X-Ray Powder Diffraction and Raman Spectroscopy of CaF_2 (Fluorite) and $CaCO_3$ (Calcite)

Experiment #5

Characterization of Materials (96.445/545)

Meg Noah

Objective

The purpose of this lab is to characterize the similarities and differences of natural and synthetic CaF2 and to study the Raman spectrum of calcite. We want to better understand synthetic fluorite because it is used for optical equipment.

Experimental Equipment

The experimental equipment used for this lab included:

- Powdered and bulk samples of synthetic fluorite, bulk natural fluorite, bulk natural calcite
- Raman Systems, Inc. (RSI) RSL Plus R-3000 series and RSI Scan® software
- Raman Systems, Inc. (RSI) RSI-Indent® software.
- The XPowder software on the laboratory computer (to use for finding Raman Line position and FWHM).
- The inXitu BTX system of hardware and software
- The XPowder software on the laboratory computer

The BTX system and XPowder software were described in detail in the last lab report.

Procedure

1. **Sample Preparation**
   The synthetic fluorite samples were already prepared by the instructor, and I donated the natural calcite and fluorite to the lab – these samples were already cleaved.
2. **Acquire Raman Exposures**
   The BTX was not operational the day of our experiment, but Dr. Stimets and Hongmei Chen had previously perfomed analysis on the powder synthetic fluorite.
3. **Acquire Raman Exposures**
   The procedure for acquiring the Raman spectra was described in the last laboratory write-up, and was used here. The bulk samples were not rotated, but the powder was.

Results and Discussion

Elements identified with X-Ray fluorescence

CaF_2 and $CaCO_3$ can't be chemically determined by X-Ray fluorescence. There is an impurity in the synthetic CaF_2 that can be found with X-Ray fluorescence, but the machine wasn't working when we did the lab.

Structure found in XPowder

Dr. Stimets and Hongmei Chen performed powder diffraction analysis of the powder synthetic

