

Raman Spectroscopy of TiO₂

Experiment #4

Characterization of Materials (96.445/545)

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Objective

The purpose of this laboratory is to identify two different phases (rutile and anatase) of TiO₂ by Raman spectroscopy. A secondary objective is to learn to use the Raman spectroscopy equipment and how to optimize the geometry of the data acquisition and the parameters such as integration time and laser power.

Experimental Equipment

The experimental equipment used for this lab included:

- Powdered TiO₂ samples Number 8 and Number
- Raman Systems, Inc. (RSI) RSL Plus R-3000 series and RSI Scan[®] software
- Raman Systems, Inc. (RSI) RSI-Indent[®] software.
- The X Powder software on the laboratory computer (to use for finding Raman Line position and FWHM).

The RSL we used had a 785 nm laser light, which is just beyond the red visible region. A red LED on the probe turns on when the laser is operating so that the beam can be focused on a sample. Safety goggles should be worn when this system is operated, but we didn't. Dark samples and samples optically opaque in the near infrared will heat up quickly with this laser focus. So, the samples are being turned. The actual spot size of the laser beam is about 100 microns. The typical low power setting for the RSL Plus is 125 mW, and the typical high power setting is 250 mW; for the R-3000 series the low setting is 90 mW and the high setting is 290 mW.

The spectrometer is supposed to be calibrated, and during typical operation this calibration is verified by measuring the peaks of a Teflon cap using the verification option of the software. We didn't have the Teflon (polytetrafluoroethylene) cap, and we didn't verify the calibration.

Procedure

1. Sample Preparation

The samples were already prepared by the instructor, and labeled with a number that didn't identify their phase. We know they are TiO₂.

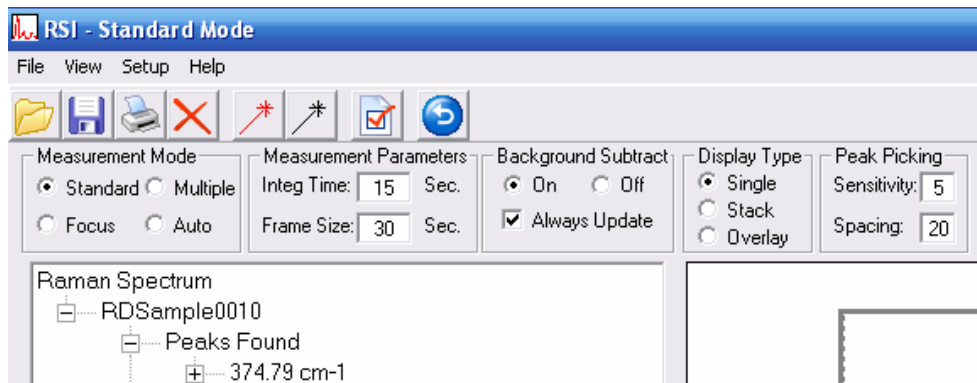
2. Loading the Raman specimen holder

The powder samples were loaded into the turning specimen holder. Scotch tape was used to keep the specimen holder from walking around the table during acquisition. We measured the rotation rate to be about 1 rotation in 5 seconds.

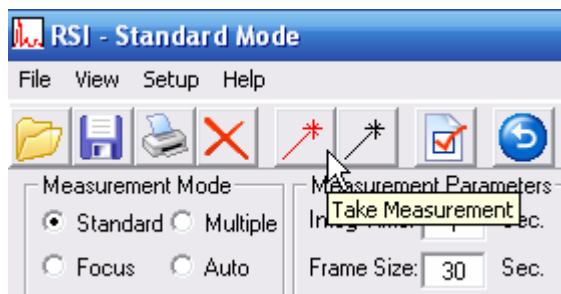
3. Acquire exposures.

First we tried Number 8, but didn't get quality data. So then we did Number 9. After acquiring data for Number 9, we tried Number 8 again. In both cases, the XRF data identified Ti, so we

concluded that the compounds were both TiO_2 . The system is activated by first turning it on and then turning a key on the laser power control box. The software on an accompanying laptop provides the user interface for operating the system and managing the data. We defined the low power as being 12 O'Clock setting on the power knob, medium as being 5 O'Clock, and high as being 10 O'Clock.



To display the control parameters, press the arrow key. We did this and tried exposures of 3, 5, and 10 seconds for sample 8, and 10 and 30 seconds for sample 9. To take a measurement, the take measurement button is clicked:



Then, the status bar on the software tells what stage of the acquisition is current: acquiring background, or collecting data, or saving data. The plot is displayed afterward, and automatically saved with sequential filenames.

