Raman Spectroscopy for the On-Line Analysis of Oxidation States of Oxygen Carrier Particles

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ASL/ISP

Chemical Looping Combustion

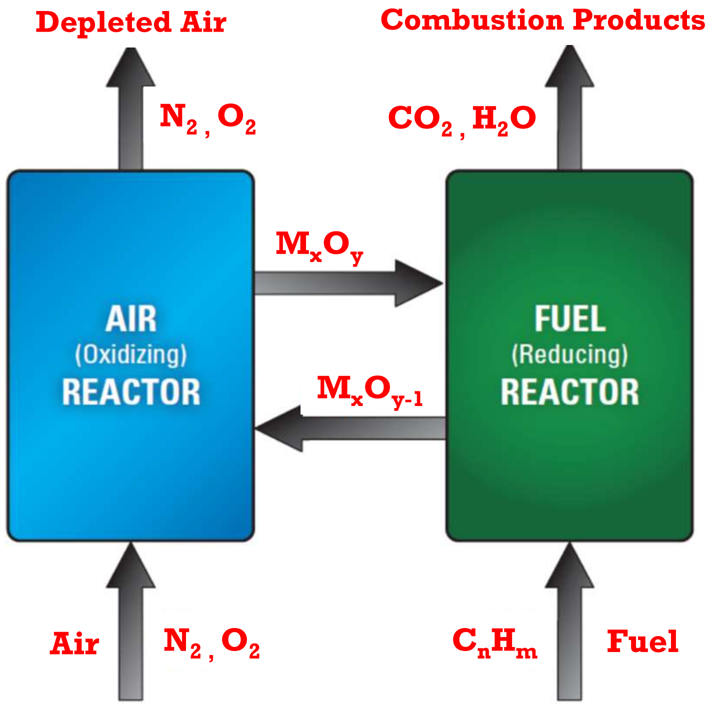


Figure 2: Two Reactor CLC Process

Goal: Combust fossil fuels in pure O_2 so as to generate pure CO_2 for storage.

Conditions, including:

- **Temperatures: 800 °C – 1000 °C**
- **Pressure: ~ 10 atm**
- **Particles constantly moving**

Optimization of process requires ability to identify oxidation state

"DOE/NETL Advanced Combustion Systems: Chemical Looping Summary," July 2013, DOE/NETL

Oxygen Carrier Particles

https://www.netl.doe.gov/newsroom/labnotes/labnotes-archive/01-2014, accessed 9/26/16

This Project:

- Fe_2O_3/Fe_3O_4
- $CaSO_4$
- CuO

Desired properties include:

- High conversion efficiency
- High reactivity
- Low agglomeration
- Long lifetime
- Low cost
- Low environmental impact

J. C. Fisher II, "Oxy(gen) combustion and Chemical Looping Combustion," DOE/NETL

Goal, Objectives, and Vision

Goal:
Develop a sensor for the on-line analysis of the oxidation state of oxygen carrier particles and demonstrate its feasibility.

Objectives:

(1) Set up and test a Raman spectroscopy system in combination with a pressurized high-temperature sample chamber.

(2) Optimize operating parameters of the Raman spectroscopy system and measure the high-temperature spectra of oxygen carriers.

(3) Develop an analysis procedure, including statistical modeling and multivariate calibration, for the interpretation of the Raman spectra.

Long-term Vision:
Monitoring system that can easily be integrated into different types of CLC systems and provide feedback for process control.

Raman Spectroscopy

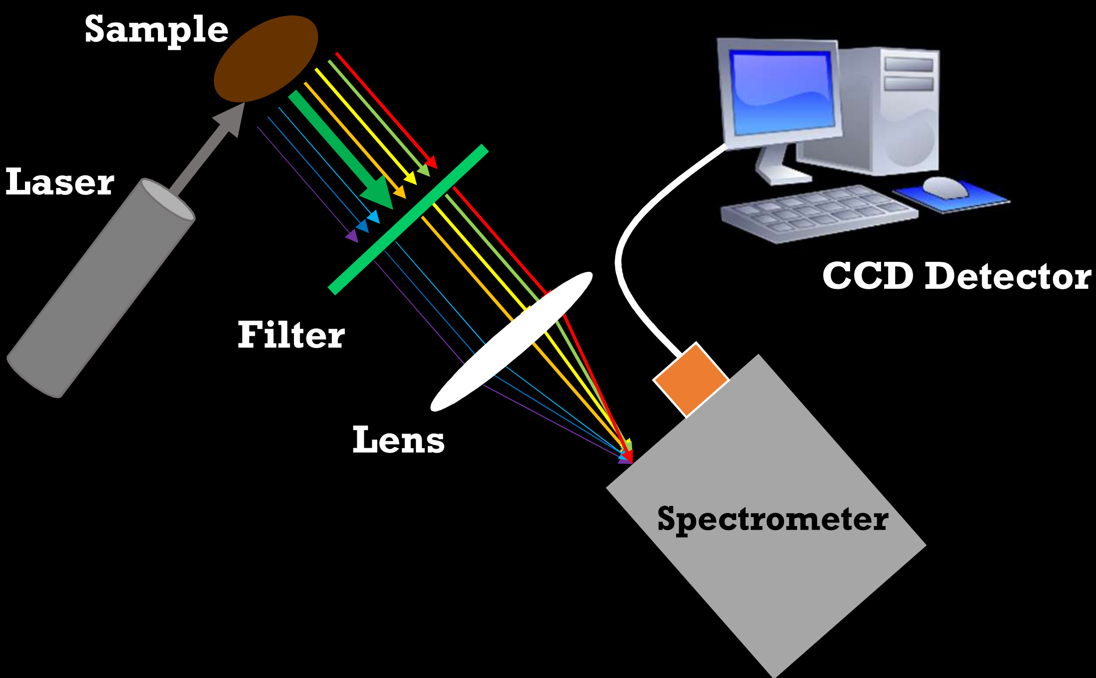
- **Widely used for the detection/identification of materials.**
- **Demonstrated for standoff/remote single-shot applications.**

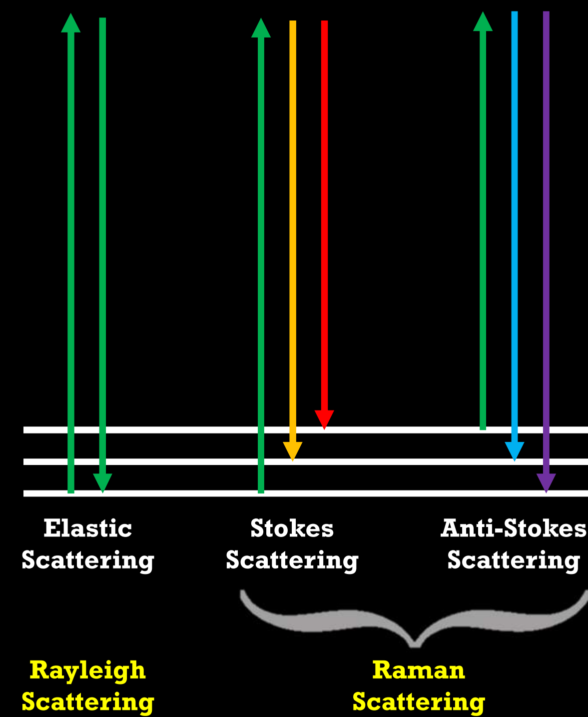
https://www.sciaps.com/raman-spectrometers/, accessed 9/30/16

Widely used and proven technique.