Figure 1: Powder Synthetic CaF_2

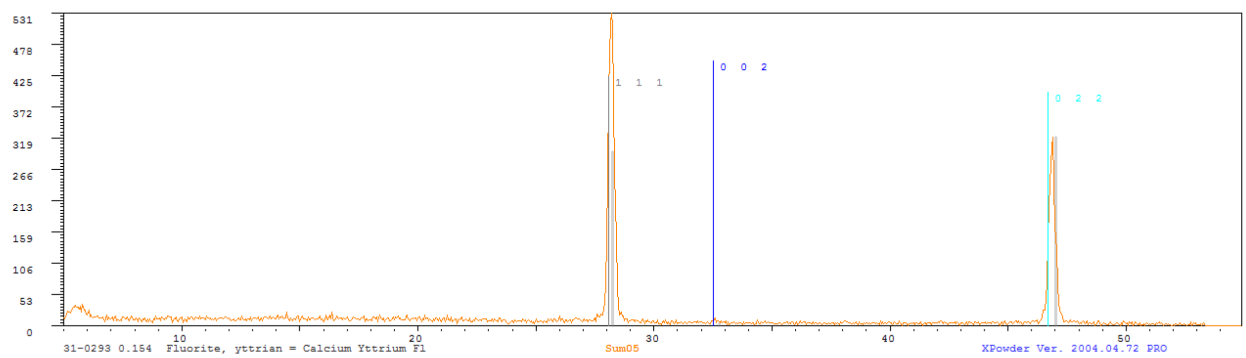


Table 1: Powder Synthetic CaF_2 Unit Cell and Diffraction Intensities

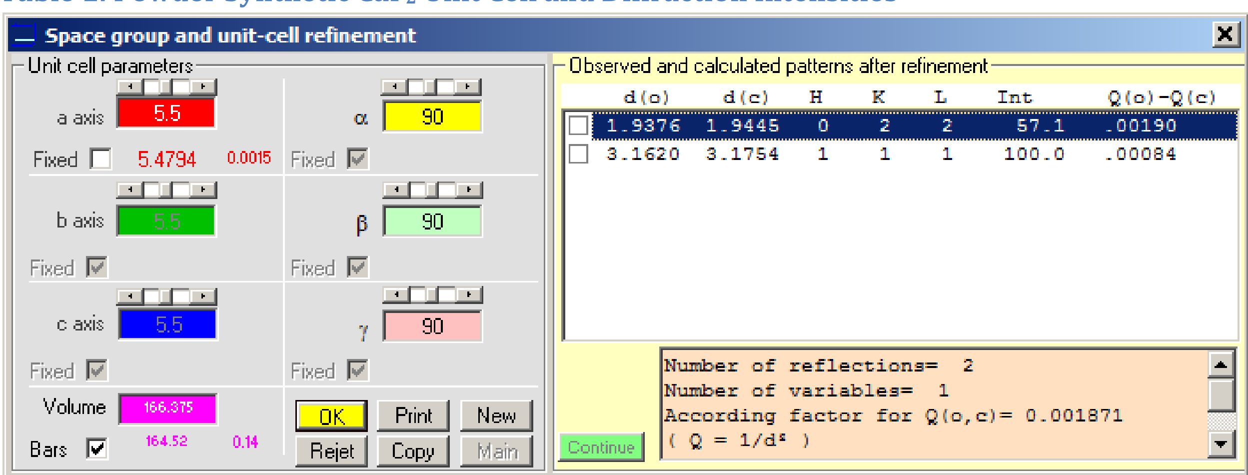


Figure 2: Powder Synthetic CaF_2

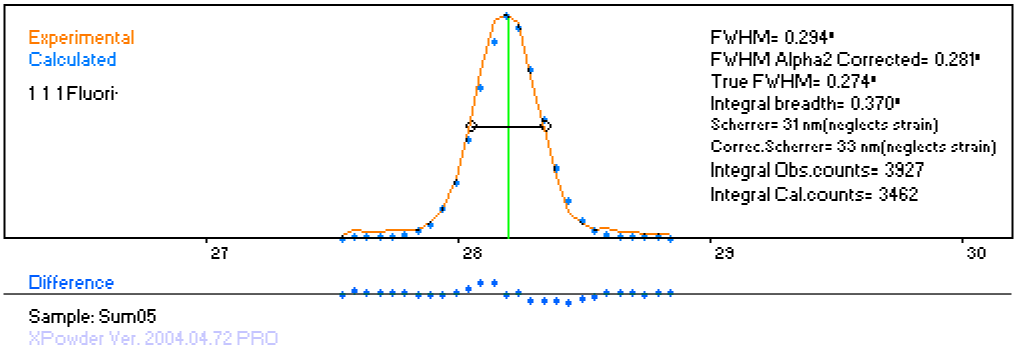
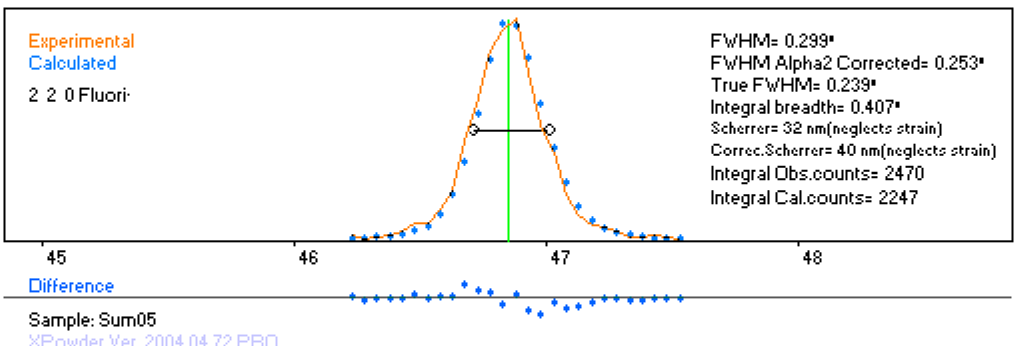


Figure 3: Powder Synthetic CaF_2



Raman Lines

Table 2: Our Measurements

Observed **Frequencies** of Raman-Active **Modes** effect on the line widths and line shapes.

Sample	RDSample CaF2	rotation period (10 seconds)	
Laser power **low** (12 o'clock)			
	2487	10s	
	2488	10s	
	2489	10s	
	2390	10s	
Beautiful Fine Spot			
High Power (10 o'clock high power)			
	2492	10s	
	2493	10s	
Beautiful Little Spot			
Medium Power (3 o'clock high power)		10s	
	2496	10s	
	2497		
	2498 bad	10s	
	2499	10s	
	2500	10s	
Meg's Sample	Purple Natural Fluorite	Raman Peak	
	10s		
	10s		
Blue Natural Fluorite			
	10s		
	10s glitch		
	10s glitch		
	2506		
	2507	10s	nice
	2508		
	2509	10s	glitch
Clear Natural Fluorite			
	10s nice		
	2511	10s	
	2514	10s	
CaCO3		10s	
	10s		
	10s		
CaCO3	2519	10s	
	2520	10s	
	2521	10s	
	2522	10s	
	2523	10s	
	2524	10s	
	2525	10s	
	2526	10s	

Figure #3 (Sum 02 2492 2493)

