A - Transformation of anatase into rutile

Anatase and rutile are two distinct phases of titanium dioxide TiO_2. The stable phase is rutile.

1. Structural study

Anatase: tetragonal system. (see PDF file)

1.1 Determine the Bravais lattice. Determine the number Z of chemical formula per unit cell.

1.2 Determine the position of the most intense diffraction peak for λ (Cu K_α).

Rutile: tetragonal system (see PDF file)

1.3 Determine the Bravais lattice.

1.4 Determine the indices and the line parameter of the line defined by the points 1 0 0 and 1 1 2.

1.5 Determine the angle between the lines [1 0 0] and [1 1 2].

1.6 Determine the indices of the plane family containing the lines [1 0 0] and [1 1 2].

1.7 Determine the Miller indices of the plane containing the points 1 0 0, 1 1 2 and -1 0 0.

2. Experimental study

The sample holder is a circular silicon wafer (face 511) with diameter 50 mm. The powder is sieved and homogeneously spread on the wafer on a circular area with diameter 35 mm. The recording parameters are:

- Sample holder: Si wafer (face 511), diameter 50 mm
- Mass of the sample: 30 mg
- Diameter of the sample: 35 mm
- recording : 10 to 80 ° 2θ
- step : 0.04 ° 2θ
- dwell time for one step : 2 s
- $\lambda(CuK_{\alpha 1})$: 1.5405981 Å
- Fixed slit opening 0.6 °
- Sample rotation yes

2.1 What is the time length of the record?

2.2 Determine the position of the diffraction peak of the wafer (Si, cubic, a = 5.4309 Å)

The apparent density of the powder on the wafer is estimated about 2.3 $g.cm^{-3}$.

2.3 Determine the thickness on the sample on the wafer.

2.4 Determine the linear absorption coefficient and the average penetration length of the X-ray beam. What conclusion can you infer?

The irradiated area of the sample is a rectangle with variable length and fixed width 12 mm.

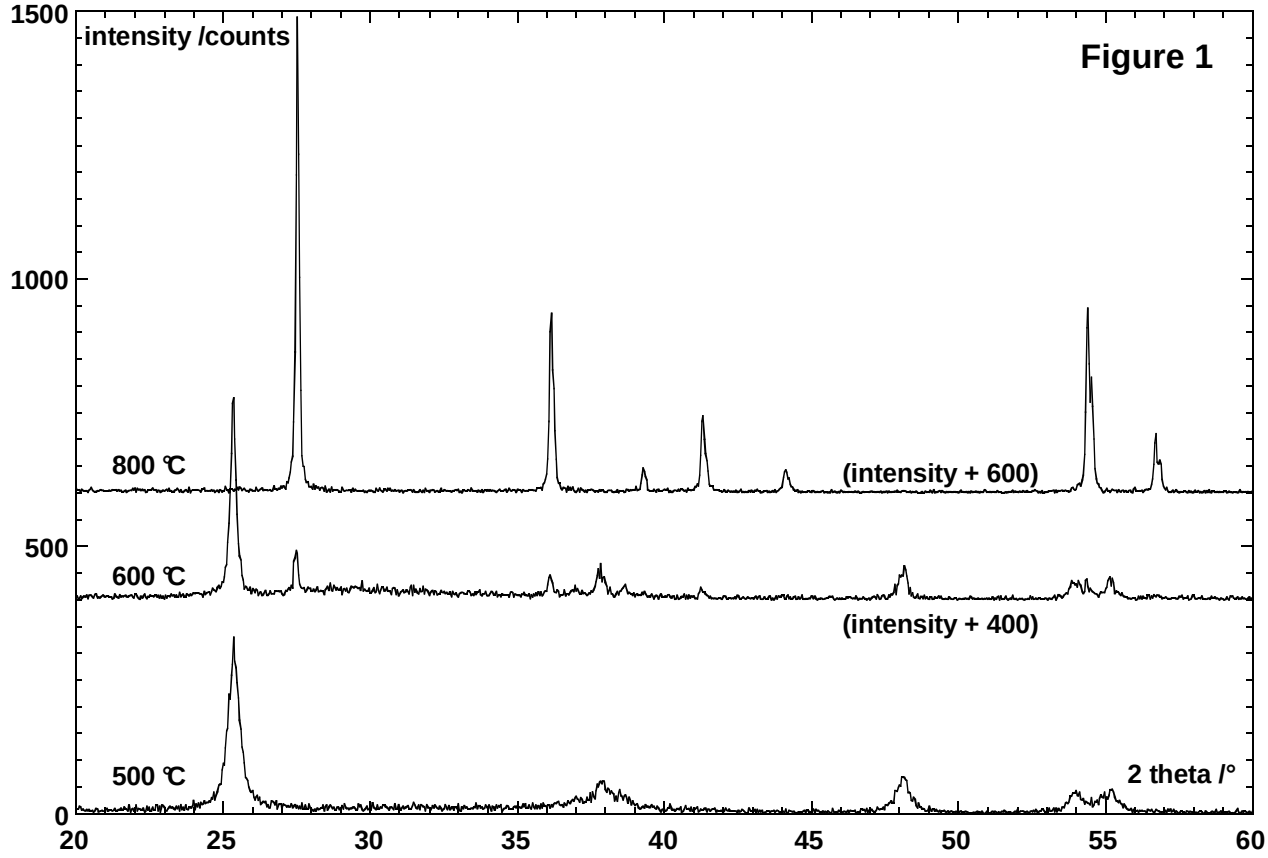
2.5 What is the maximum length of the irradiated area?