Raman Spectroscopy

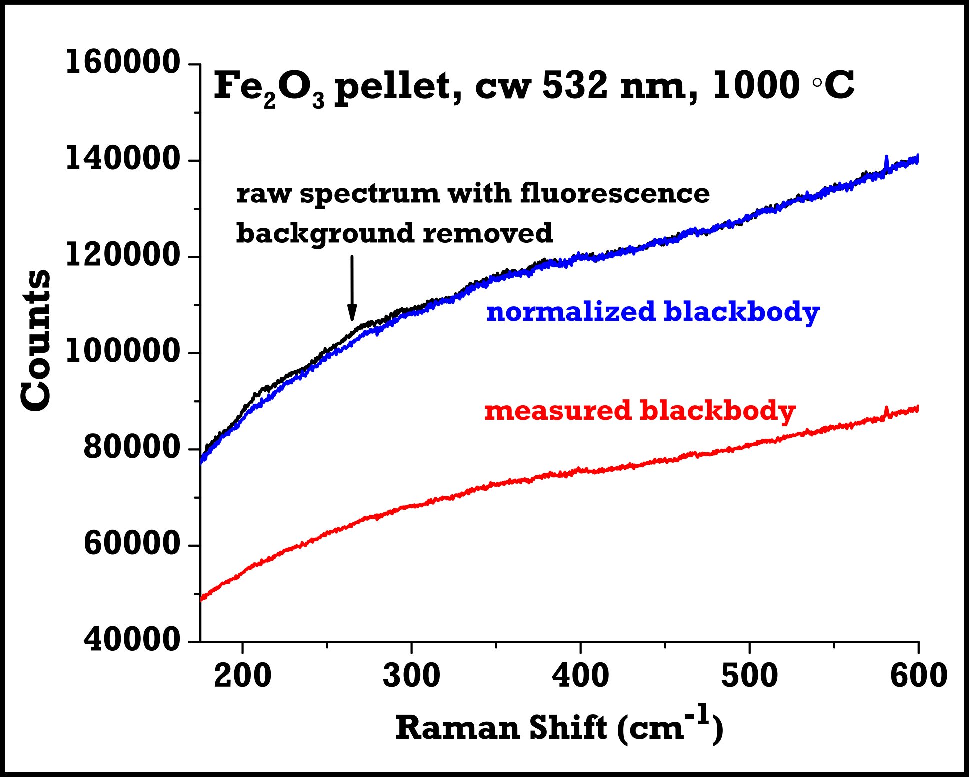
scattering $\propto \left(\frac{1}{\lambda}\right)^4$





Provides vibrational information unique to material.

Corrections for Raman Spectra

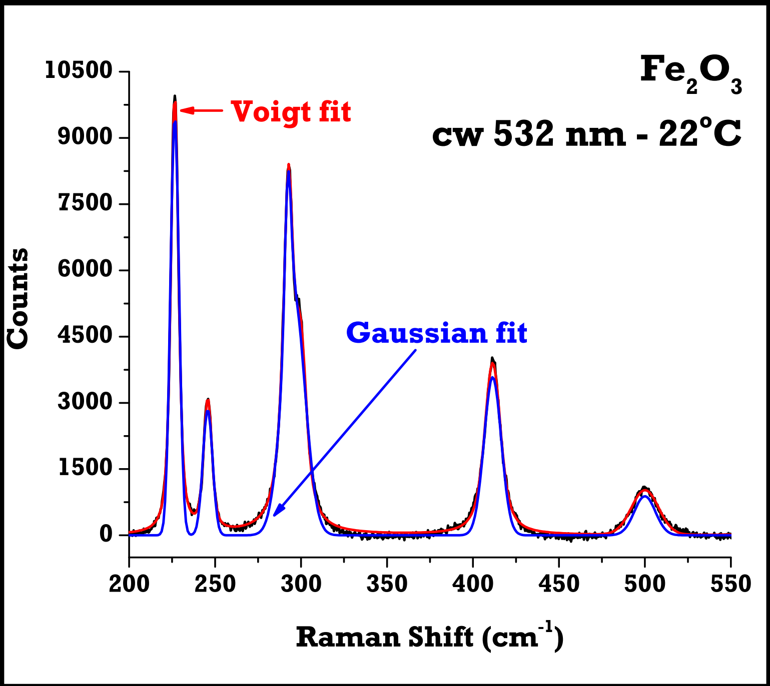


Processing:

- Instrumental transfer function
  - Filters
  - Spectrometer
  - Detector
  - Other optical elements
- Background
  - Fluorescence
  - Blackbody
  - Cosmic radiation
  - Stray light
  - Laser fluctuation
- Multi-peak fitting
  - Peak position
  - FWHM
  - Peak area

Raman spectra require various corrections.

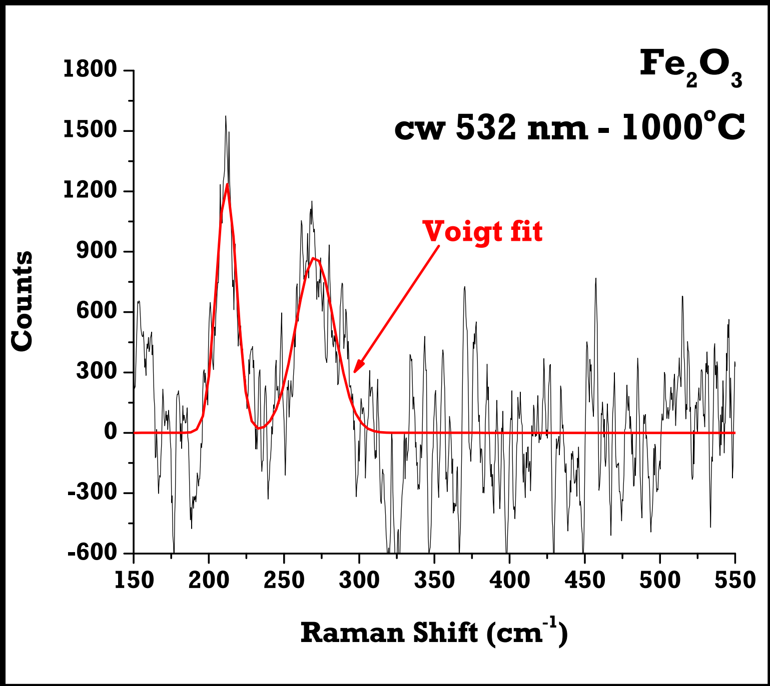
Fitting of Raman Bands



FWHM—thermal broadening

Band center—band migration due to heating

Integrated– calculate temperature from Stokes/antiStokes bands



Peak fitting provides important information for calibration models.

Raman Analysis

- **Heat known materials (e.g., Fe_2O_3, Fe_3O_4) to high temperature (e.g., 800 °C, 900 °C, and 1000 °C) and measure Raman spectra.**
- **Perform Inverse calibration (determine composition and temperature):**

$$x = \alpha_0 + \alpha_1 R_1 + \alpha_2 R_2 + \cdots + \alpha_h R_h$$

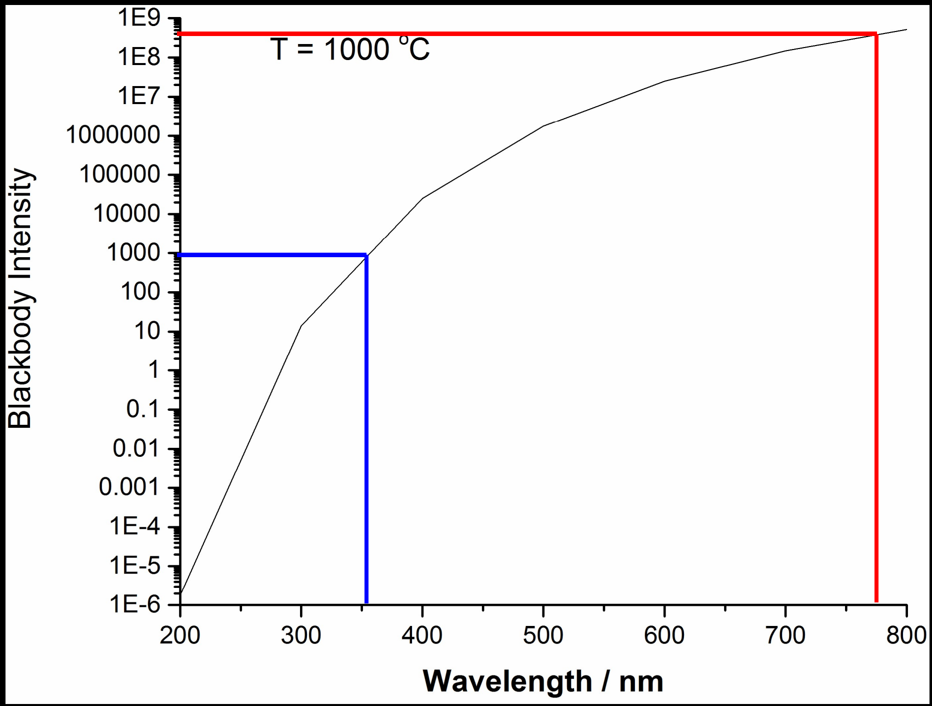
$$T = \beta_0 + \beta_1 R_1 + \beta_2 R_2 + \cdots + \beta_k R_k$$

x: **Composition (e.g., mol% Fe_2O_3)**
T: **Temperature**
α_i, β_i: **fitting parameters**
R_i: **subsets of the Raman parameters (frequency; FWHM; area)**

Yields T and x in the form of linear combinations of the Raman parameters.