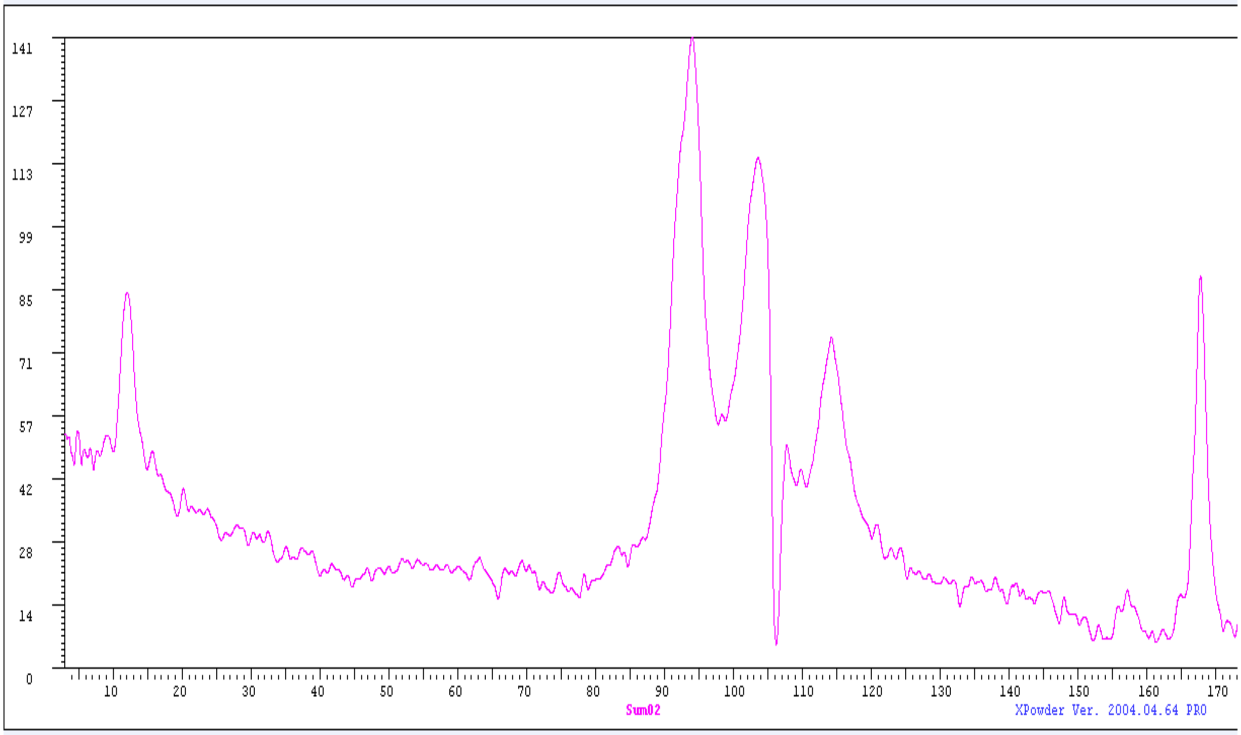


Figure #4 (Sum 03 2496 2497 2500)

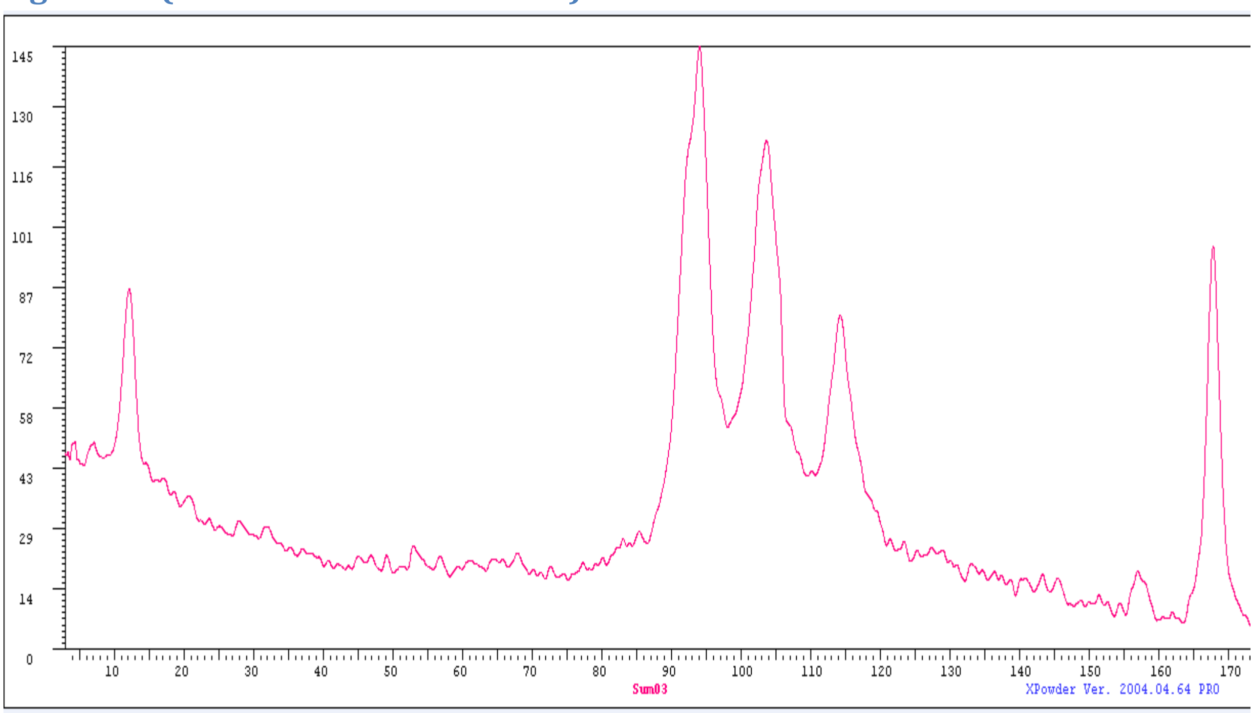


Figure #5 (Sum 04 2510 2511 2512 2514 One nice peak)

um 04 2510 2511 2512 2514 One nice peak)

