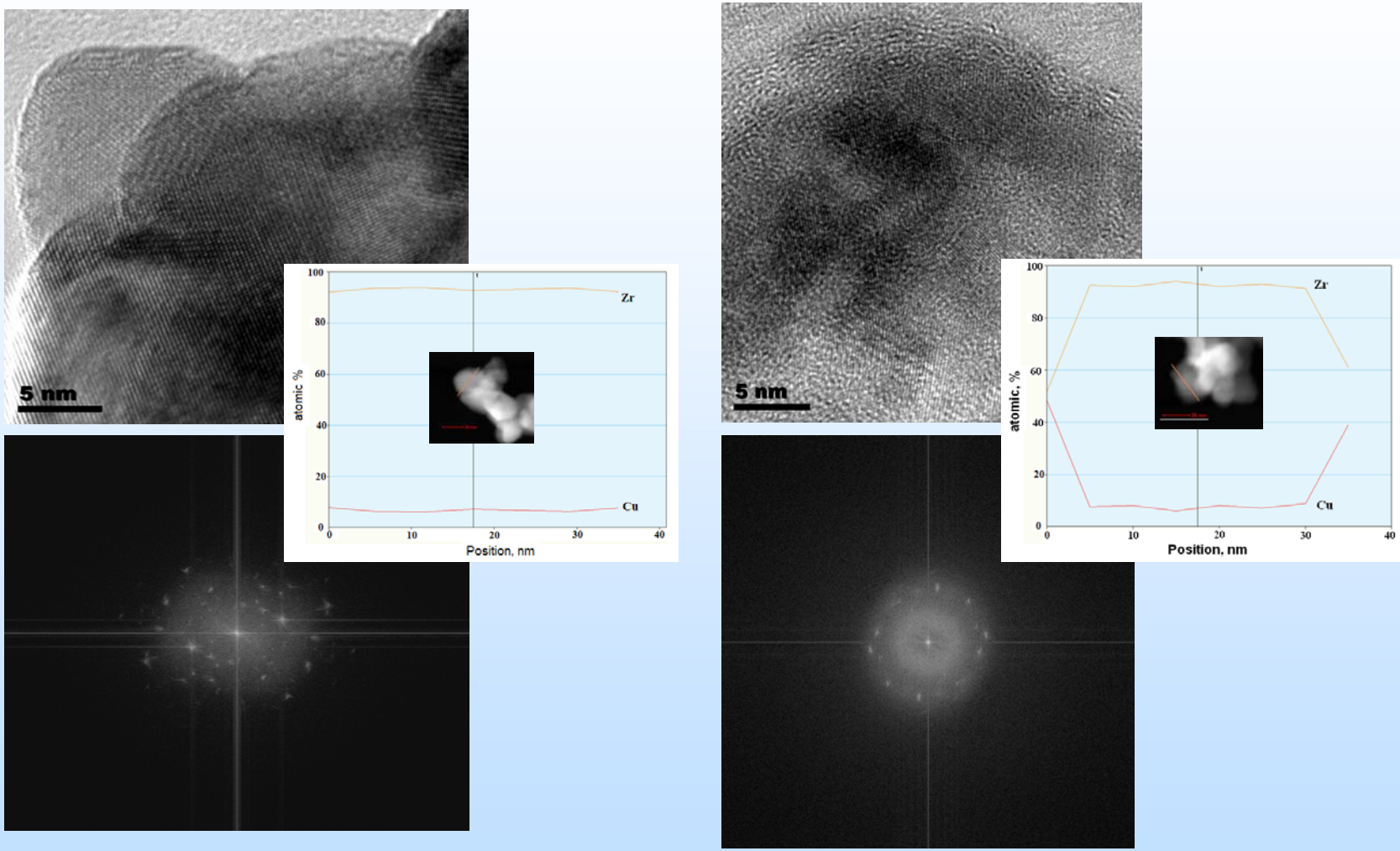

**XRD spectra of the CDZ particles after being treated at 550°C in: a – fresh sample; b – 2 h in 400 ppmv CO; c – 2 h in air; d – after four cycles of switching between air and 400 ppmv CO with a final step of 10 h in 400 ppmv CO.**

- **Over reduction in >1% CO**



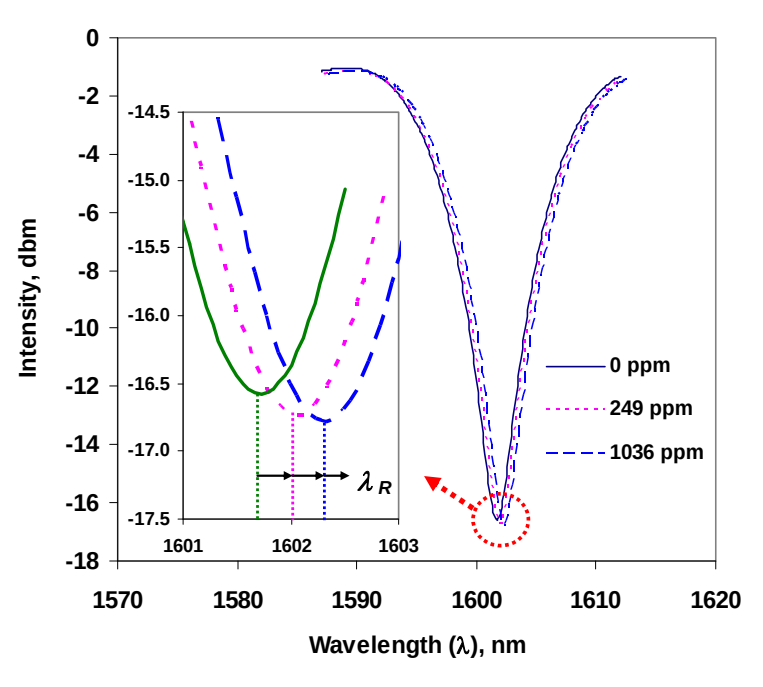

**XRD spectra of the CDZ particles after being treated at 550°C: a – fresh sample, b – in 1vol% CO for 2 h, c – after three cycles of switching between air and 1vol% CO ending with 2 h in 1vol% CO, d – after 2 h in air**