1. Li, H., et al. "Feasibility Study of Using High-Temperature Raman Spectroscopy for On-Line Monitoring and Product Control of the Glass Vitrification Process," Energy", PNNL/DOE 1998.
2. Piepel, G. F., et al. "Statistical Modeling of Raman Spectroscopy data from high-temperature glass melts for on-line monitoring of temperature and composition." Quality Engineering 2001, 13, 667-677

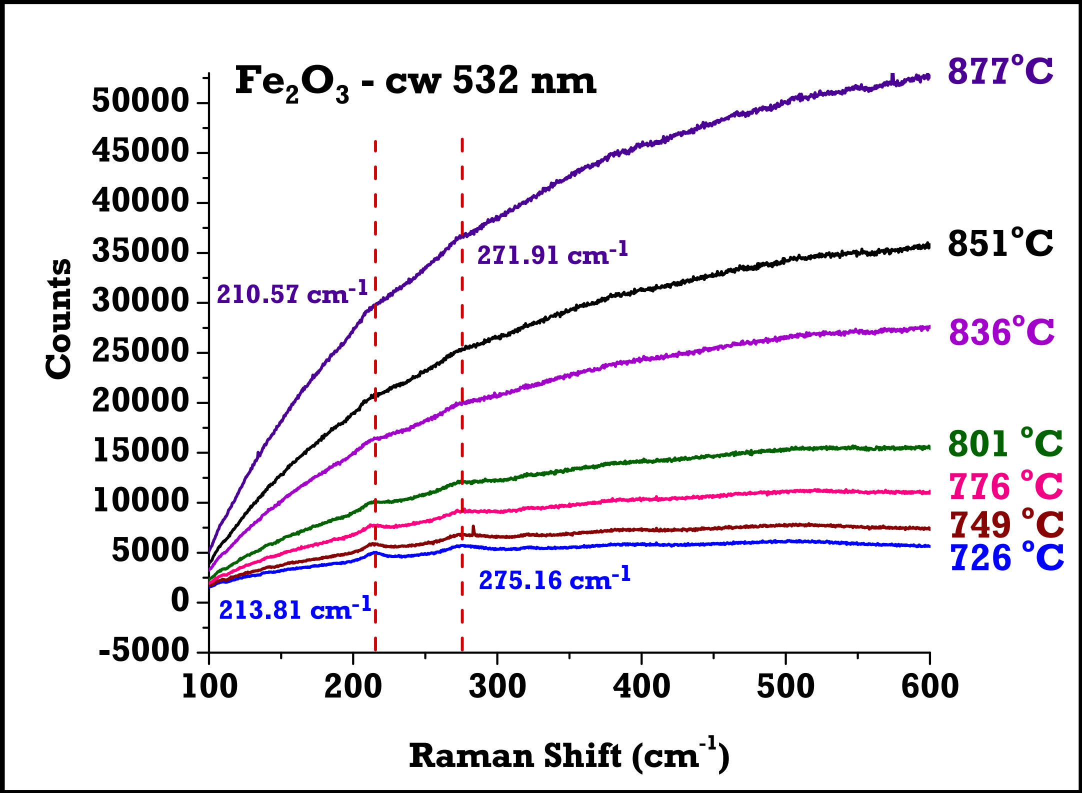
Blackbody Radiation at 1000 °C



$$I_\lambda = \frac{2hc^2}{\lambda^5\left(e^{\left(\frac{hc}{\lambda kT}\right)} - 1\right)}$$

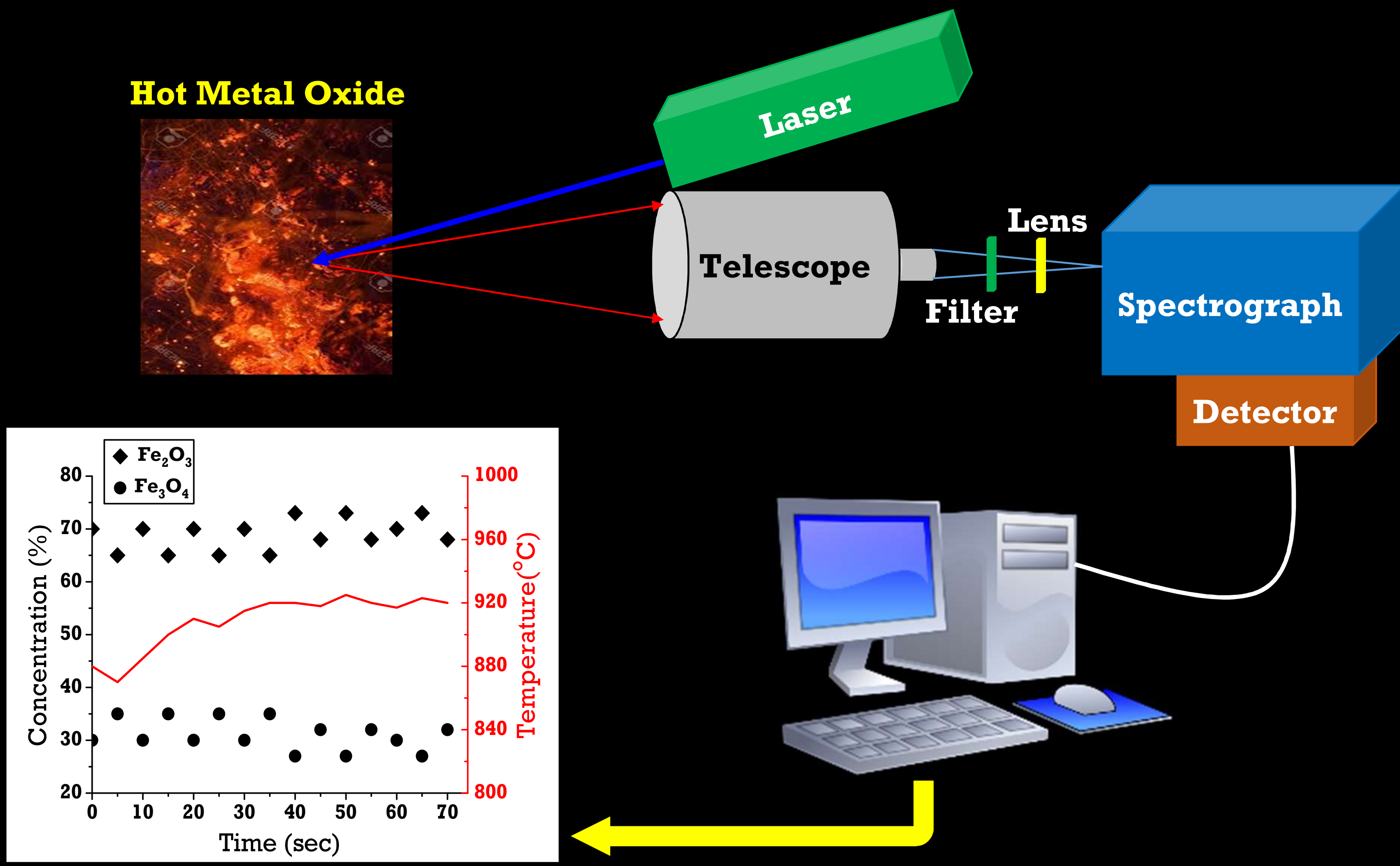
Using 355 nm instead of 785 nm reduces background by more than 5 orders of magnitude.