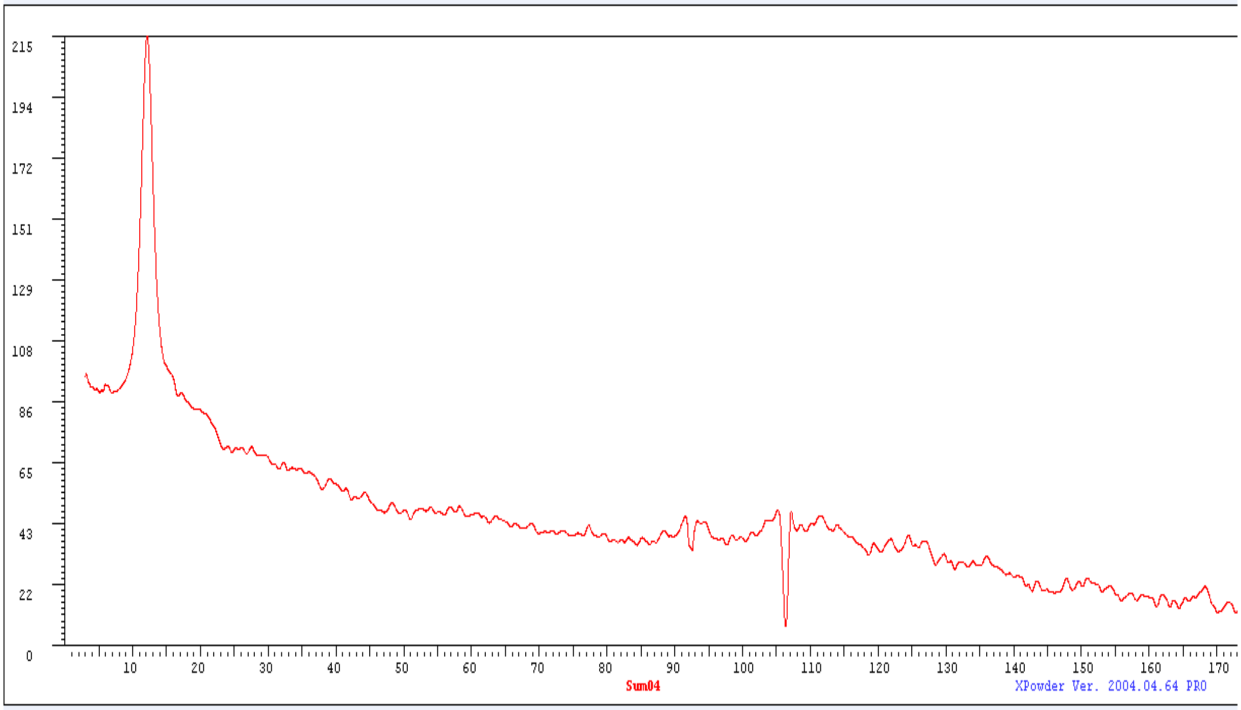


Figure #6 (Sum 05 2501 2502) Purple

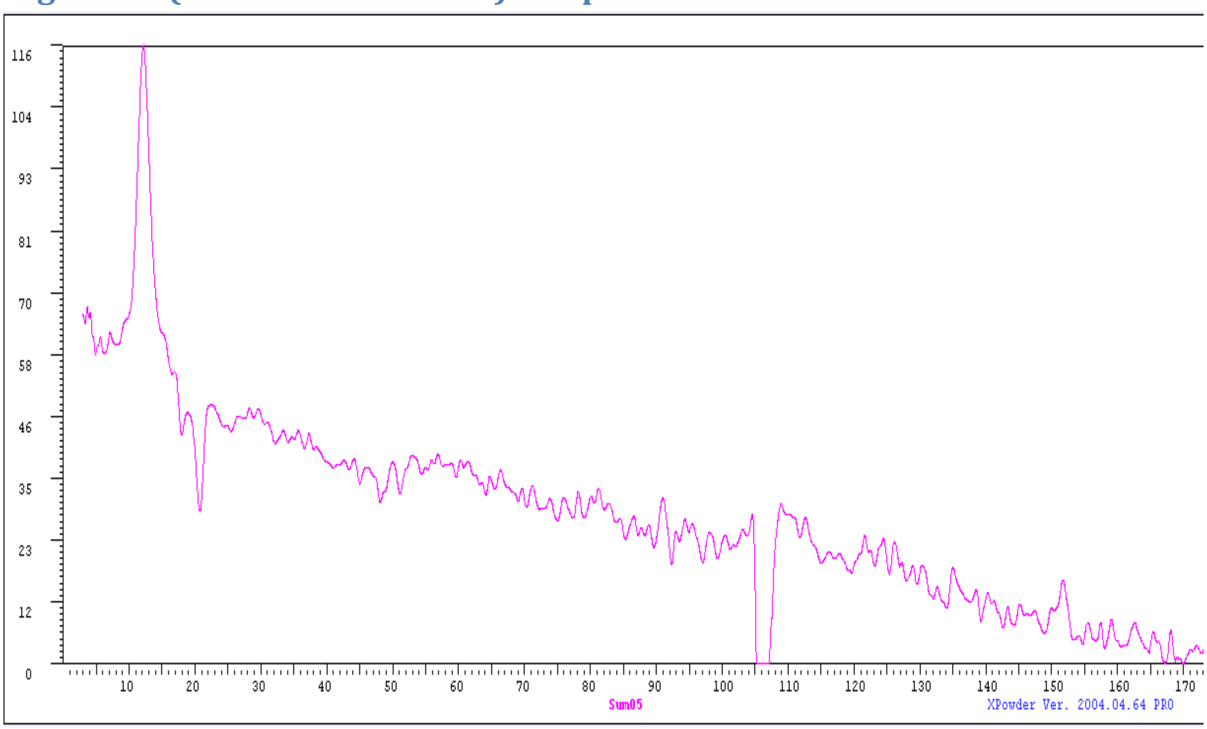


Figure #7 Blue (Sum 06 2503 2504 2505 2506)