4. Save Exposures and Data

We saved the data to disk, converted the csv (comma separated value text format) for use in X Powder to find the Raman lines and FWHM values. Using this hack in X Powder, the offset of the plots is manually set from 3.01 (default) to 0.01. The line positions which X Powder interprets as a 2θ value, are calibrated by multiplying by 10 and adding 200 to get to wavenumber (cm^{-1}) values. The positions of the center of the line, the right and left side half peak positions are found interactively and calibrated to cm^{-1} .

Results and Discussion

Determination of Optimal Settings

Trial and error seems to be the only method for finding the optimal settings. To get good signal to noise statistics, typically longer integration times are used. But with this system, there is no way to set the gain values. Figure 1 shows the saturated values that are acquired when long integration times are used; here sample 8 was measured with a 20 second integration time at the lowest power setting. To find the optimal integration time, we simply tried different time settings and visually assessed the quality of the scan. For sample 9, Figure 2 shows the difference of a quality spectrum (blue) when integration time was 30 seconds, and one with too low of a signal to noise (red) when 10 seconds was used both for the lowest power laser setting. The optimal integration time was significantly different for sample 9 and sample 8. But it did not seem to depend on the power setting of the laser, although the highest power setting showed the most variation in the data sets from set to set (Figure 3). Good statistics can be acquired by averaging multiple runs, and using low or medium power settings. The next section shows that the FWHM did not depend very much on the settings. Figure 4 shows the bizarre behavior of some of the CCD pixels. Occasionally the data are fine, but more often than not, they are either missing or spiked. This is probably telegraph noise (Hung, 1990).

Figure 1: Saturated Values (Sample 8, 20 second integration time, lowest power setting)

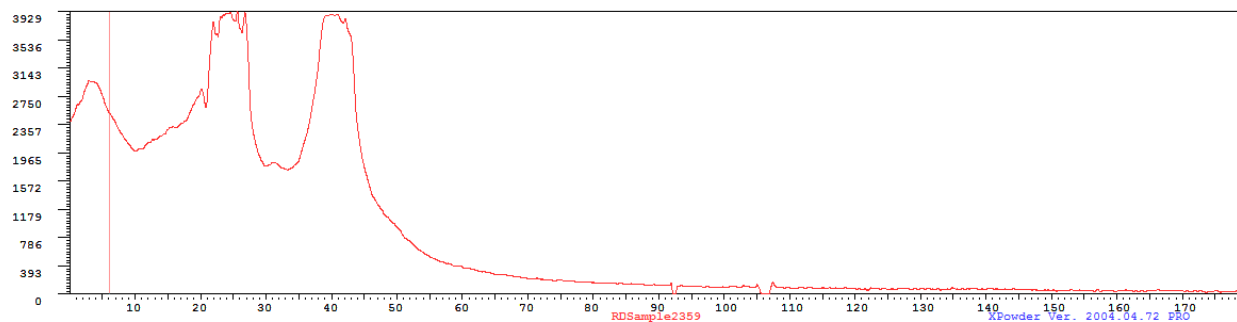


Figure 2: Sample 9 with 30s (good) and 10s (too low) integration times

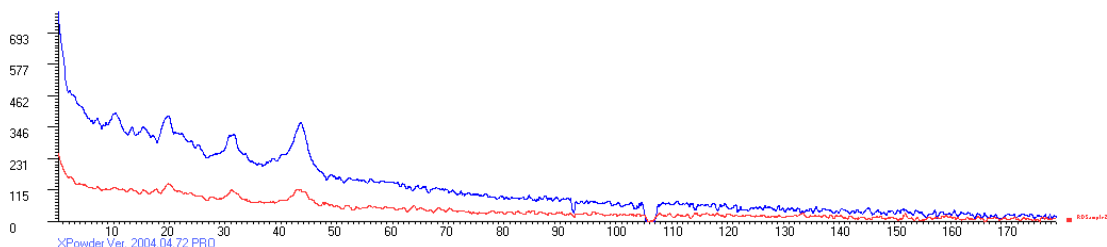


Figure 3: Stacked Acquisitions Show Signal Variations (Sample 9, 30 second, highest power)