Blackbody Radiation - Fe_2O_3

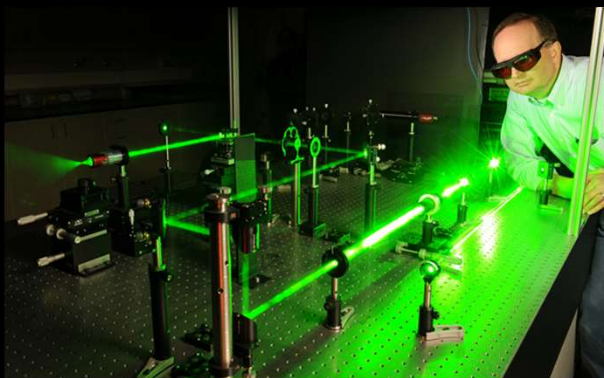


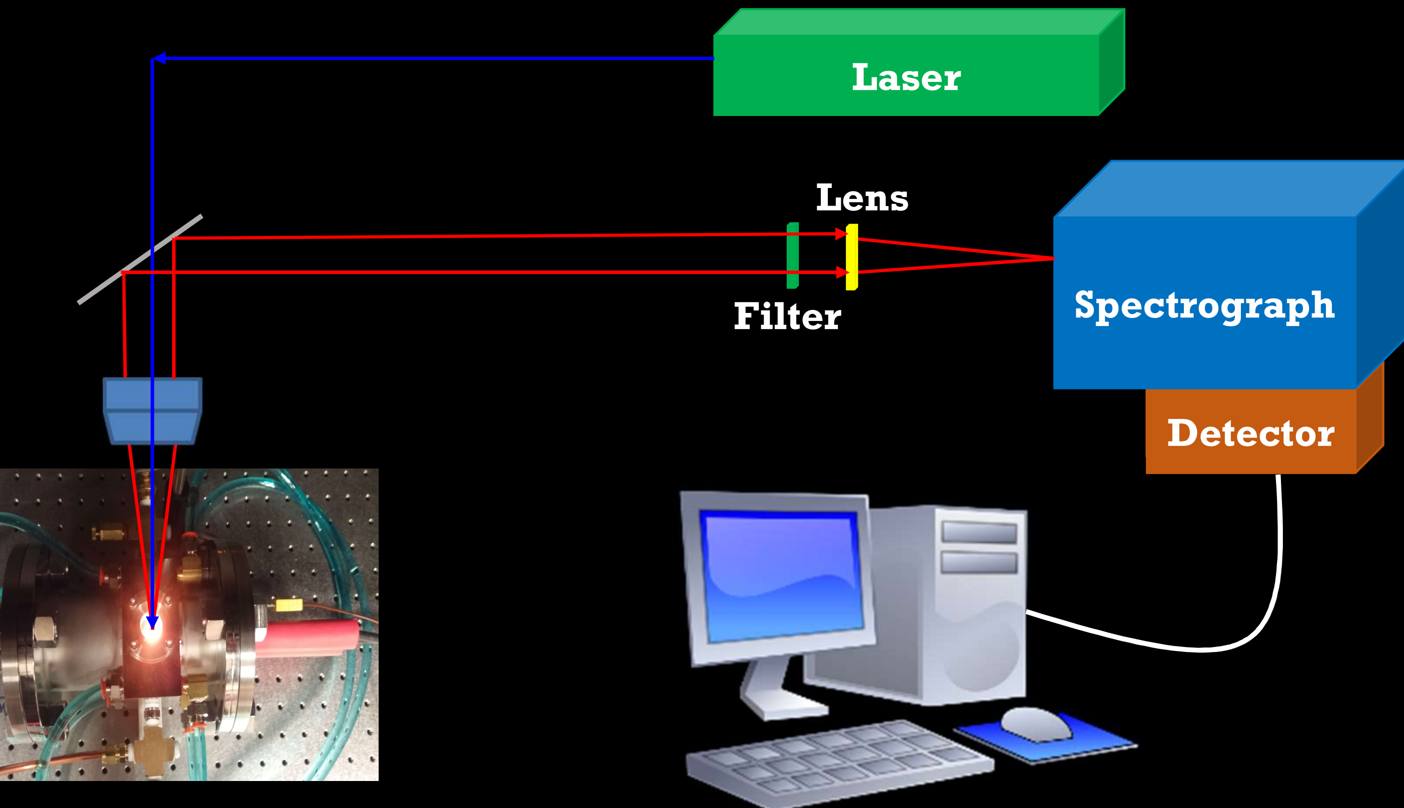
Effects of blackbody radiation apparent using 532 nm excitation.

Envisioned Raman Spectroscopy Field Setup



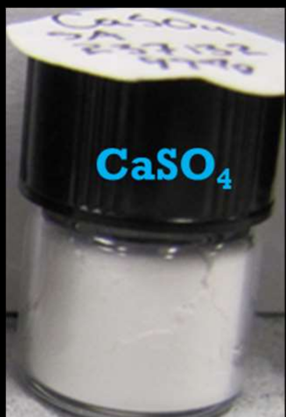
Initial Laboratory Setup





Calibration measurements on well-defined samples.

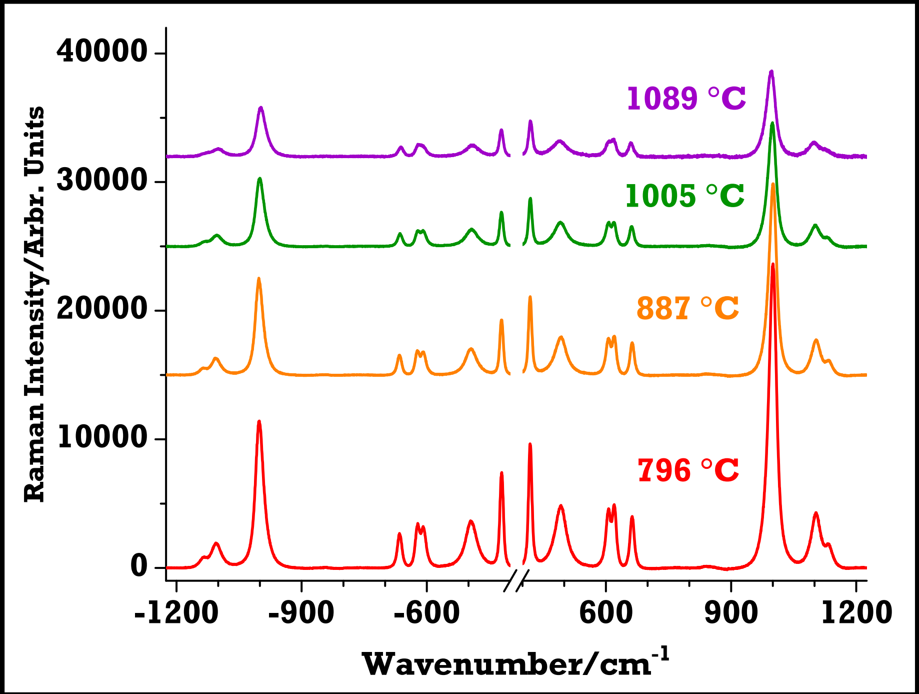
Investigation of OCPs



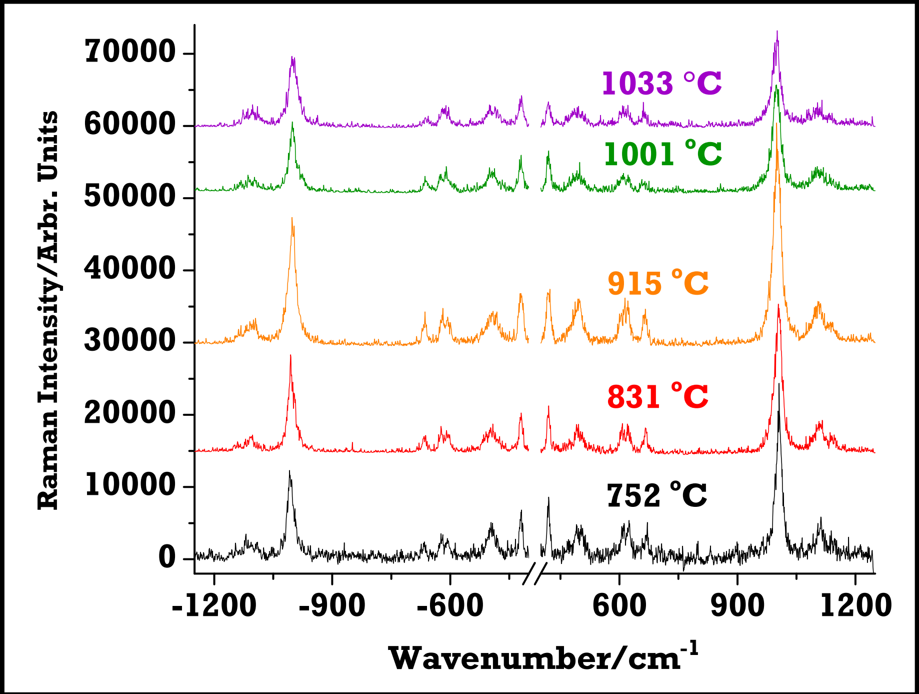
- **Calcium Sulfate Studies**
  - Pulsed/time gating approach successful for temperatures >1000°C
- **Iron Oxide Studies**
  - Pulsed lasers generally not successful because of instability under intense light.
  - CW lasers have proved promising