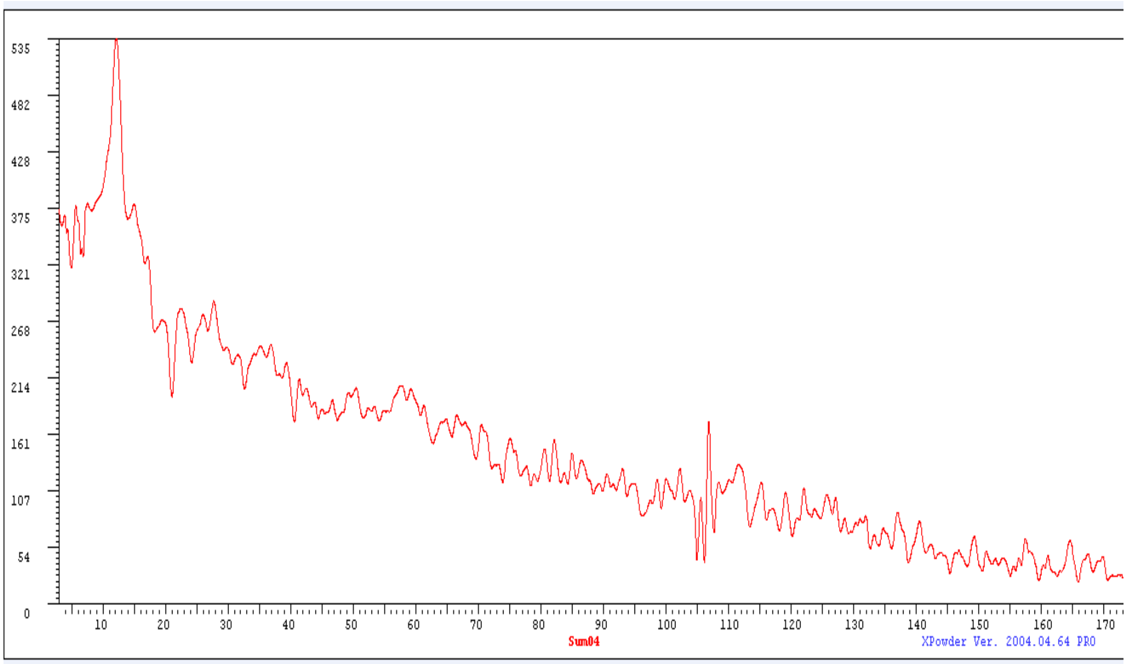


Figure #8 blue Sum 07 (2501 2502 2503 2506 2507 2508)

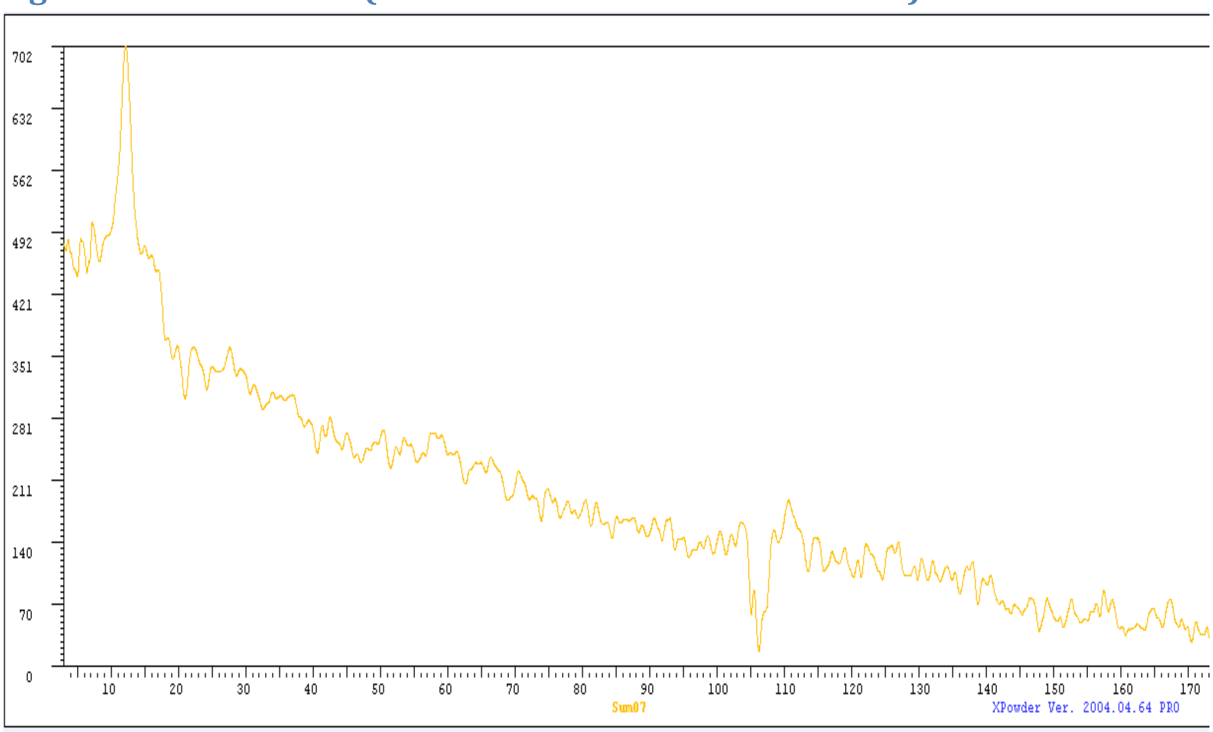


Figure #9 Sum 08 (2515 2516 2517 2518)

