Qualitative phase analysis (phase ID)

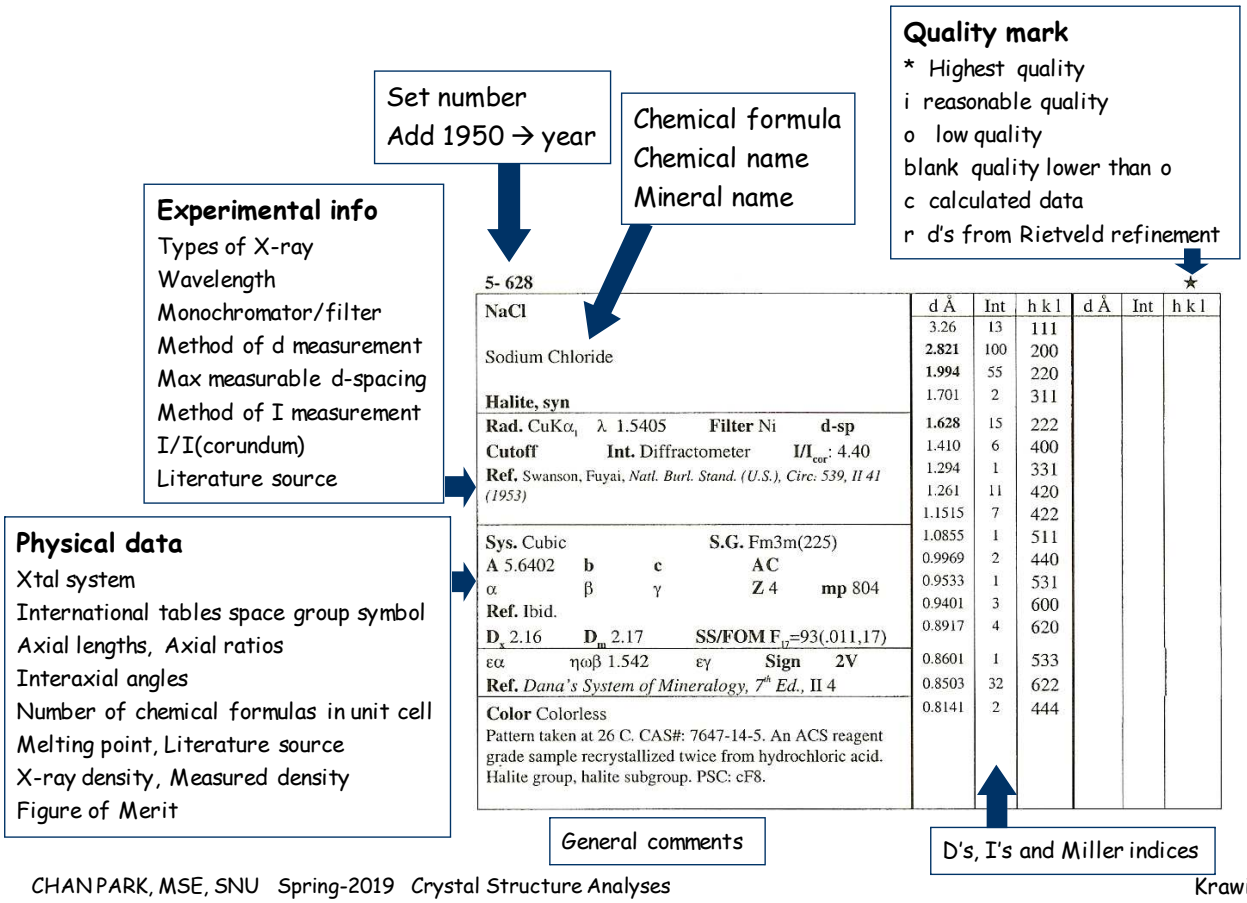
Structure Analysis
Materials Science & Engineering
Seoul National University
CHAN PARK