$CaSO_4$ – High Temperature Measurements

532 nm



CW, 100 ms



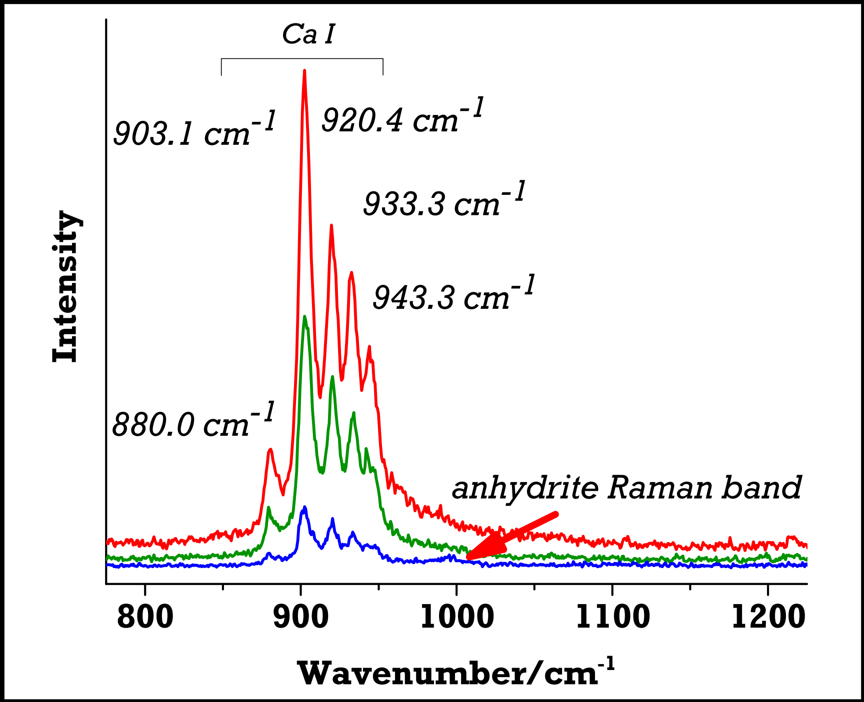
Single shot, long-pulse, 130 μs

Characteristic Raman peaks observed above 1000°C.

J. Kirtley, V. Leichner, B. R. Anderson, H. Eilers, *J. Raman Spectrosc.* **2018**.

$CaSO_4$ – LIBS

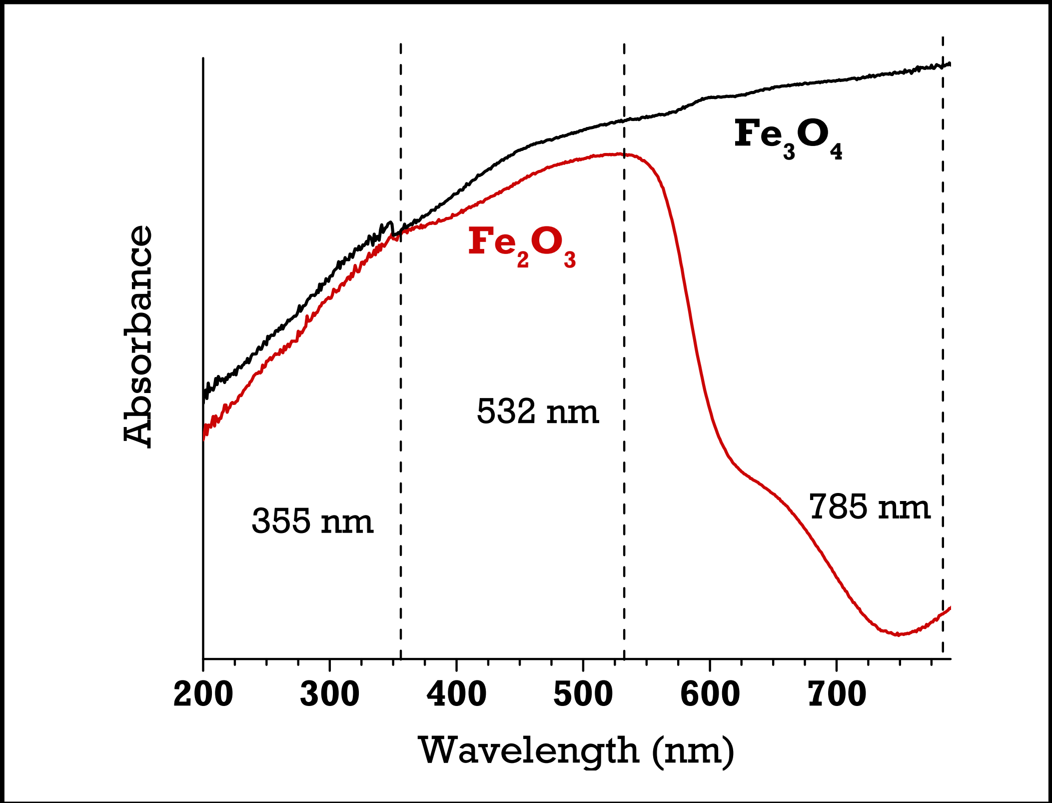
532 nm



Laser induced breakdown spectra (LIBS) observed using laser pulses of sufficient intensity.

J. Kirtley, V. Leichner, B. R. Anderson, H. Eilers, *J. Raman Spectrosc.* **2018**.

Fe_2O_3/Fe_3O_4 – Challenges with Absorption



Ideally, we want high scattering and low absorption.

Fe_2O_3 – Optimizing Light Intensity & Wavelength

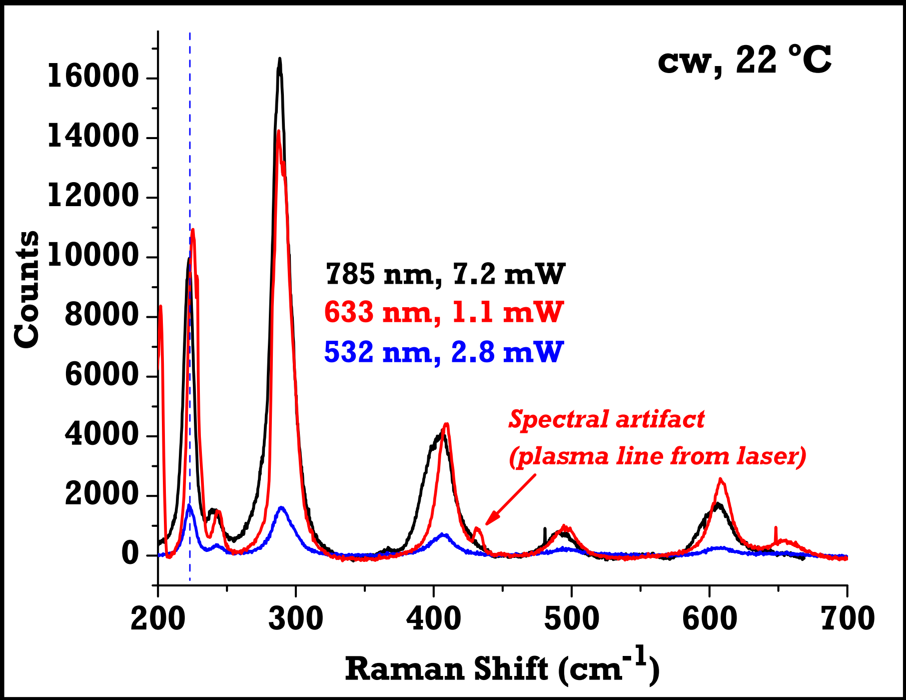
Using CW:

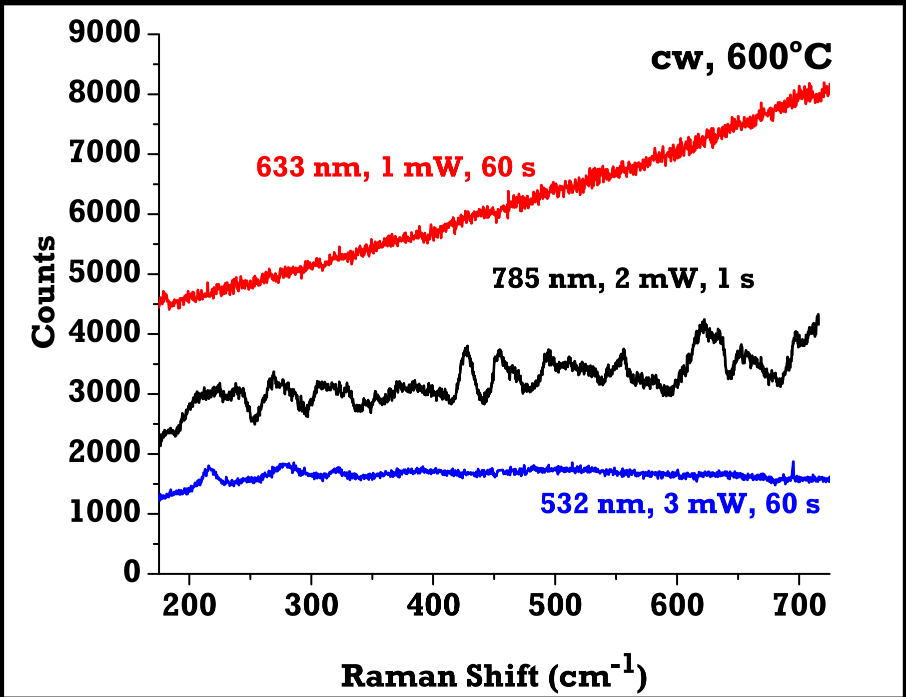
	360 nm**	532 nm*	633 nm*	785 nm*
Intensity	$\leq 10^6$ W/cm^2	$\leq 10^5$ W/cm^2	$\leq 10^5$ W/cm^2	$\leq 10^5$ W/cm^2
Highest Temperature	1050 °C	700 °C	400 °C	600 °C

***Using hematite powders (212 µm-600 µm)**
****Light intensity only estimated, used densely packed powder**

Light intensity must be low to avoid LIBS (creating an advantage for UV excitation).

Fe_2O_3 – Comparison of Wavelengths

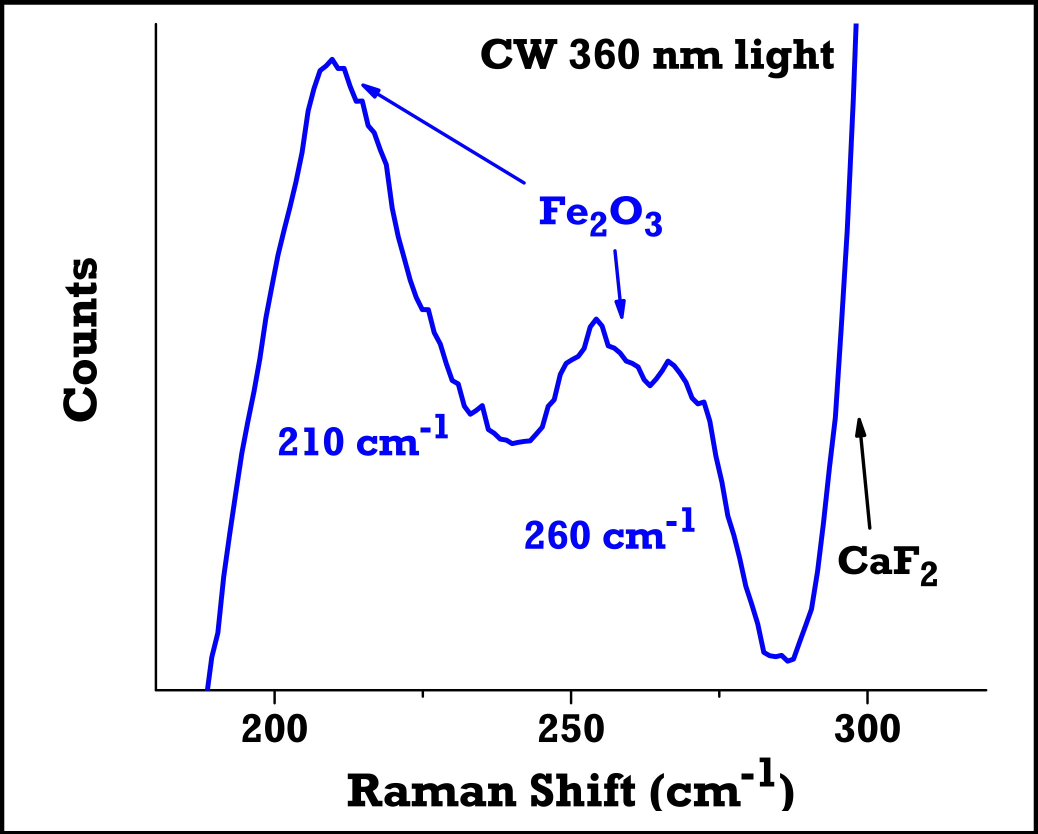




Shorter wavelengths best for avoiding blackbody.

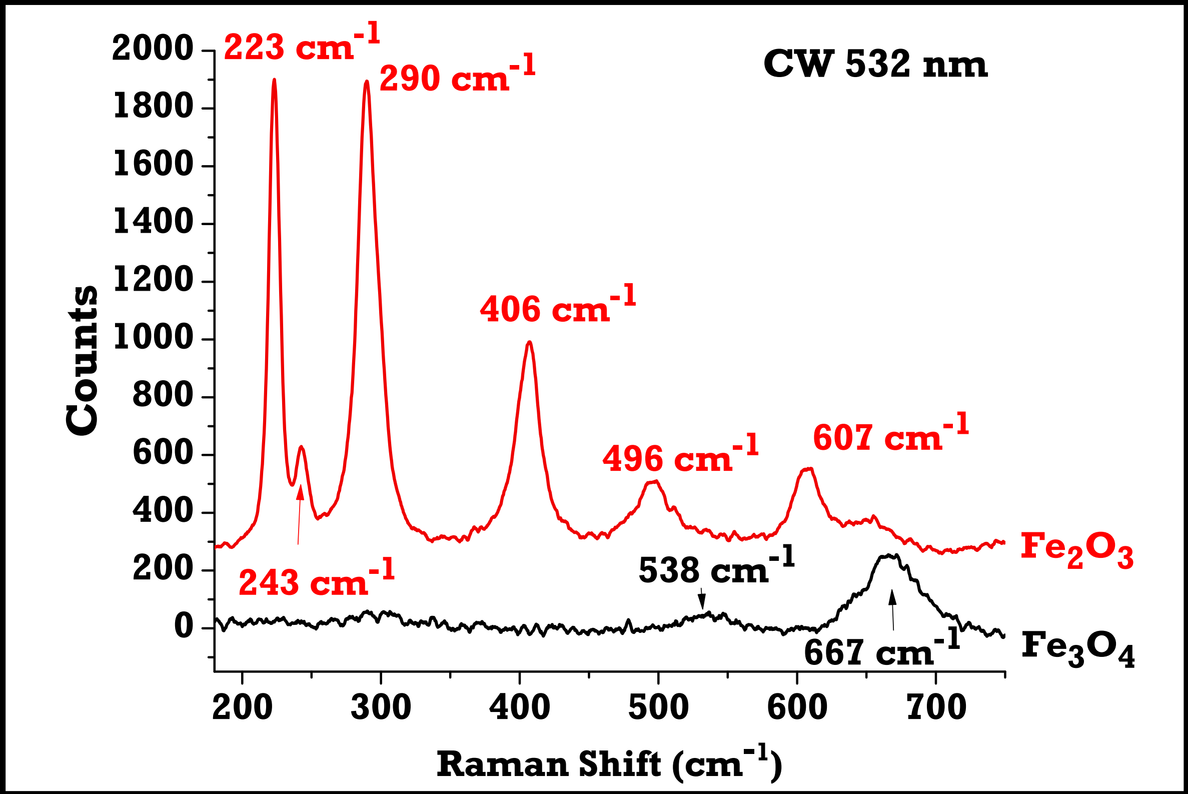
Fe_2O_3 at 1000 °C

Fe_2O_3 spectra at 1000 °C have been successfully collected using <u>360 nm and 532 nm excitation.</u>



Benchmark high temperature spectrum.