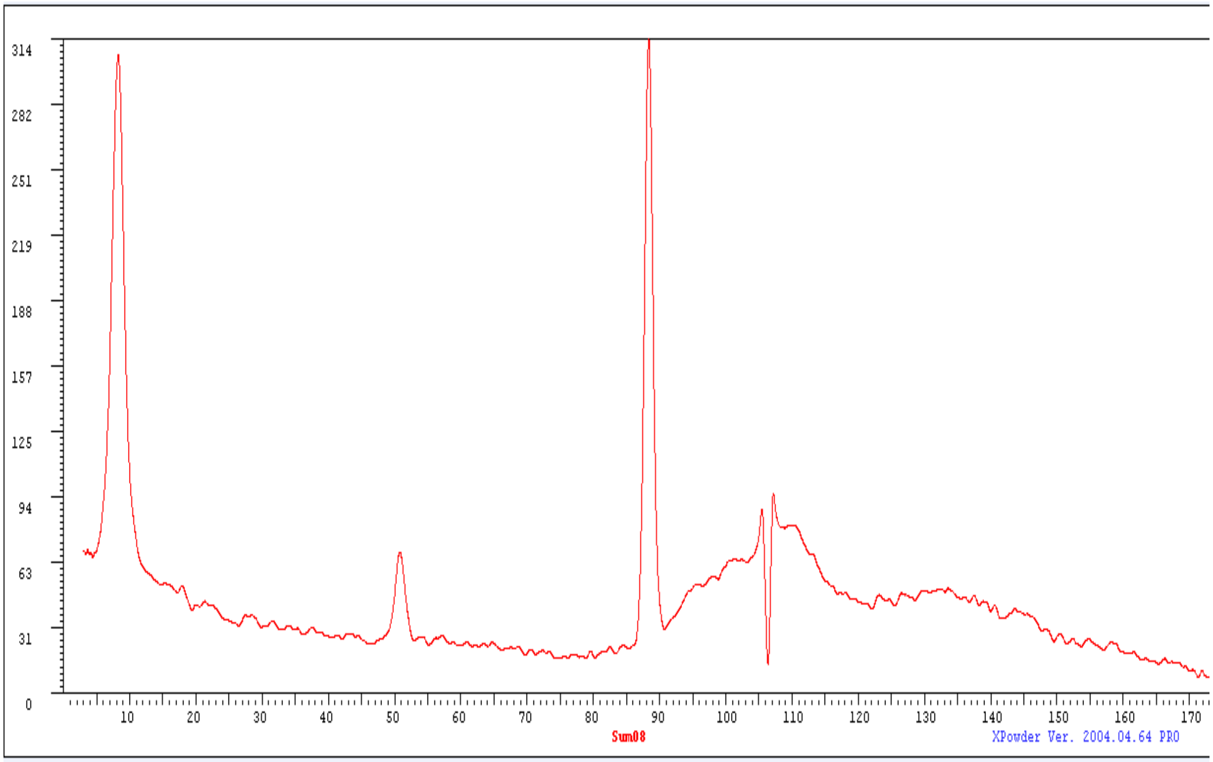


Figure #10 (Sum 09 2519 2520 2521 2522)

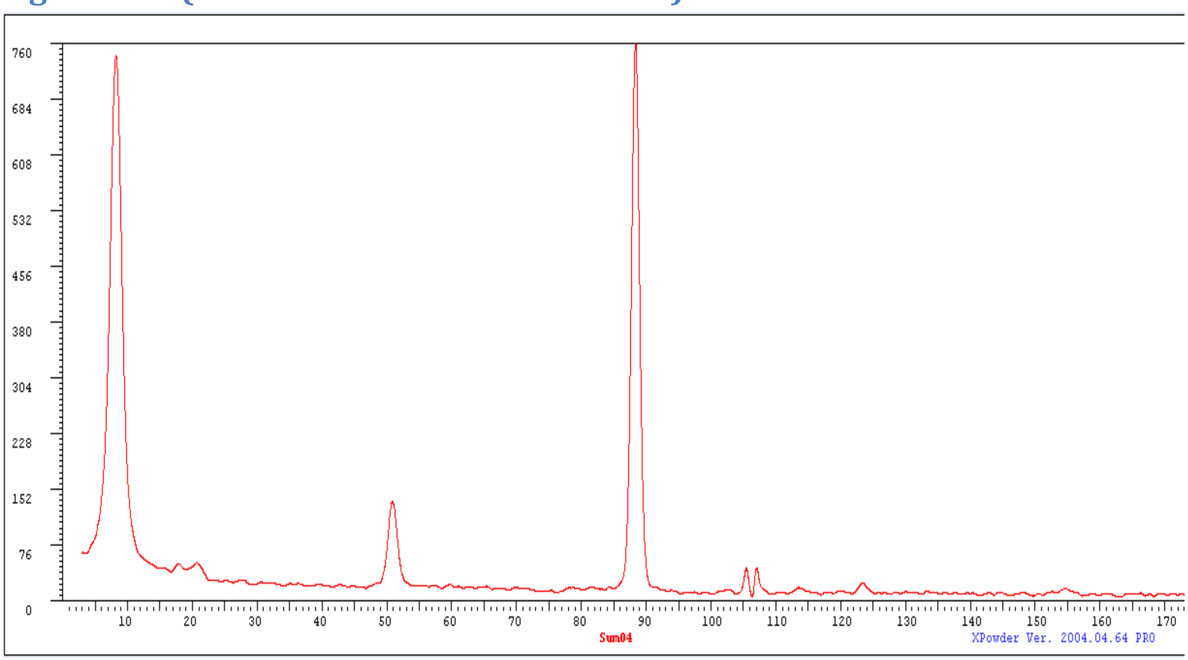
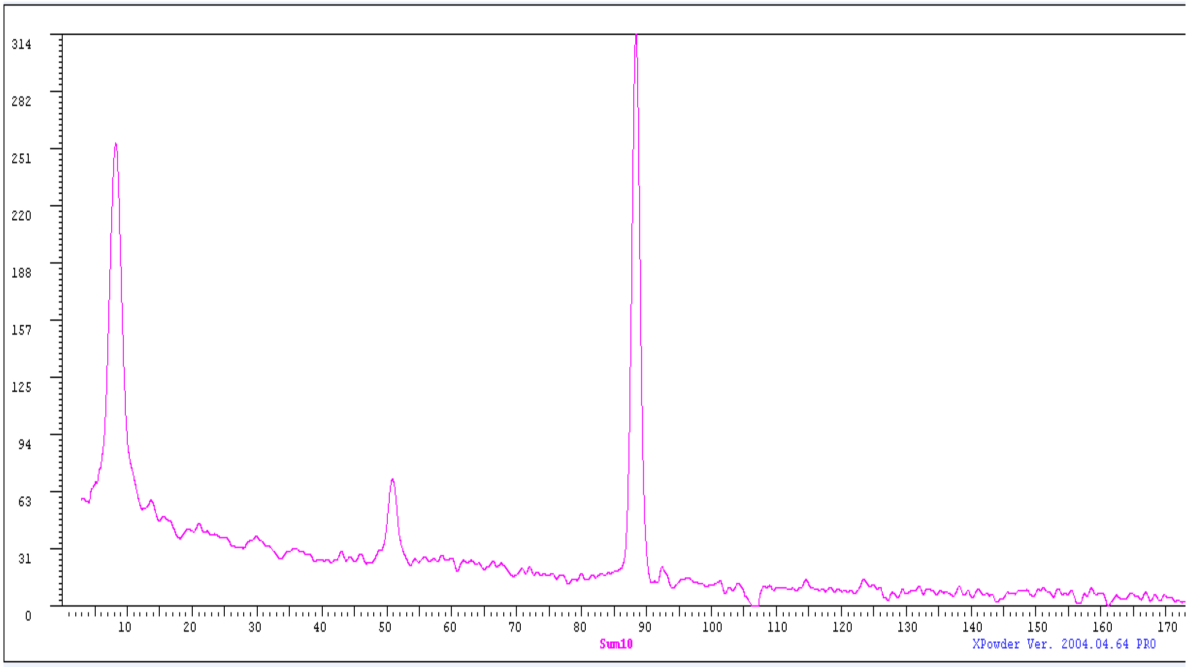