2.6 What is the minimum 2θ angle to avoid the irradiated part to exceed the area of the

sample? Radius of the goniometer circle 200 mm; opening slit 0.6 °.

3. Data analysis

Diffractograms of three samples treated respectively at 500, 600 and 800 °C (Fig. 1).



3.1 What are the Miller indices of the most intense peaks for each phase?

3.2 Discuss the evolution of the diffractograms.

3.3 For an equimolar mixture of each phase, determine the intensity ratio $I_{rutile}/I_{anatase}$ (largest peak of each phase) from the PDF files.

Fig. 2 displays an enlargement of the diffractogram.

3.4 Taking the height of a diffraction peak as a measure of the intensity, determine the percentage of each phase for the three samples.

3.5 How many experimental points define the diffraction peaks for the sample treated at 600 °C? Conclusion.

3.6 Give an estimation of the average size of the anatase crystallites at 500 °C and 600 °C. Conclusion.

4. Study of the background.

Fig. 3 presents the diffractogram of the sample treated at 500 °C, for the 2θ range 28 to 35 °.

4.1 How many experimental data in this range?

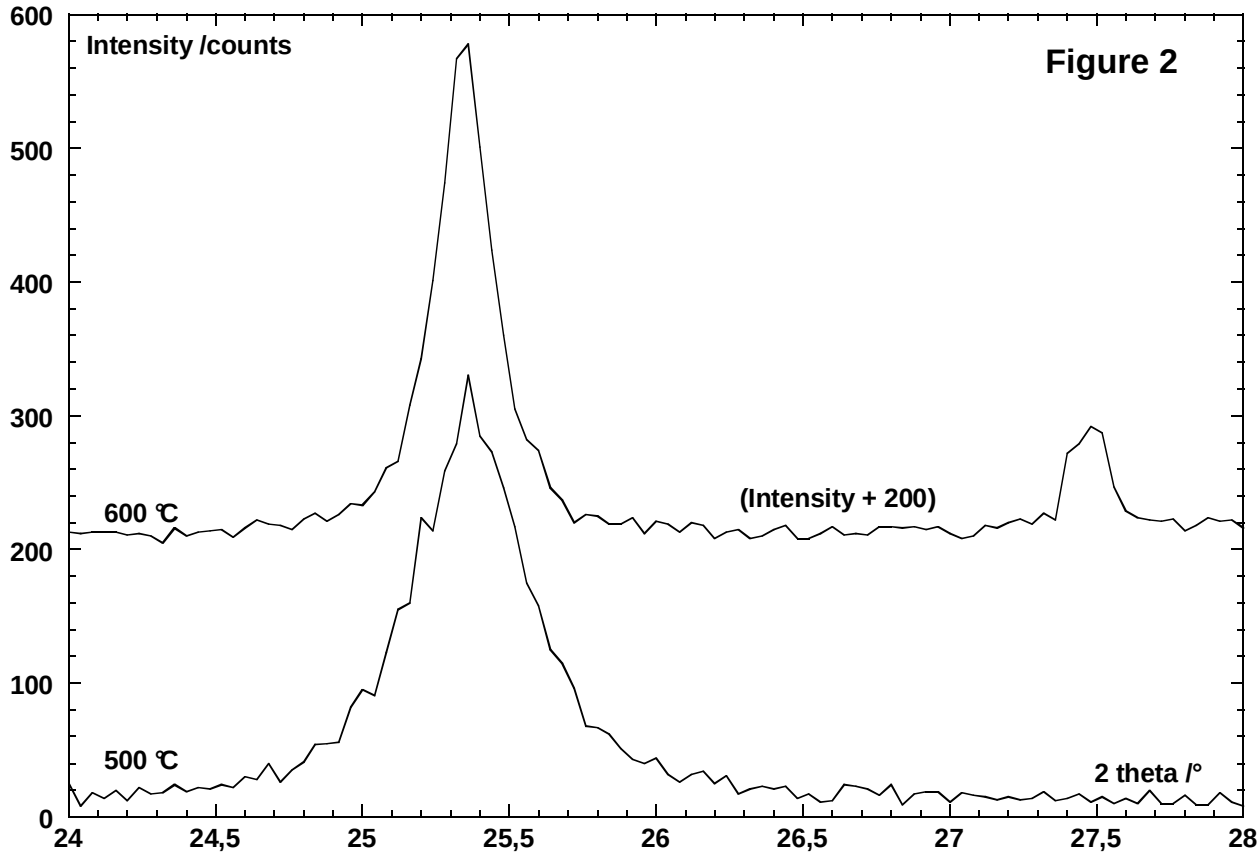
A statistical analysis of these data gave the following results:

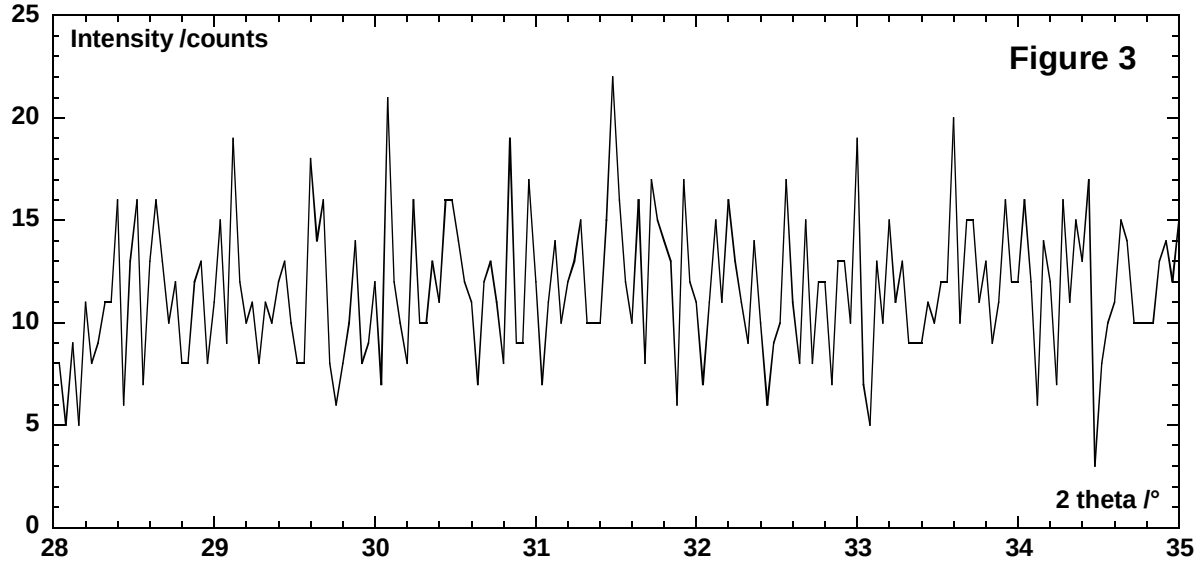
Minimum: 3 maximum: 22 mean: 11.57 standard deviation: 3.39

4.2 Do these values agree with a Gaussian background corresponding to a counting statistic?

On the Fig. 3, draw the horizontal lines corresponding to the mean value and to the ±2σ space below and above the mean value.

4.3 How many points you expect outside the ±2σ space? Is it in agreement with the experimental data?





Good luck

PDF Anatase

Pattern : 21-1272 *Radiation =* 1.540598 *Quality :* High

TiO_2

Titanium Oxide
Anatase, syn

Lattice :
S.G. : I41/amd (141)

a =
c =
Z =

Mol. weight = 79.90
Volume [CD] = 136.31
Dx = 3.893
I/Icor = 3.30

Color: Colorless
Sample source or locality: Sample obtained from National Lead Co., South Amboy, New Jersey, USA.
General comments: Anatase and another polymorph, brookite (orthorhombic), are converted to rutile (tetragonal) by heating above 700 C.
General comments: Pattern reviewed by Holzer, J., McCarthy, G., North Dakota State Univ, Fargo, North Dakota, USA, *ICDD Grant-in-Aid* (1990). Agrees well with experimental and calculated patterns.
Additional pattern: Validated by calculated pattern.
Temperature of data collection: Pattern taken at 25 C.
Additional pattern: See ICSD 9852 (PDF 71-1166).
Data collection flag: Ambient.