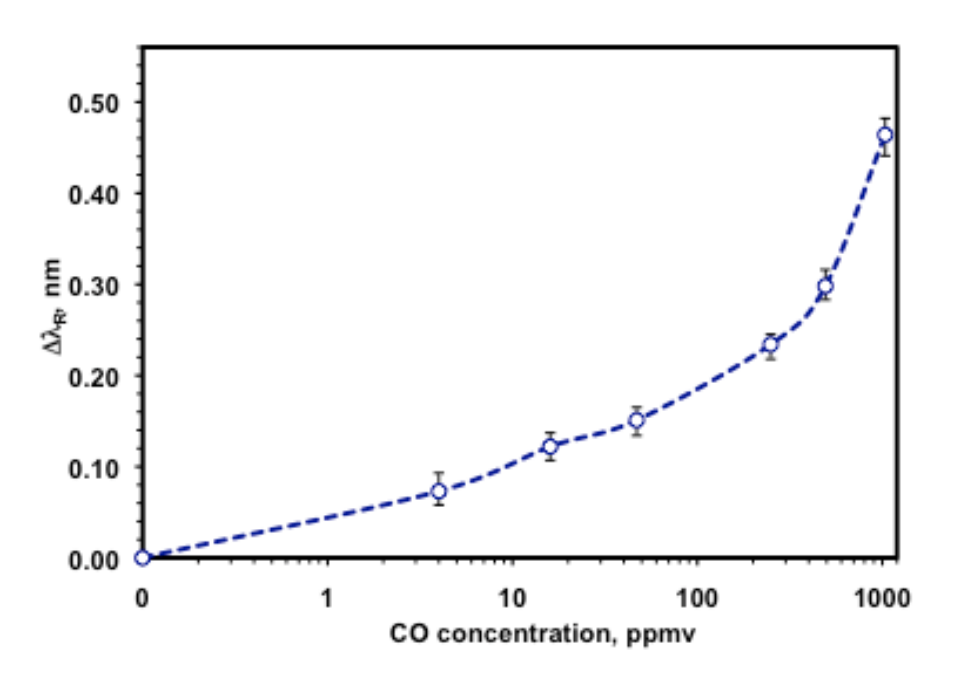
# CDZ instability in high Concentration CO




TEM images and electron diffraction patterns of the 16% Cu doped CDZ nanoparticles: (left) – fresh CDZ particle; (right column) after reduction in 1vol% CO for 10 h.

# 16%Cu CDZ-LPFG for low concentration CO measurement

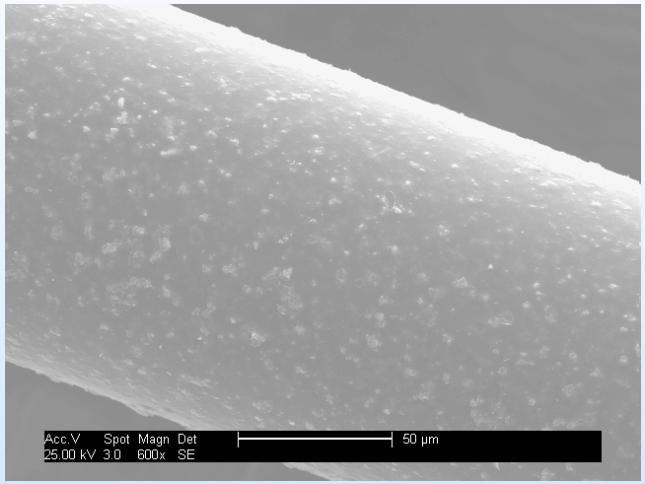


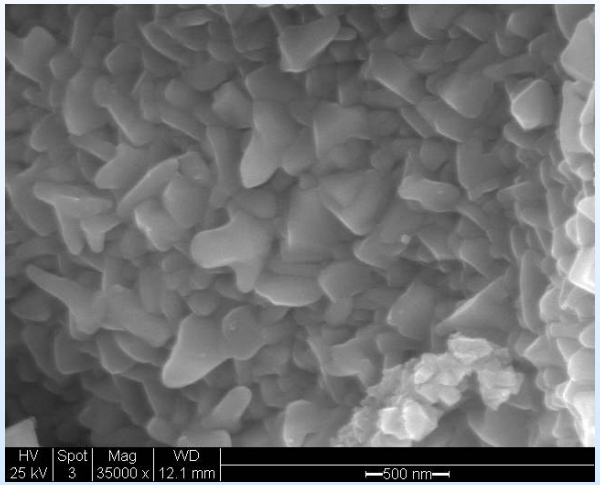



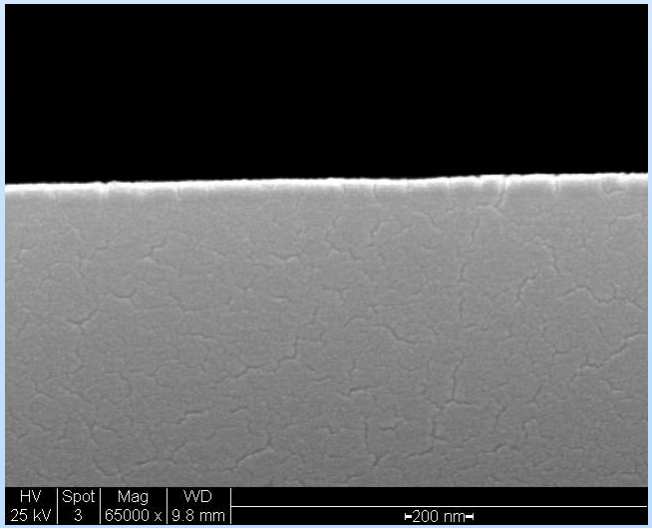

CDZ-LPFG transmission spectra gases of different CO concentrations (left) and sensor output $\Delta\lambda_R$ as a function of CO concentration at 550$^o$C (right)