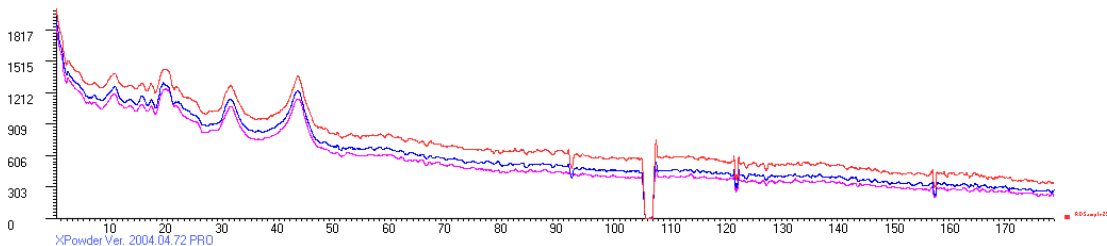
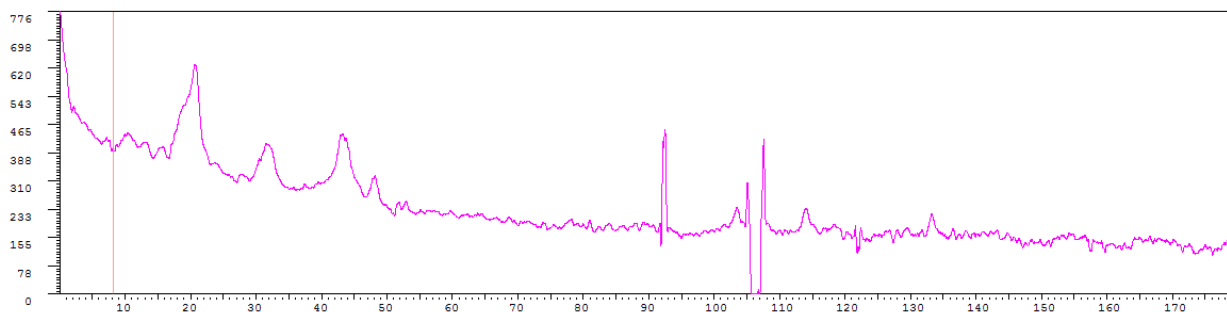


Figure 4: Telegraph Noise



Determination of Optimal Settings

Using a hacked procedure for X Powder, the Raman lines for Sample 8 and Sample 9 were determined and are in Table 1 and Table 2. The co-added spectra are provided in Figure 5 and Figure 6.

Table 1: Sample 8 Raman Line Measurements

Number of Runs	Power Setting	Exposure time	Line Center cm^{-1}	FWHM cm^{-1}	Line Center cm^{-1}	FWHM cm^{-1}
3	Medium	5 s	443.8	42	604.9	40
3	Low	5 s	443.5	40	605.7	40
3	High	3 s	443.0	40	605.6	40

Table 2: Sample 9 Raman Line Measurements

Number of Runs	Power Setting	Exposure time	Line Center cm^{-1}	FWHM cm^{-1}	Line Center cm^{-1}	FWHM cm^{-1}	Line Center cm^{-1}	FWHM cm^{-1}
4	Low	30 s	397.5	45	514.6	35	635	42
3	Medium	30 s	395.9	38	514.6	35	633.3	41
3	High	30 s	397.5	43	514.6	35	633.3	40

Figure 5: Sample 8 High Power (Bottom), Medium Power (Middle), Low Power (Top)