Figure 11 (Sum 10 2523 2524)



Figure#12 (Sum 11 2525 2526)

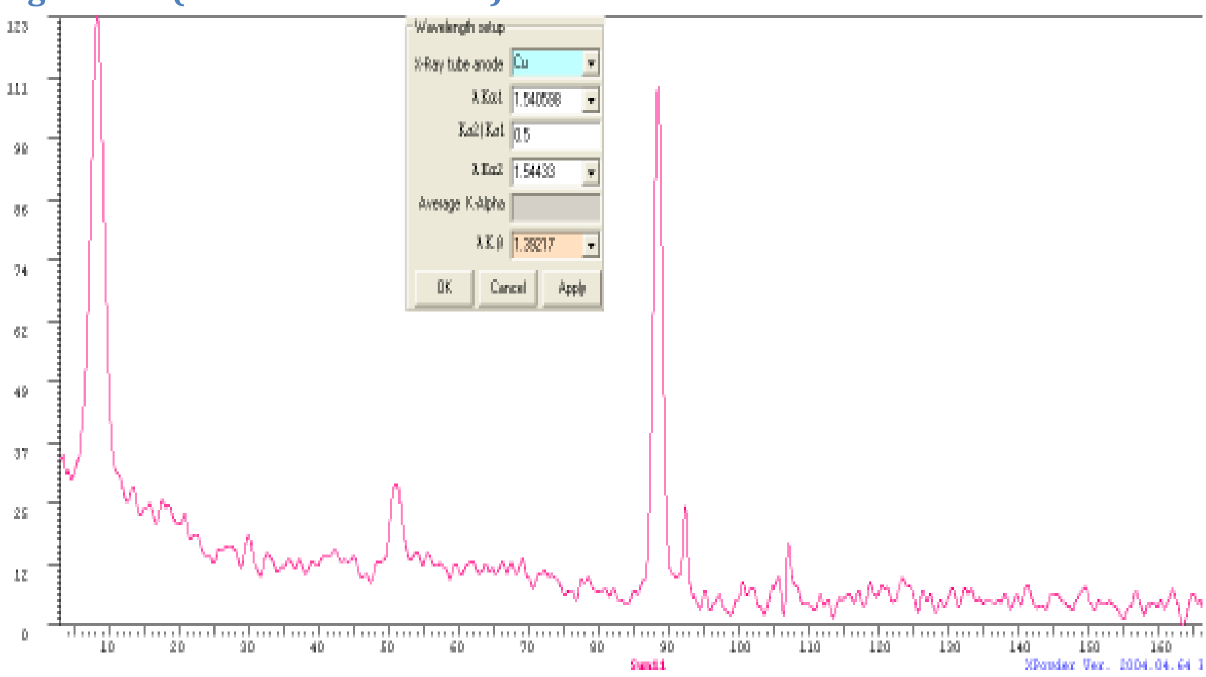


Figure #13(Sum 01 2487 2488 2489 2490)