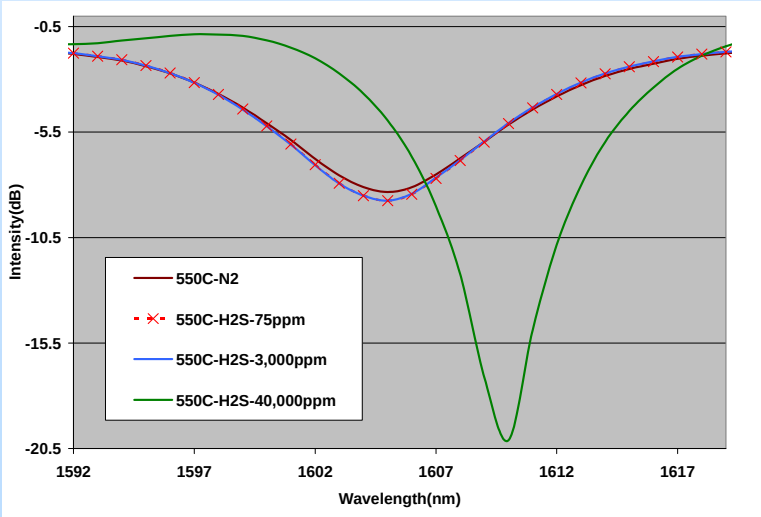
# 3. $H_2S$ sensor Materials

- **$SnO_2$ – irreversible response, not suitable**



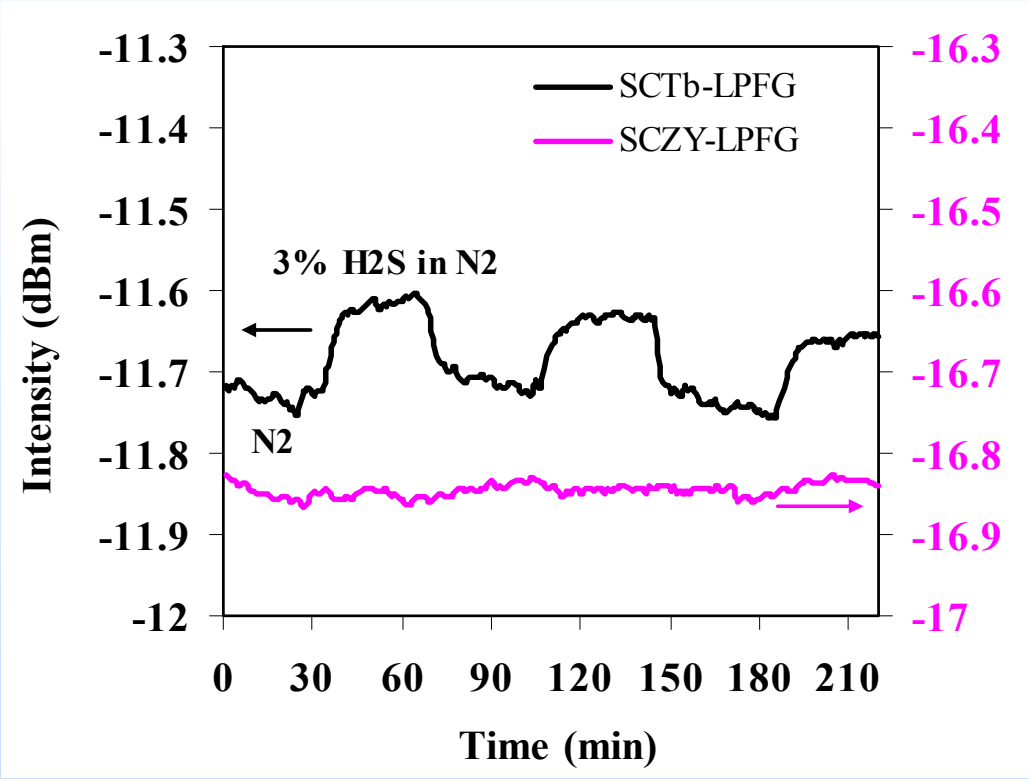



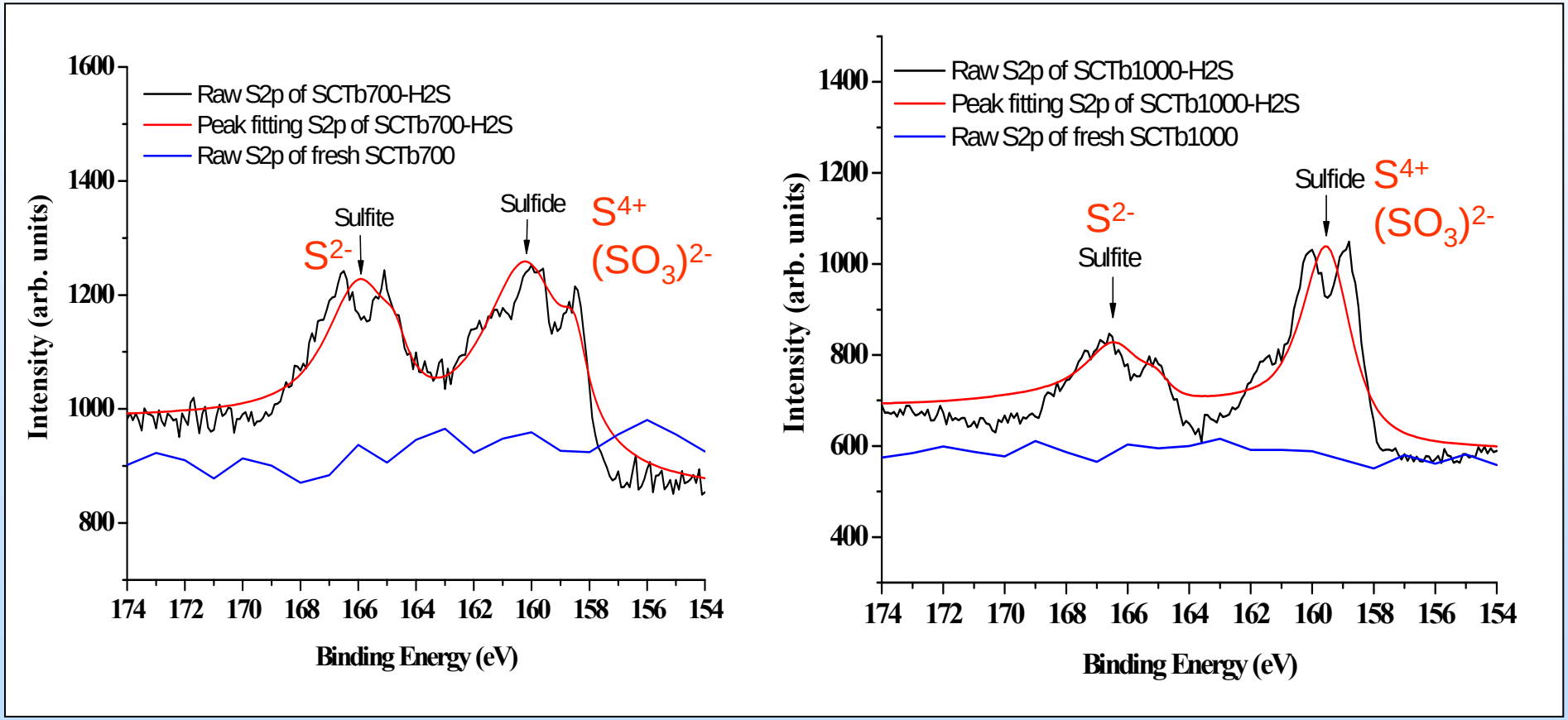
# Proton-conducting perovskite

**Temporal responses of SCTb- and SCZY-LPFG sensors to switching between pure $N_2$ and 3% $H_2S$ in $N_2$ response**



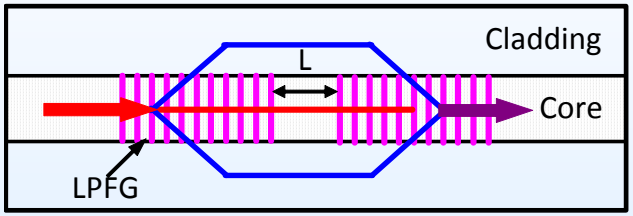