d (Å)	I	h	k	l
3.52000	100	1	0	1
2.43100	10	1	0	3
2.37800	20	0	0	4
2.33200	10	1	1	2
1.89200	35	2	0	0
1.69990	20	1	0	5
1.66650	20	2	1	1
1.49300	4	2	1	3
1.48080	14	2	0	4
1.36410	6	1	1	6
1.33780	6	2	2	0
1.27950	2	1	0	7
1.26490	10	2	1	5
1.25090	4	3	0	1
1.18940	2	0	0	8
1.17250	2	3	0	3
1.16640	6	2	2	4
1.16080	4	3	1	2
1.06000	2	2	1	7
1.05170	4	3	0	5
1.04360	4	3	2	1
1.01820	2	1	0	9
1.00700	2	2	0	8
0.99670	2	3	2	3
0.95550	4	3	1	6
0.94640	4	4	0	0
0.92460	2	3	0	7
0.91920	2	3	2	5
0.91380	2	4	1	1
0.89660	4	2	1	9
0.88900	2	2	2	8
0.88190	2	4	1	3
0.87930	2	4	0	4
0.84640	2	4	2	0
0.83080	2	3	2	7
0.82680	4	4	1	5
0.81020	2	3	0	9
0.79740	4	4	2	4
0.79280	2	0	0	12

PDF rutile

Pattern : 21-1276 **Radiation =** 1.540598 **Quality :** High

TiO_2

Titanium Oxide
Rutile, syn
Also called: titania

Lattice : Tetragonal
S.G. : P42/mnm (136)

a = 4.59330
c = 2.95920

Z = 2

Mol. weight = 79.90
Volume [CD] = 62.43
Dx = 4.250
Dm = 4.230
I/Icor = 3.40

d (Å)	i	h	k	l	
3.24700	100	1	1	0	
2.48700	50	1	0	1	
2.29700	8	2	0	0	
2.18800	25	1	1	1	1
2.05400	10	2	1	0	
1.68740	60	2	1	1	
1.62370	20	2	2	0	
1.47970	10	0	0	2	
1.45280	10	3	1	0	
1.42430	2	2	2	1	
1.35980	20	3	0	1	
1.34650	12	1	1	2	
1.30410	2	3	1	1	
1.27390	1	3	2	0	
1.24410	4	2	0	2	
1.20060	2	2	1	2	
1.17020	6	3	2	1	
1.14830	4	4	0	0	
1.11430	2	4	1	0	
1.09360	6	2	2	2	
1.08270	4	3	3	0	
1.04250	6	4	1	1	
1.03640	6	3	1	2	
1.02710	4	4	2	0	
1.01670	1	3	3	1	
0.97030	2	4	2	1	
0.96440	2	1	0	3	
0.94380	2	1	1	3	
0.90720	4	4	0	2	
0.90090	4	5	1	0	
0.88920	8	2	1	3	
0.87740	8	4	3	1	
0.87380	8	3	3	2	
0.84370	6	4	2	2	
0.82920	8	3	0	3	
0.81960	12	5	2	1	
0.81200	2	4	4	0	
0.78770	2	5	3	0	

General comments: No impurity over 0.001%.
Sample source or locality: Sample obtained from National Lead Co., South Amboy, New Jersey, USA.
General comments: Two other polymorphs, anatase (tetragonal) and brookite (orthorhombic), converted to rutile on heating above 700 C.
Optical data: A=2.9467, B=2.6505, Sign=+
General comments: Optical data on specimen from *Dana's System of Mineralogy, 7th Ed.*, I 555.
Reflectance: Opaque mineral optical data on specimen from Sweden: $R_3R\%$=20.3, Disp.=Std.
Vickers hardness number: VHN_{100}=1132-1167.
General comments: Pattern reviewed by Syvinski, W., McCarthy, G., North Dakota State Univ, Fargo, North Dakota, USA, *ICDD Grant-in-Aid* (1990). Agrees well with experimental and calculated patterns.
General comments: Additional weak reflections [indicated by brackets] were observed.
Additional pattern: Validated by calculated pattern.
General comments: Naturally occurring material may be reddish brown.
Color: White
Temperature of data collection: Pattern taken at 25 C.
Data collection flag: Ambient.