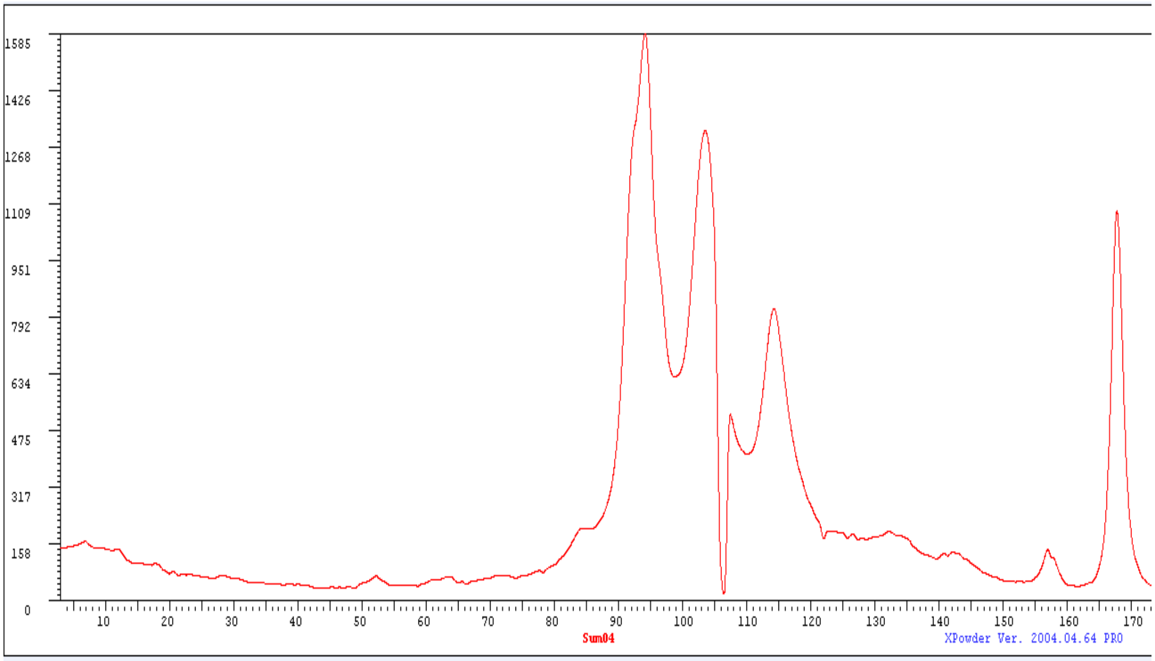


Table 3: Raman Line Measurements (cm-1)

Sum 01 (2487 2488 2489 2490)					5 peaks								
w1	Δw	w2	Δw	w3	Δw	w4	Δw	w5	Δw				
1141	50	1231	37	1343	40	1773	27	1879	25				
Very Strong		Strong		moderate		weak		Strong					
Sum 02 (2492 2493)													
w1	Δw	w2	Δw	w3	Δw	w4	Δw	w5	Δw				
1095	64	1104	48	1198	312	1312	39	1849	21				
moderate		Strong		strong		moderate		strong					
Sum 03 (2496 2497 2500)													
w1	Δw	w2	Δw	w3	Δw	w4	Δw	w5	Δw	w6	Δw		
320	16	1135	38	1231	38	1344	33	1773	22	1817	25		
Moderate (Intensity : 87)		Strong		Strong		moderate		weak		Strong			
Sum 04 (2510 2511 2512 2514) One nice peak													
w1	Δw												
322	23												
Strong (Intensity: 215)													
Purple Sum 05 (2501 2502)													
w1	Δw	w2	Δw										
322	22	1711	24										
Strong (Intensity: 116)													
Blue Sum 06 (2503 2504 2505 2506)													
w1	Δw												
315	23												
Strong (Intensity: 535)													
Blue Sum 07(2501 2502 2503 2506 2507 2508)													
w1	Δw												
320	19												
Strong (intensity: 702)													
Sum 08(2515 2516 2517 2518)													
w1	Δw	w2	Δw	w3	Δw								
282	21	708	17	1085	15								
Strong (Intensity: 312)		weak		Strong									

Table 3: Raman Line Measurements continued

Sum 09(2519 2520 2521 2522)											
w1	Δw	w2	Δw	w3	Δw	w4	Δw	w5	Δw		
282	21	710	16	1083	20	1254	9	1276	10		
Strong (intensity: 758)		weak		Strong		weak		weak			
Sum 10(2523 2524)											
w1	Δw	w2	Δw	w3	Δw						
282	22	708	16	1083	18						
Strong (intensity: 252)		weak		Strong							
Sum 11(2525 2526)				(three peaks)							
w1	Δw	w2	Δw	w3	Δw						
281	24	710	13	1085	15						
Strong		weak		Strong							

Conclusions

X-Powder determined the lattice constant a value equals **5.4795**. The corresponding intensity equals 99 for 111 mode and **57** for 012 mode. Table 4 shows the measured modeled line intensities for CaF2, which are very close to the relative strengths that we measured. In previous modeling of X-Ray lines, we didn't use the correct atomic form factor that uses Cromer-Mann Coefficients for the CaF2 it is:

$$f^{o}(\sin\theta/\lambda) = \sum_{i=1}^{4} a_i \cdot e^{-b_i(\sin\theta/\lambda)^2} + c$$

Cromer-Mann coefficients for CA, z = 20				
f/i	1	2	3	4
a	8.627	7.387	1.590	1.021
b	10.442	0.660	85.748	178.437
c	1.375	-	-	-
Z calculated from Cromer-Mann coefficients= 20.000				
Cromer-Mann coefficients for F , z = 9				
f/i	1	2	3	4
a	3.539	2.641	1.517	1.024
b	10.283	4.294	0.262	26.148
c	0.278	-	-	-
Z calculated from Cromer-Mann coefficients= 8.999				

Table 4: Modeled CaF2 Line Intensities

(h,k,l)	M	d(Ang)	T(Deg)	fF	fCa	nfF	nfCa	S(hkl)	LP(T)	Intensity	
(1 1 1)	8	3.14714	28.33	7.14	14.09	0.00	4.00	56.35	3.82	97014.7	100.0
(2 2 0)	4	1.92722	47.12	5.42	11.34	8.00	4.00	88.70	1.25	39304.5	40.5
(2 0 0)	4	2.72550	32.83	6.72	13.39	-8.00	4.00	-0.20	2.78	0.4	0.0
(1 0 0)	4	5.45100	16.25	8.13	16.25	-0.00	0.00	-0.00	12.15	0.0	0.0
(1 1 0)	4	3.85444	23.06	7.60	14.97	0.00	0.00	0.00	5.90	0.0	0.0
(2 1 0)	8	2.43776	36.84	6.34	12.79	0.00	0.00	0.00	2.16	0.0	0.0

The position, the full width at half maximum and the intensity of the Taman line 322 cm^-1 for each sample has been shown. The rare earth could absorb photons in a band extending several hundred cm^-1 on either side of the 785-nm laser line are **Nd, Dy, Er, Tm.** Among these rare earths, **Nd, Dy** have an energy level below the excited level so that, when the electron relaxes to this lower level, it can emit a photon of somewhat lower energy and longer wavelength which looks like a Raman shift.