# Sulfur in SCTb phase

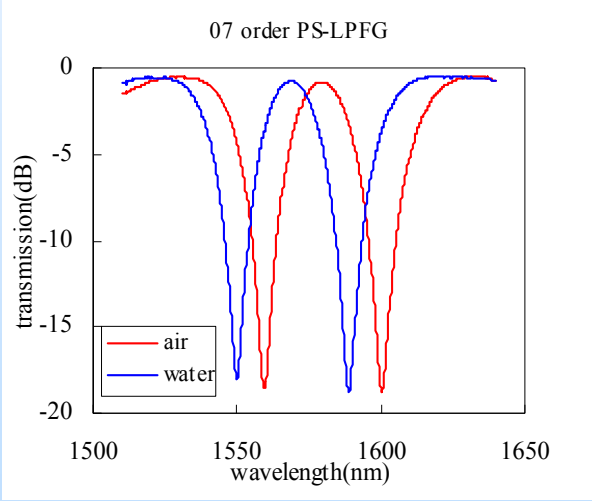
**XPS Spectra of S2p in both fresh and treated SCTb:**
**(left) calcined at 700C; (right) calcined at 1000C.**

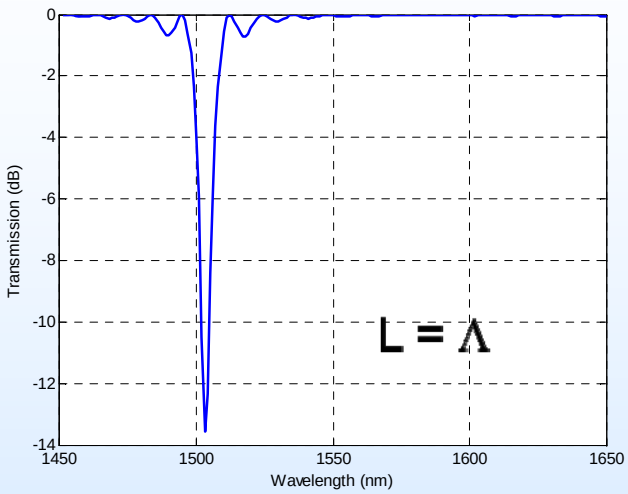


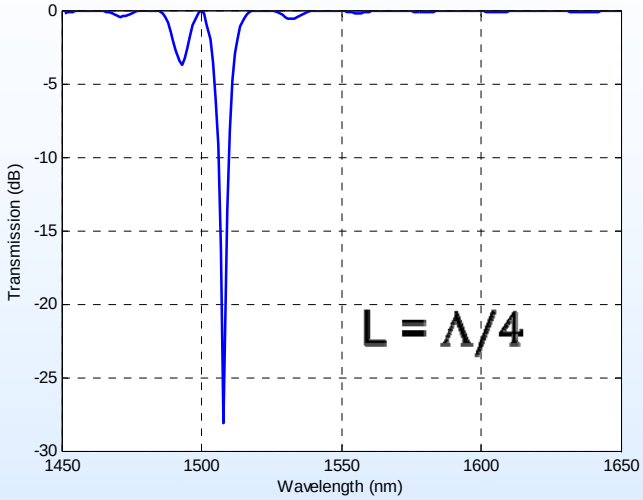
# Design and Fabrication of New Fiber Device