B – Analysis of chalk used at University

The diffractogram of the white chalk used in France and in Rumania is given in Annex. The recording parameters are:

- Sample holder: standard (plastic)
  - Mass of powder: 528 mg
  - Volume of powder: 778 mm^3
  - Diameter: 24 mm
- record: 5 to 80 ° 2θ
- step: 0,02 ° 2θ
- dwell time per step: 1 s
- $\lambda(CuK_{\alpha 1})$: 1.5405981 Å
- Fixed slit 1 °

The major species of the chalk used in France is calcium carbonate $CaCO_3$ (calcite, see PDF sheet) whereas it is calcium sulfate dehydrate $CaSO_4 \cdot 2H_2O$ (gypsum, see PDF sheet) .

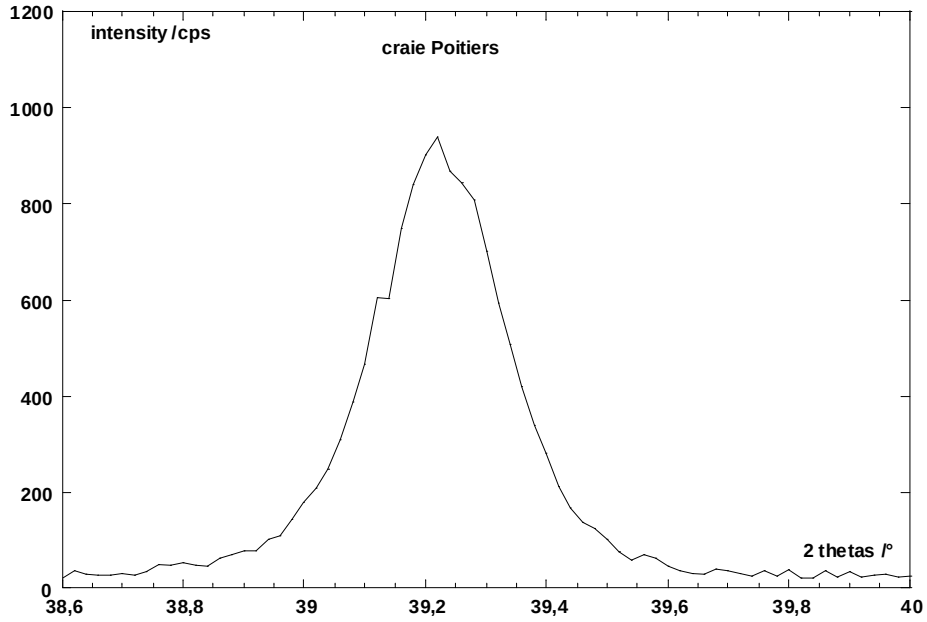
1. Study of the diffractogram

1.1 Determine the time length of the record.

1.2 Determine the d-spacing of the peak plotted below.

1.3 How many experimental points are used to draw this peak? Is this number sufficient for a profile study?

1.4 From this peak, determine the mean crystallite size for the phase calcite.



A careful examination of the PDF sheet and the experimental d-spacing show a systematic shift between these values. This shift can be assigned to a sample displacement.

1.5 From the most intense peak (d = 3.05597 Å), determine the direction and the value of

this displacement.

1.6 Determine the correction to be done for the last diffraction peak (d = 1.88155 Å). Perform this correction and compare with the value in the PDF sheet.

2. Study of the calcite phase

The Bravais lattice in the PDF sheet is R (rhombohedral), but the data of the unit cell correspond to a hexagonal cell.

2.1 Define the cell parameters and determine the volume.

2.2 Determine the number of formula in the cell.

2.3 Another species is present (hydrated boehmite) and is used as a binder between the calcite particles. What can you say about this species?