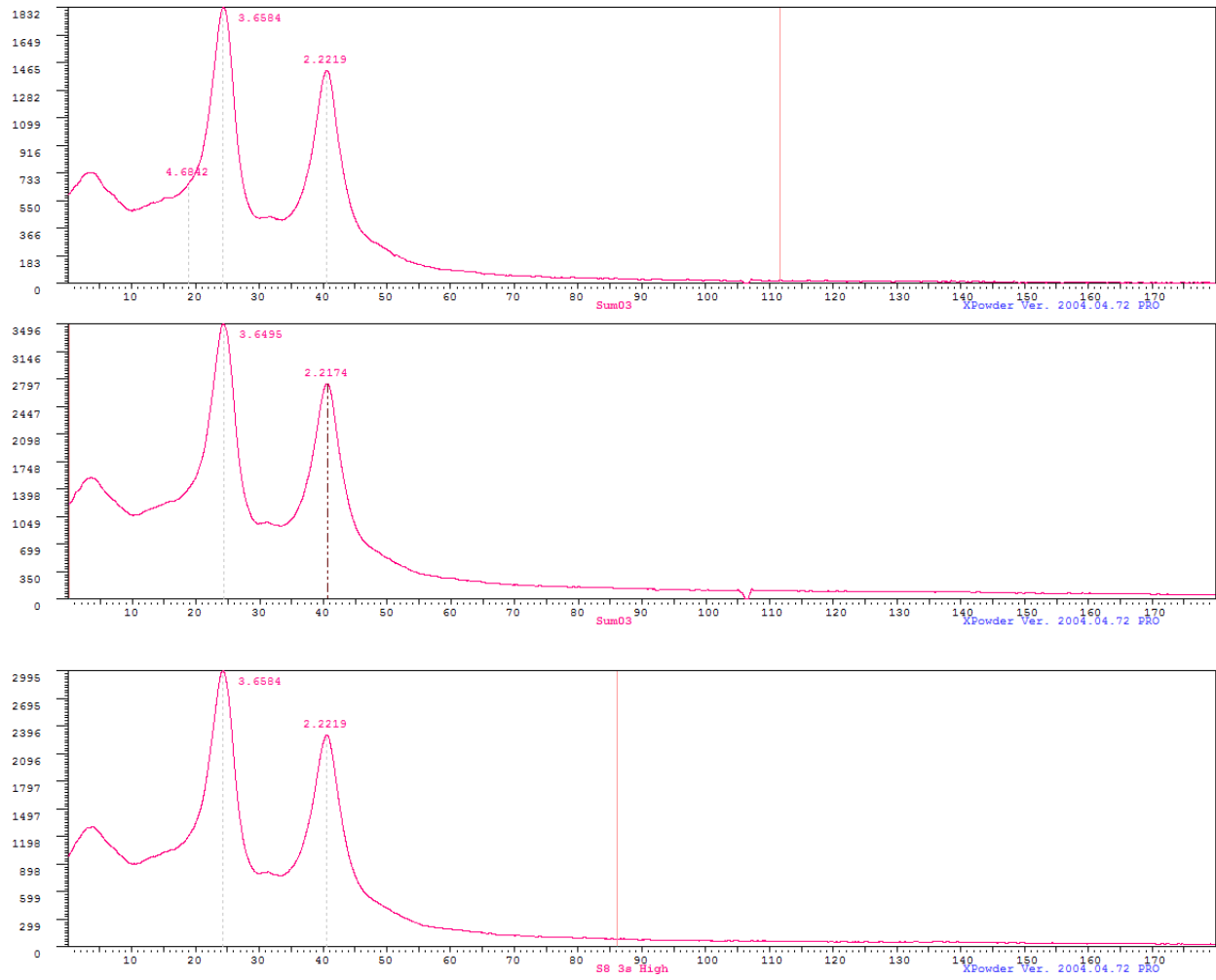
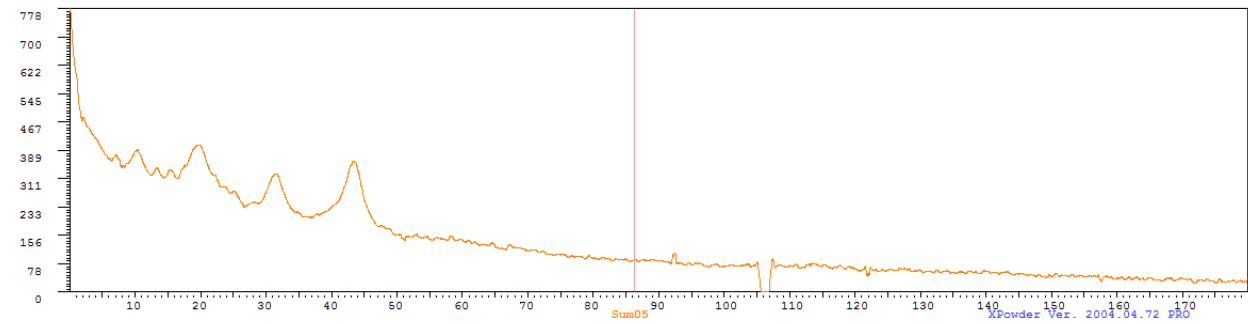
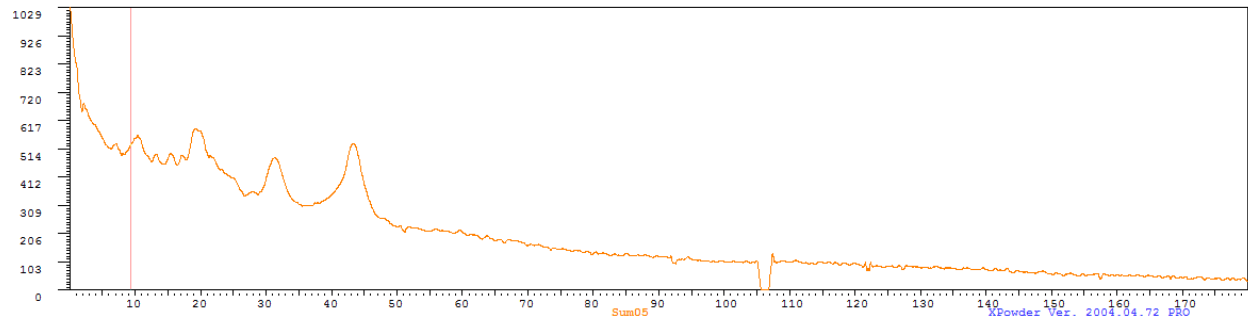
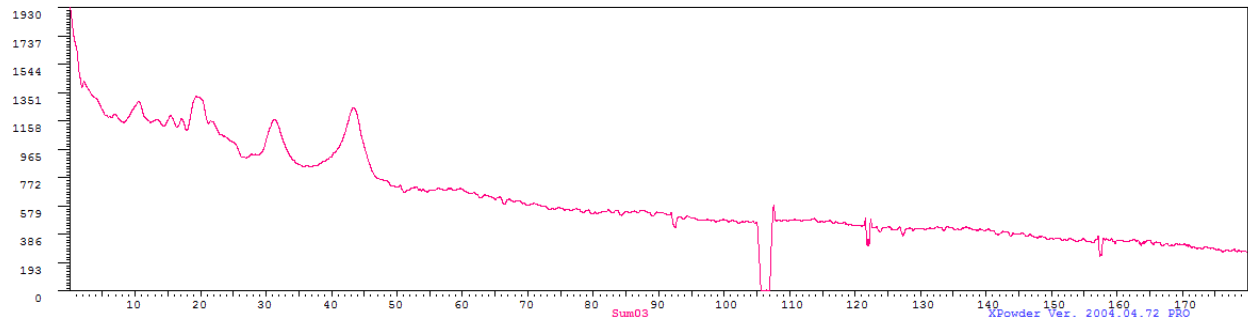