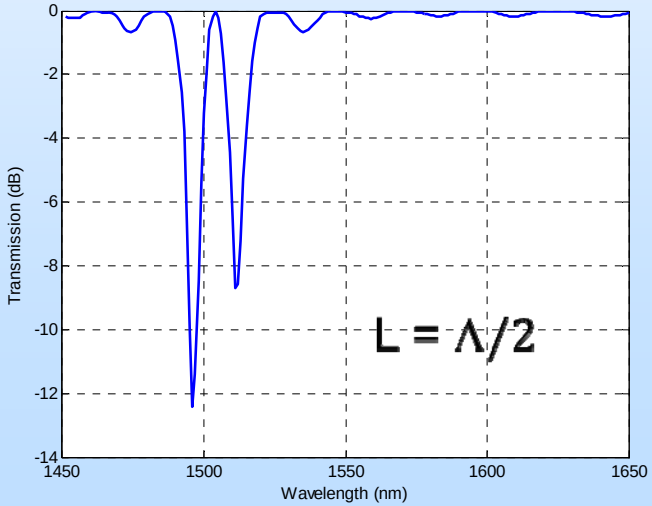
# Phase Shifted LPFG

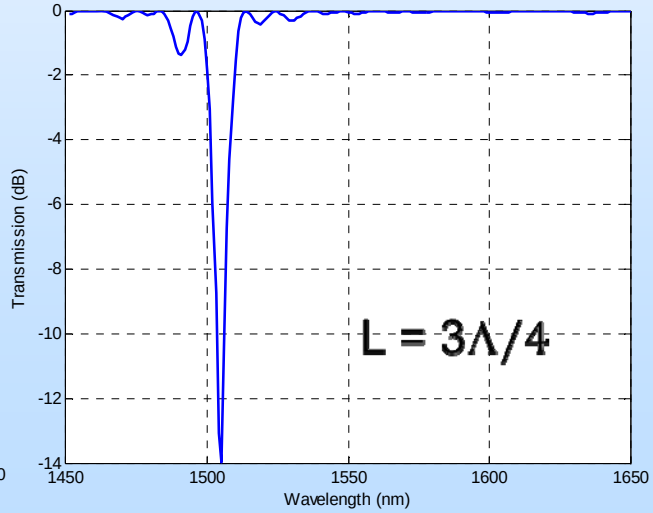


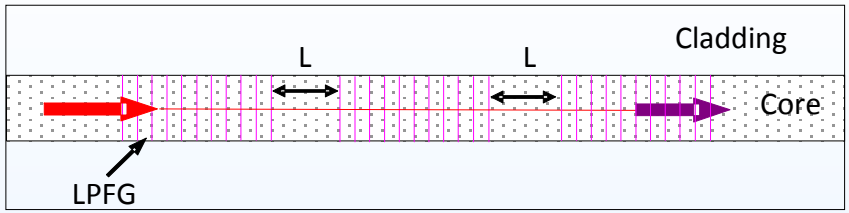



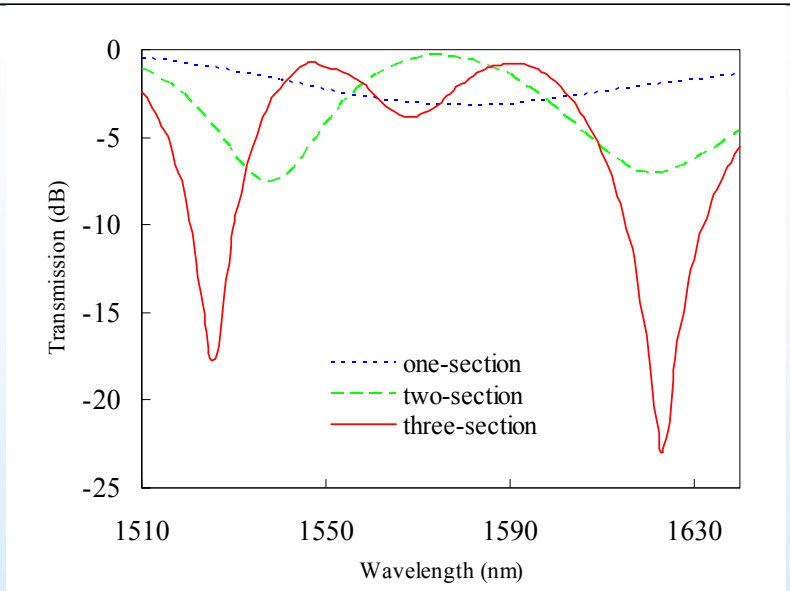



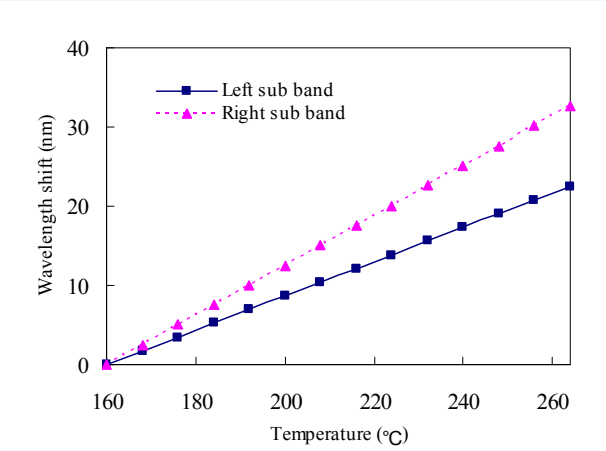



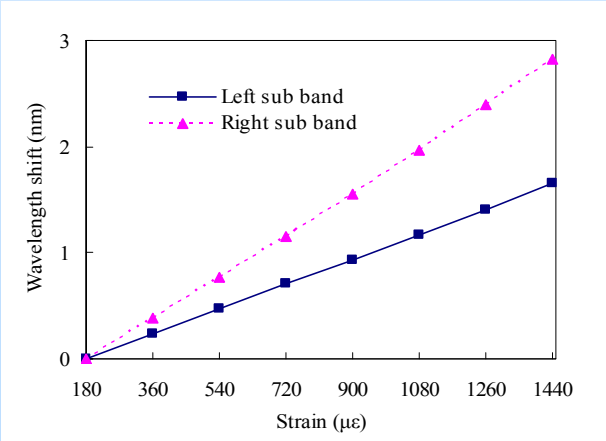



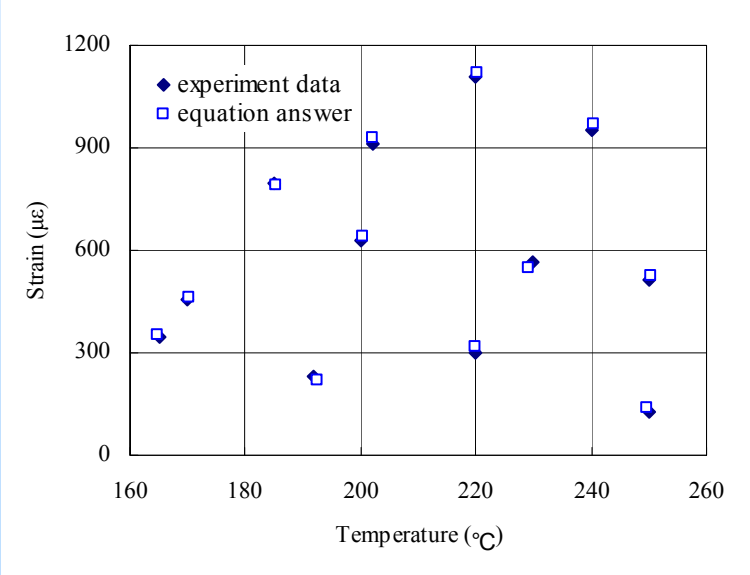
# 3-Section Phase Shifted LPFG



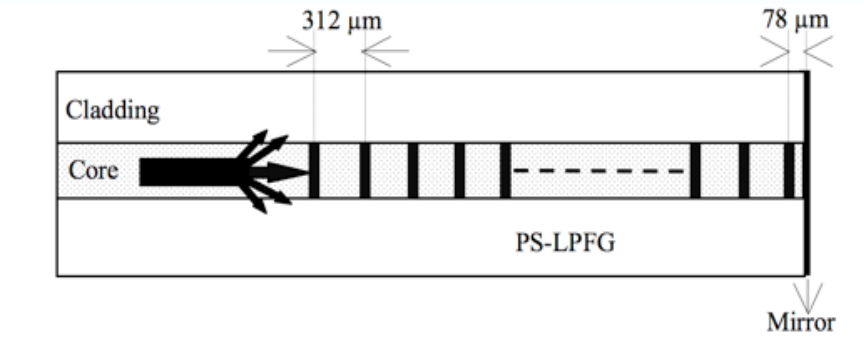



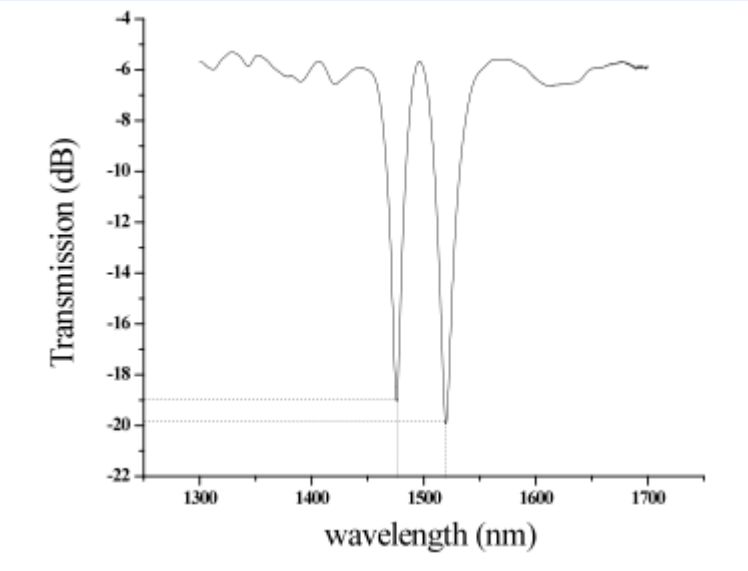



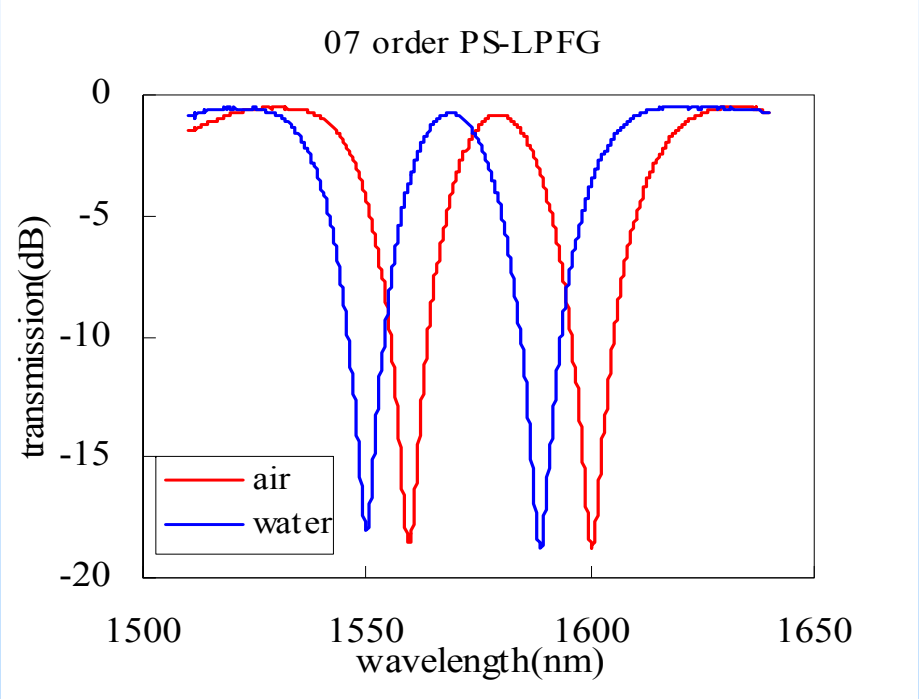



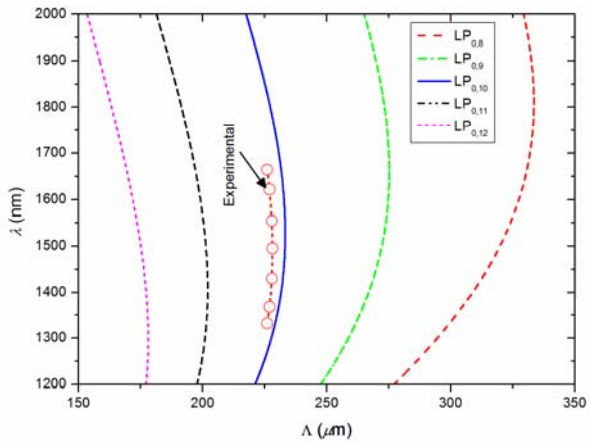
# Reflective Phase Shifted Grating

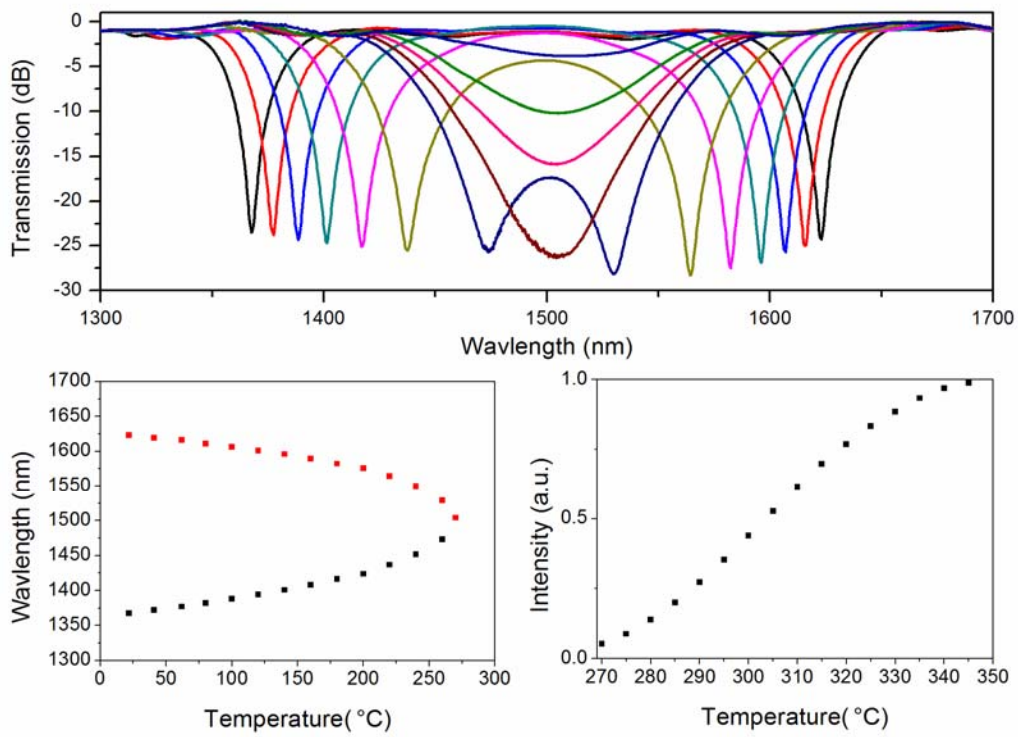


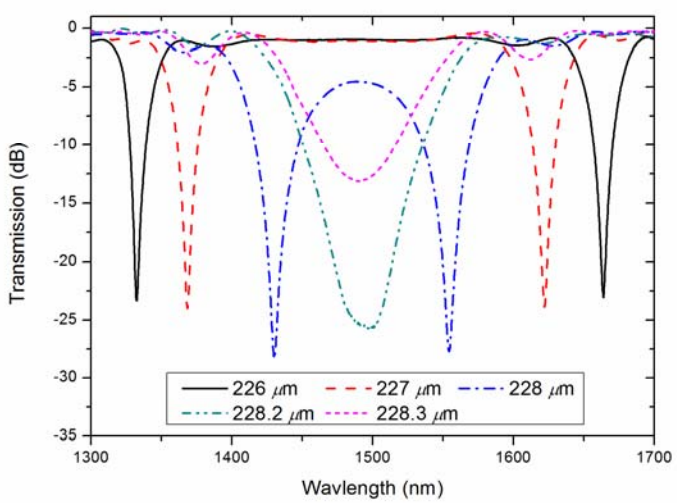



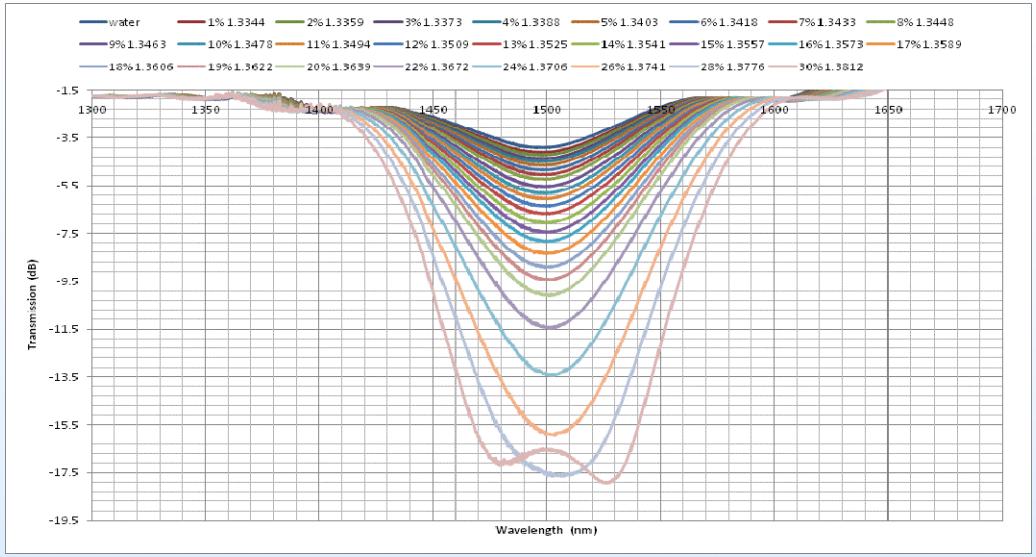
# Turning Point LPFG

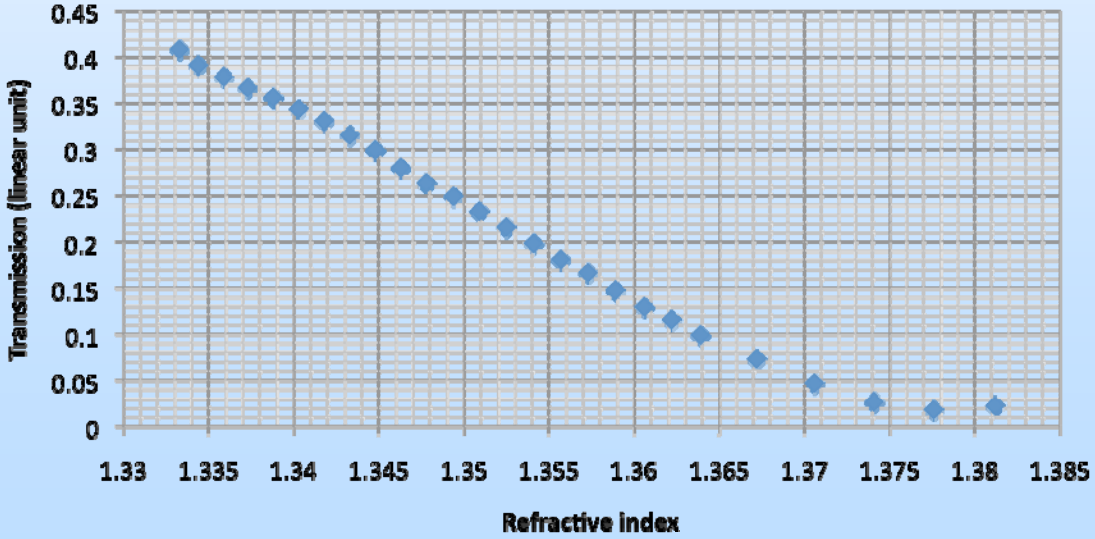