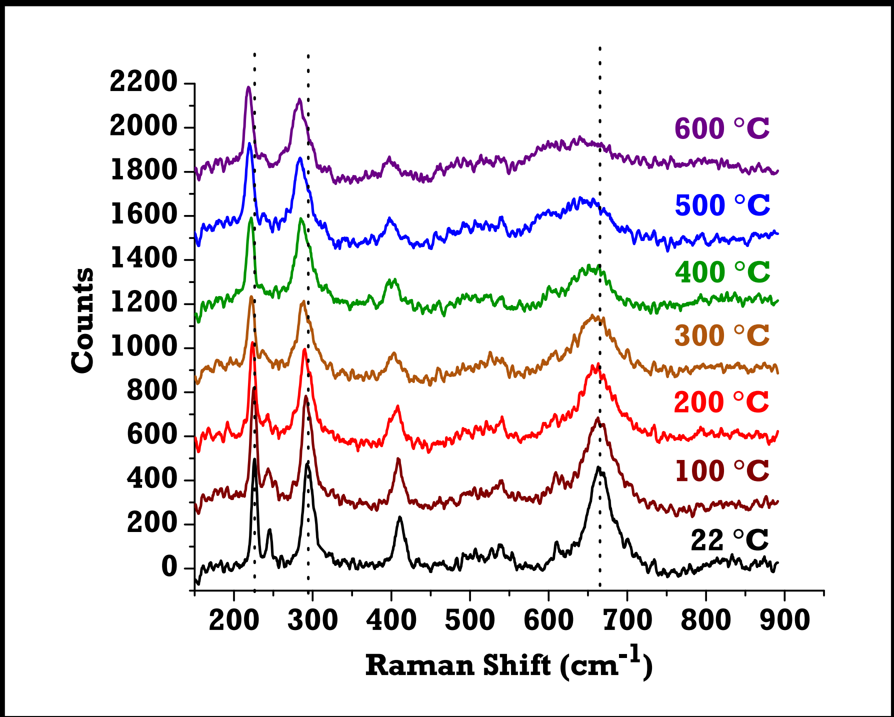
Reference Fe_2O_3 and Fe_3O_4 Spectra at RT



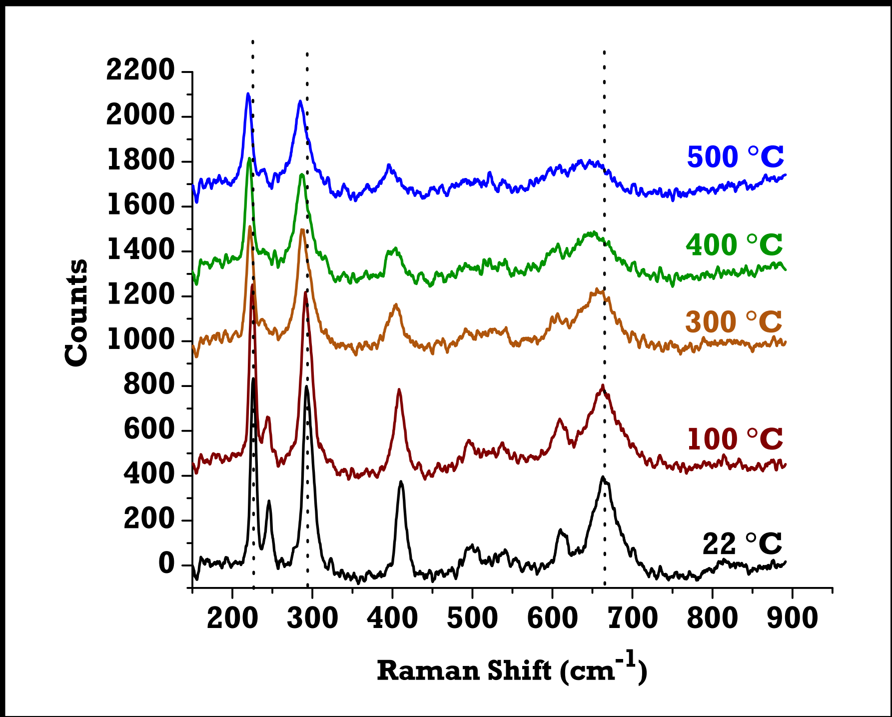
Raman signatures of powders optimized prior to heating mixture sample.

Fe_2O_3/Fe_3O_4 Powder Mixture

Heating



Cooling

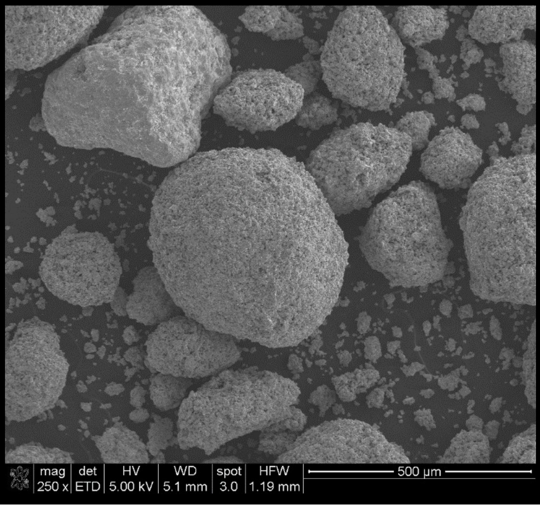


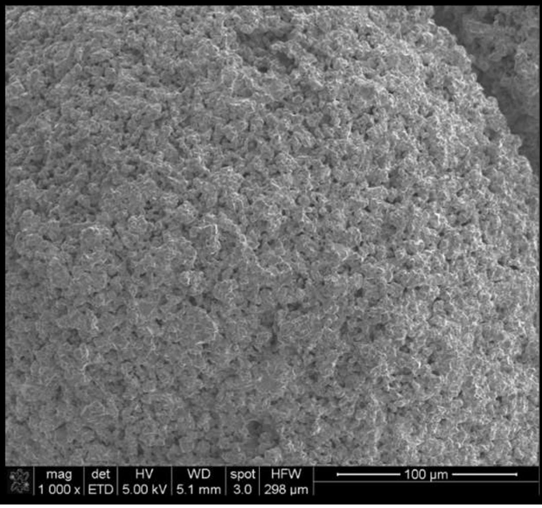
Fe_2O_3/Fe_3O_4 can be differentiated up to 600°C using CW 532 nm.

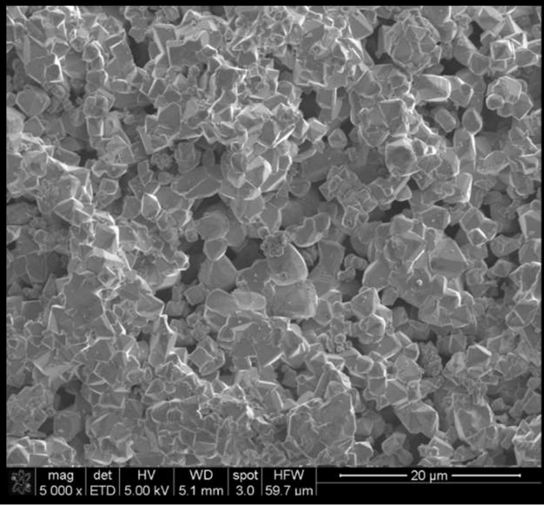
Next Steps

- **Optimize Collection of Raman Spectra**
  - Further investigate UV Raman
  - Finalize selection of laser wavelength
  - Utilize lock-in amplifier with photomultiplier tube to minimize spectral noise/background
- **Test NETL Samples**
  - Collect reference spectra prior to heating