3. C – Absorption of X-ray

3.1 Determine the mass absorption coefficient and linear absorption coefficient for calcite powder.

3.2 Determine the mean penetration length of X-ray for this sample.

3.3 Determine the depth of the sample holder. Is this sample holder adapted for precise intensity measurements?

4. Study of the gypsum phase (monoclinic system)

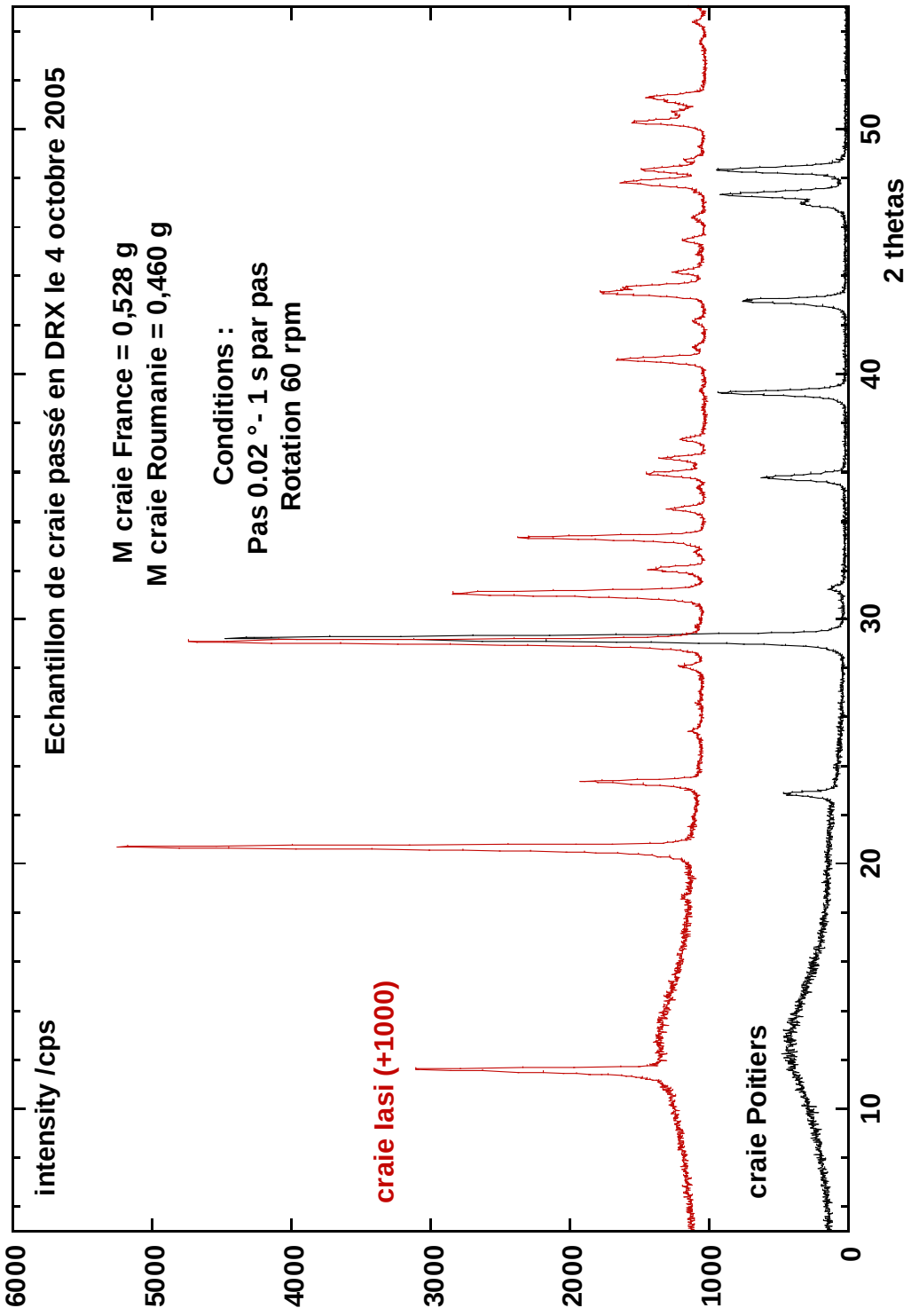
4.1 What are the translations associated to a Bravais lattice C?

4.2 What are the corresponding systematic absences?

4.3 Determine the Bravais lattice for gypsum phase.

Bon courage

Diffractograms



Pattern : 5-586 ANNEXE 2 **Radiation =** 1.540598 **Qual**

$CaCO_3$

Calcium Carbonate
Calcite, syn

maille Rescagonale

Lattice : Rhombohedral
S.G. : R-3c (167)

a = 4.98900
c = 17.06200
Z =

Mol. weight = 100.09
Volume [CD] = 367.78
Dx = 2.711
Dm = 2.710
I/Icor = 2.00

Optical data: A=1.487, B=1.659, Sign=-
Color: Colorless
Sample source or locality: Sample from Mallinckrodt Chemical Works.
Analysis: Spectroscopic analysis: <0.1% Sr; <0.01% Ba; <0.001% Al, B, Cs, Cu, K, Mg, Na, Si, Sn; <0.0001% Ag, Cr, Fe, Li, Mn.
Temperature of data collection: Pattern taken at 26 C.
General comments: Other form: aragonite.
General comments: Pattern reviewed by Parks, J., McCarthy, G., North Dakota State Univ., Fargo, North Dakota, USA, *ICDD Grant-in-Aid* (1992).
General comments: Agrees well with experimental and calculated patterns.
General comments: Additional weak reflections [indicated by brackets] were observed.
Additional pattern: See ICSD 16710, 20179, 28827, 18164, 18165 and 18166 (PDF 72-1214 and 72-1937); ICSD 73446 (PDF 81-2027); ICSD 79673 (PDF 83-577); ICSD 79674 (PDF 83-578).
Data collection flag: Ambient.