# Turning Point LPFG



# PUBLICATIONS

***Peer-reviewed journal papers:***

- K. Remmel, H. Jiang, X. Tang, J. Dong, X. Lan, H. Xiao, Investigation on Nanocrystalline Copper-Doped Zirconia Thin Films for Optical Sensing of Carbon Monoxide at High Temperature. *Sensors and Actuators B-Chemical* (**2011**) *Under review*.
- X. Tang, J. Provenzano, Z. Xu, J. Dong, H. Duan, H. Xiao, Acidic ZSM-5 Zeolite-Coated Long Period Fiber Grating for Optical Sensing of Ammonia. *Journal of Materials Chemistry* 21 (**2011**) 181-186.
- X. Tang, K. Remmel, X. Lan, J. Deng, H. Xiao, J. Dong, Perovskite-Type Oxide Thin Film Integrated Fiber Optic Device for High Temperature Hydrogen Measurement. *Anal. Chem.* 81 (**2009**) 7844-7848.

***Conference papers/presentations:***

- J. Dong, X. Tang, H. Xiao, T. Wei, Novel Fiber Optical Gas Sensors Based on Ceramic Membrane Materials for Energy Systems. (invited talk) *Gordon Research Conference – Membrane Materials and Processes*, New London, NH, USA, July 27 - 31, 2010.
- X. Tang, Z. Xu, S.-J. Kim, J. Dong, Ammonia Gas Sensing by Zeolite-Fiber Optic Device: Effects of Surface Modification and Operation Temperature . *AIChE Annual Meeting*, Salt Lake City, UT, USA, Nov. 7 -12, 2010.
- X. Tang, Z. Xu, J. Dong, H. Duan, H. Xiao, Development of Nanocrystalline Thin Films of Proton Conducting Perovskite Oxides for High Temperature H2 Separation and Optical Probing in Fossil Fuel Gase**s**. *AIChE Annual Meeting*, Salt Lake City, UT, USA, Nov. 7 -12, 2010.
- Y. Zhang, X. Lan, T. Wei, H. Duan, H. Xiao, Side-coupled optical fiber devices for sensing applications. *SPIE Symposium on Defense, Security + Sensing*, Orlando, FL, USA, Apr. 5-9, 2010.
- X. Tang, K. Remmel, D. Sandker, Z. Xu, J. Dong, Proton Conducting Perovskite-Type Ceramics for Fiber Optic Sensors for Hydrogen Monitoring at High Temperature. *SPIE Symposium on Defense, Security + Sensing*, Orlando, FL, USA, Apr. 5-9, 2010.
- Hongbiao Duan, Xinwei Lan, Tao Wei, Yinan Zhang and Hai Xiao, Characteristics and application of phase-shifted long-period fiber grating fabricated by CO2 laser. *SPIE Symposium on Defense, Security + Sensing*, Orlando, FL, USA, Apr. 5-9, 2010.
- J. Dong, X. Tang, K. Remmel, H. Xiao, Nanostructured Inorganic Thin Film Enabled Fiber Optic Sensors for Gas Sensing in Energy and Environmental Systems, *MS&T Conference*, Pittsburgh PA, Oct. 2009.