CuO-Fe_2O_3-Al_2O

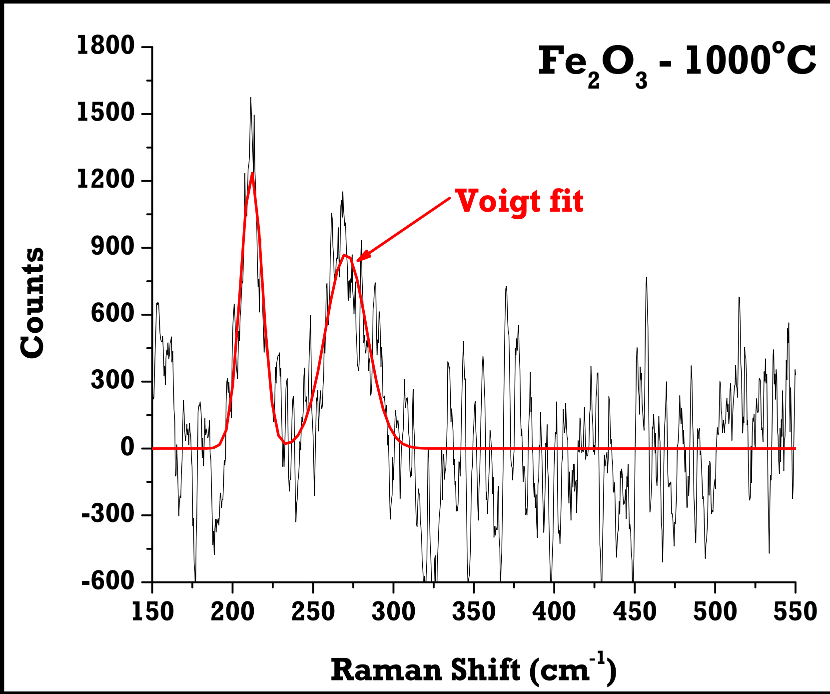




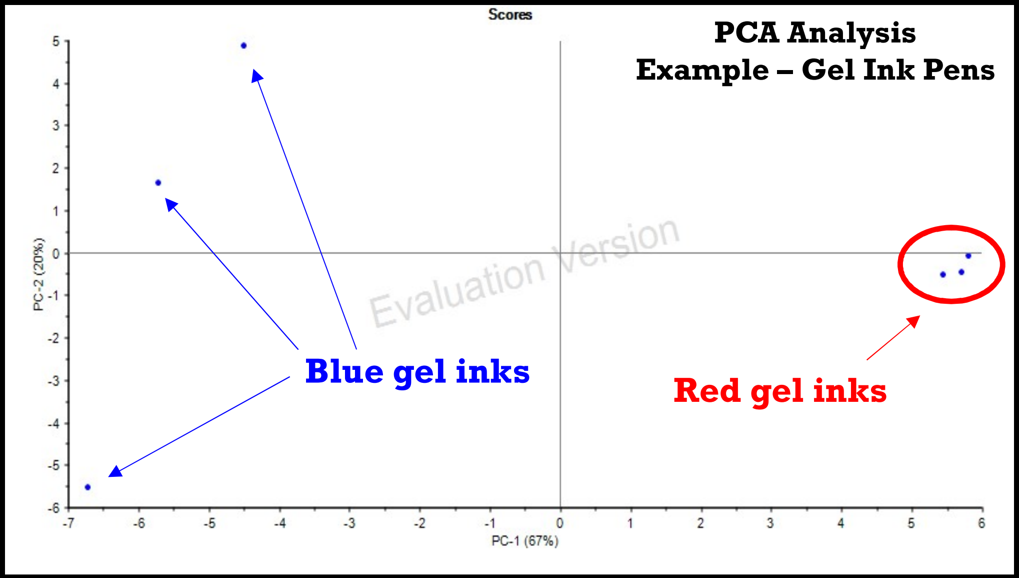


Next Steps

- **Perform Multivariate Statistical Analysis**
  - Collect reference measurements for calibration
  - Test chemometric software for our analysis
  - Determine relative mole fraction of OCPs at a given temperature



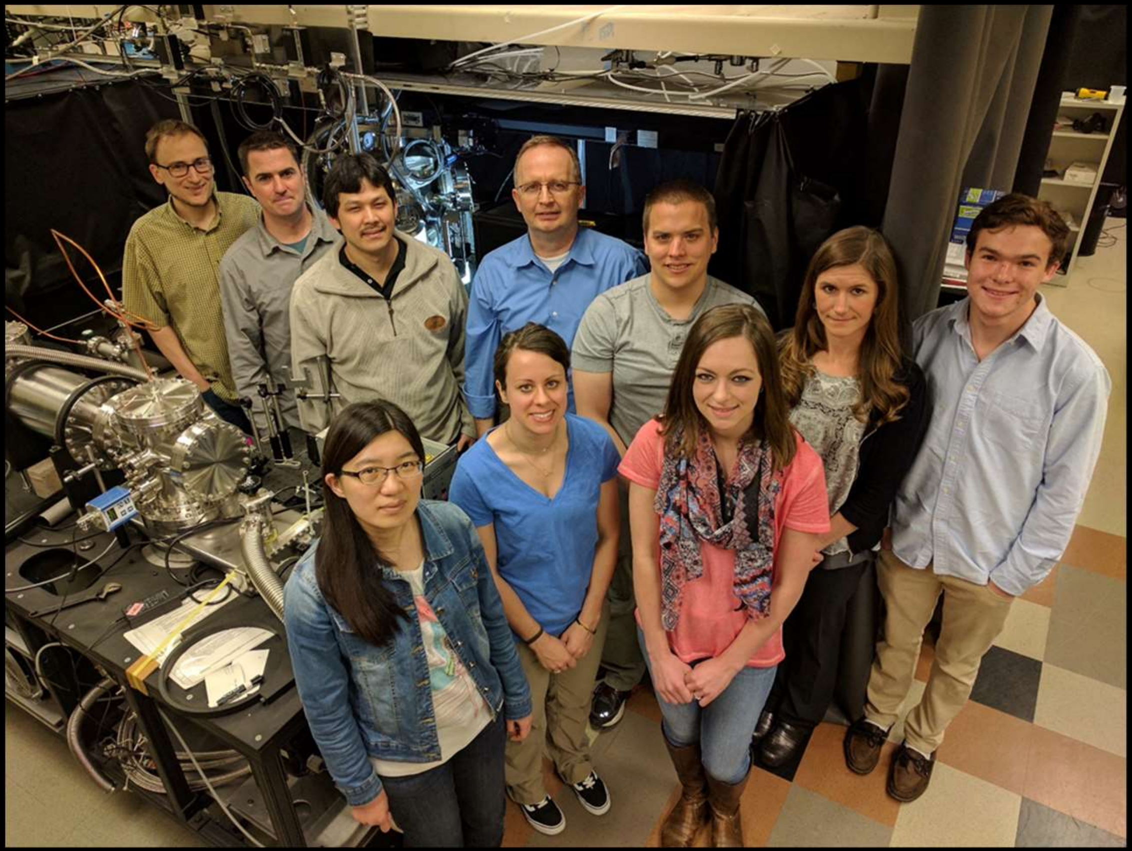
Multiple linear regression (MLR) could be a useful chemometric technique for our analysis.



Summary

- $CaSO_4$
  - Yields good spectra for both cw and low intensity pulses
  - Successfully measured spectra above 1000°C
  - LIBS observed with high intensity pulses
- Fe_2O_3 and Fe_3O_4
  - Shorter wavelengths and low intensity light ideal for avoiding LIBS and blackbody radiation
  - Benchmark Fe_2O_3 spectrum at 1000 °C achieved
  - Fe_2O_3 /Fe_3O_4 Raman spectra collected up to 600 °C
- Publications/Presentations
  - John Kirtley, Victoria Leichner, Benjamin Anderson, Hergen Eilers, "A comparison of pulsed and continuous lasers for high-temperature Rama n measurements of anhydrite," J. Raman Spectrosc. 10.1002/jrs.5356
  - John Kirtley, Victoria Leichner, and Hergen Eilers, "Raman spectroscopy of oxygen carrier particles in harsh environments," Invited Presentation, SPIE-DSS, April 16, 2018, Orlando, FL

Questions?



Thanks to DOE/NETL: FE0027840

ASL/ISP