d (Å)	I	h	k	l
3.86000	12	0	1	2
3.03500	100	1	0	4
2.84500	3	0	0	6
2.49500	14	1	1	0
2.28500	18	1	1	3
2.09500	18	2	0	2
1.92700	5	0	2	4
1.91300	17	0	1	8
1.87500	17	1	1	6
1.62600	4	2	1	1
1.60400	8	1	2	2
1.58700	2	1	0	10
1.52500	5	2	1	4
1.51800	4	2	0	8
1.51000	3	1	1	9
1.47300	2	1	2	5
1.44000	5	3	0	0
1.42200	3	0	0	12
1.35600	1	2	1	7
1.33900	2	0	2	10
1.29700	2	1	2	8
1.28400	1	3	0	6
1.24700	1	2	2	0
1.23500	2	1	1	12
1.18690	1	3	1	2
1.17950	3	2	1	10
1.17280	1	0	1	14
1.15380	3	1	3	4
1.14250	1	2	2	6
1.12440	1	1	2	11
1.06130	1	2	0	14
1.04730	3	4	0	4
1.04470	4	3	1	8
1.03520	2	1	0	
1.02340	1	2	1	13
1.01180	2	3	0	12
0.98950	1	3	2	1
0.98460	1	2	3	2
0.97820	1	1	3	10
0.97670	3	1	2	14
0.96550	2	3	2	4
0.96360	4	0	4	8
0.95620	1	0	2	
0.94290	2	4	1	0
0.93760	2	2	2	12

Pattern : 33-311 ANNEXE 3 **Radiation =** 1.540598 **Quality :** High

$CaSO_4 \cdot 2H_2O$

Calcium Sulfate Hydrate
Gypsum, syn

Lattice : Base-centered monoclinic
S.G. : C2/c (15)

a = 6.28450
b = 15.20790 ***beta*** = 114.09
c = 5.67760
a/b = 0.41324 ***Z*** = 4
c/b = 0.37333

Mol. weight = 172.17
Volume [CD] = 495.37
Dx = 2.308
Dm = 2.320
I/Icor = 1.83

Optical data: A=1.521, B=1.523, Q=1.530, Sign=+, 2V=58°
Color: Colorless
Sample preparation: Sample prepared by adding H2 S O4 to a Ca (N O3)2 solution; the precipitate was filtered out, washed in water and bottled while moist; the crystals were dried immediately before use with care taken to prevent dehydration.
Temperature of data collection: Pattern taken at 25 C.
Additional pattern: To replace 6-46 and validated by calculated pattern 36-432.
General comments: Preferred orientation enhances 0k0 reflections.
Additional pattern: See ICSD 2057 (PDF 70-982).
Data collection flag: Ambient.

Winchell, A., Elements of Optical Mineralogy, volume 2, page 157 (1951).
Natl. Bur. Stand. (U.S.) Monogr. 25, volume 17, page 16 (1980).

Radiation : CuKa1 ***Filter :*** Monochromator crystal
Lambda : 1.54060 ***d-sp :*** Diffractometer
SS/FOM : F30= 51(0.0120,49) ***Internal standard :*** Si

d (Å)	I	h	k	l
7.63000	100	0	2	0
4.28300	100	0	2	1
3.79900	17	0	4	0
*3.79900	17	1	3	0
3.17200	4	1	1	1
3.06500	75	0	4	1
2.87300	45	-2	2	1
2.78900	10	-1	1	2
2.73200	2	1	3	1
2.68500	35	1	5	0
*2.68500	35	2	2	0
2.59700	6	-1	5	1
2.53400	2	0	6	0
2.49500	11	-2	0	2
2.47600	1	-1	3	2
2.45200	6	0	2	2
2.40600	4	-2	4	1
2.29100	1	2	4	0
2.21900	15	1	5	1
2.14200	2	0	4	2
2.08600	25	-2	4	2
2.07400	15	-1	5	2
*2.07400	15	-3	1	1
2.04800	6	1	1	2
2.03200	1	1	7	0
1.99200	4	-1	7	1
1.96300	3	-2	6	1
1.89980	16	0	8	0
*1.89980	16	2	6	0
1.87950	12	2	4	1
1.86500	3	-1	1	3
1.81180	13	0	6	2
1.79950	6	-2	2	3
1.78440	9	0	8	1
1.77850	12	-2	6	2
1.70930	1	1	5	2
1.68460	3	0	2	3
1.66400	6	-2	4	3
1.64560	4	2	6	1
1.62090	9	-2	8	1
*1.62090	9	1	9	0
1.60050	1	-1	9	1
1.58460	4	2	8	0
1.53270	2	0	8	2
1.52090	1	0	10	0
*1.52090	1	-4	2	2
1.51190	1	-2	8	2
1.49820	1	1	9	1
1.49470	1	-2	6	3
1.45910	3	-3	7	2
*1.45910	3	0	10	1
1.43920	5	-4	4	1
1.43540	3	3	7	0
1.42780	2	2	8	1
*1.42780	2	0	6	3
1.41780	3	-2	0	4
1.40150	2	-4	2	3
1.36570	5	2	6	2
*1.36570	5	-2	10	1
1.34400	1	1	11	0
*1.34400	1	2	10	0
1.33240	2	-1	11	1
1.32620	4	-2	8	3
1.32340	4	-4	6	2
1.27850	1	0	8	3
1.27220	1	1	11	1
1.26740	1	0	12	0
1.24810	3	4	6	0
*1.24810	3	-4	0	4
1.24410	2	2	10	1
1.23360	3	2	8	2
1.23090	2	-4	2	4
*1.23090	2	0	12	1