Figure 6: Sample 9 High Power (Bottom), Medium Power (Middle), Low Power (Top)



Conclusions

The optimization of RSI Raman equipment settings has already been discussed. The values found for the Raman lines of Sample 8 and Sample 9 were compared to values from the literature. Table 3 shows the values reported by Ma (2007). We can easily conclude that Sample 8 is the rutile phase and sample 9 is the anatase phase. The anatase values are well within experimental error. All three measurable Raman vibration modes (B_{1g} , A_{1g} , and E_g) were active. The other E_g modes are below the measurement capabilities of our system. The multiphonon 235.5 cm^{-1} mode of the rutile sample was evident in the spectra, but the value and width were not extrapolated. The 825.5 cm^{-1} was not evident, not even in the saturated exposure (Figure 1). Ma used a 514 nm laser (20 mW) to do the measurements in Table 3. It is likely that our system is too far into the infrared to see this mode. The E_g and A_{1g} modes were measured.

Table 3: Raman Shifts Measured by Ma (2007).

	This article	Arsov et al. [24]	Assignment [25]
Rutile			
	140.2	143	B_{1g}
	235.5	236	Multi-photon process
	445.8	447	E_g
	609.8	612	A_{1g}
	825.5	826	B_{2g}
Anatase			
ν_1	140.9	144	E_g
ν_2	196.3	197	E_g
ν_3	396.0	399	B_{1g}
ν_4	515.4	516	A_{1g}
ν_5	515.4	516	B_{1g}
ν_6	632.7	639	E_g

References

- [1] Operation Manual For RSLplus • R-3000 series • RSIscan® software, www.ramansystems.com
- [2] Hung, K. K., P. K. Ko, Chenming Hu, and Yiu Chung Cheng, Random Telegraph Noise of Deep-Submicrometer MOSFET's, IEEE Electron Device Letters, Vol 11, No. 2, February 1990.
- [3] Ma H.L., J.Y. Yang, Y. Dai, Y.B. Zhang, B. Lu, G.H. Ma, "Raman study of phase transformation of TiO₂ rutile single crystal irradiated by infrared femtosecond laser," Applied Surface Science 253, 2007