C – Reference for powder XRD

Silicon powder reference from NIST (National Institute for Standards and Technology, Standard Reference Materials 640d) is a reference for diffraction peak position and profile for powder XRD. The list of the peaks (given automatically by the computer), the diffractogram with enlargements and the PDF sheet of silicon are given after the text. The recording conditions are as follows:

2θ range:	5 to 132 °
Step:	0.02 °
Dwell time:	1 s
X-ray source:	Cu K_α
Fixed aperture slit:	1 °
Sample holder:	plastic
Sample diameter	25 mm
Thickness:	1 mm
Sample mass:	684 mg

5. Conditions of the record

5.1 Determine the time length of the record.

5.2 Determine the apparent density of the silicon sample

5.3 Determine the linear absorption coefficient and the mean penetration depth.

5.4 Is the sample holder adapted for this record?

6. Data analysis

6.1 From peak n° 9, calculate the wavelength used for the automatic determination of the d-spacing.

The list contains 10 diffraction peaks, but they are not all displayed on the PDF sheet of silicon.

6.2 Could you give an explanation?

The precise wavelength for λ(Cu $K_{\alpha1}$) is 1.540598 Å

6.3 Determine the value of the wavelength λ(Cu $K_{\alpha2}$) from the diffraction peaks 11 and 12 at 106.683 and 107.053 °. What is the interest to choose these peaks?

A more precise analysis of the diffraction peaks, taking into account the $K_{\alpha1}$ and $K_{\alpha2}$ components, gave the following results corresponding to the component $K_{\alpha1}$:

peak 1	28.392 °	peak 5	76.345 °
peak 2	47.263 °	peak 7	87.999 °
peak 3	56.087 °	peak 9	94.925 °
peak 4	69.091 °	peak 11	106.683 °

6.4 Determine the d-spacing corresponding to the peaks 2, 4, 7, 9 and 11

6.5 For each peak, determine the cell parameter of the cubic cell; determine the mean value and the standard deviation.

6.6 Compare the experimental mean value with the value given with the reference a = 5.43123 ± 0.00008 Å. Conclusion

6.7 Are the values of the cell parameter random or could you detect a systematic error?

7. The face centered cubic structure of silicon

7.1 Define the translations of the Bravais lattice F.

7.2 What is the condition on the Miller indices to observe the diffraction peaks (no demonstration)

7.3 What are the peaks satisfying this condition but not present in the PDF sheet and in the diffractogram?

We can deduce that there is a second condition on the Miller indices to explain the absence of these peaks. This condition is related to the structure of silicon (diamond-type structure).

The structure of silicon displays two independent Si atoms with coordinates 0 0 0 and ¼ ¼ ¼ . The remaining atoms in the unit cell are obtained from the translations linked to the Bravais lattice F.

7.4 Determine the structure factor for the two independent atoms and show that the second condition is:

- when h, k and l are even: $h + k + l = 4n$
- when h, k and l are odd no specific condition

8. Standardization of the powder diffractometer

8.1 From the cell parameter of silicon (a = 5.43123 Å), determine the 2θ values corresponding to the diffraction peaks 1 to 5 for $\lambda(Cu\ K_{\alpha 1})$.

8.2 Write a correction table with the following columns:

Peak #	(hkl)	calculated 2θ	observed 2θ	difference

8.3 What can you say about the difference

8.4 Correct the 2θ values for two peaks measured on another sample respectively at 35.125 ° and 62.453 °