Jenkins & Snyder Chap 12

Krawitz Chap 8

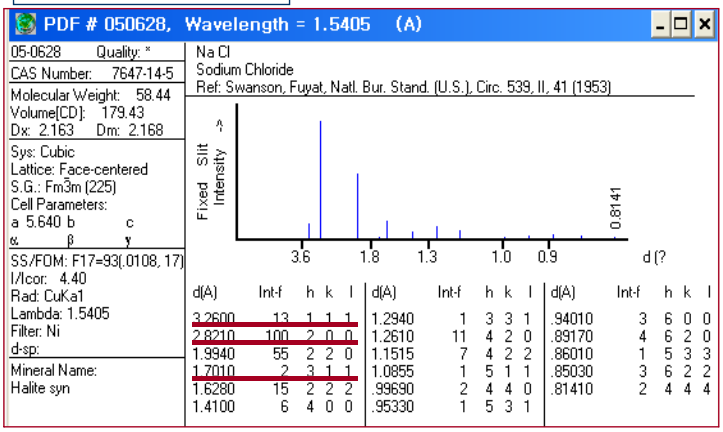
Cullity Chap 9

PDF card



PDF card & Quality mark

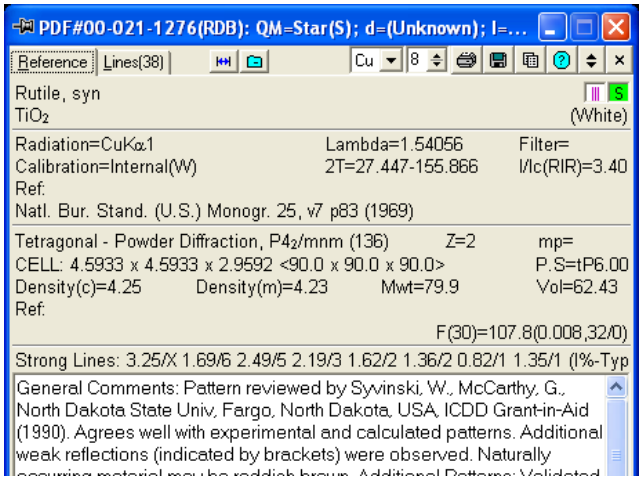
CAS; chemical abstracts service registry number

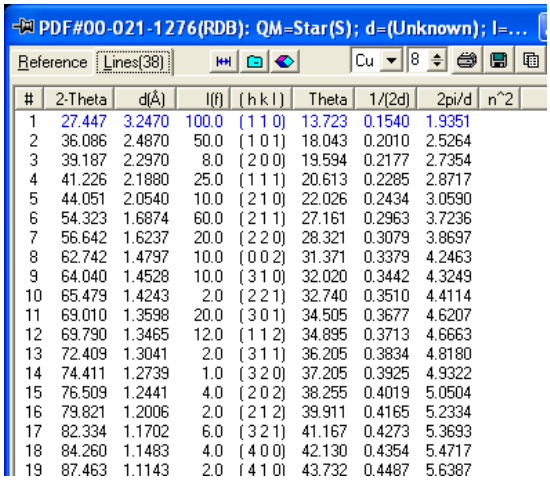


- * Highest quality
  - ✓ average Δ2θ < 0.03 degree, all lines were indexed, I measured quantitatively
- i reasonable quality
  - ✓ average Δ2θ < 0.06 degree, indexed with no more than two lines being unaccounted for, I measured quantitatively
- o low quality
  - ✓ low precision, poorly characterized, no unit cell data
- blank quality lower than o
- c calculated data
- r d's from Rietveld refinement

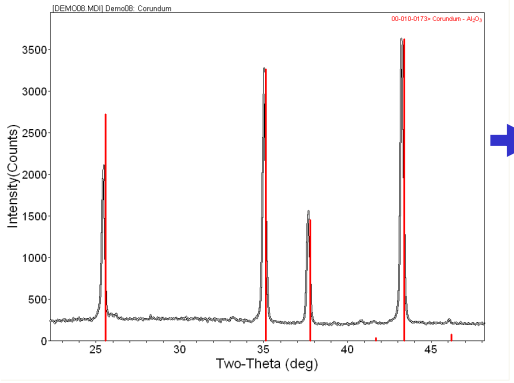
PDF card

- Modern computer programs can help you determine what phases are present in your sample by quickly comparing your diffraction data to all of the patterns in the database.
- The PDF card for an entry contains a lot of useful information, including literature references.





Powder diffraction data



Raw Data

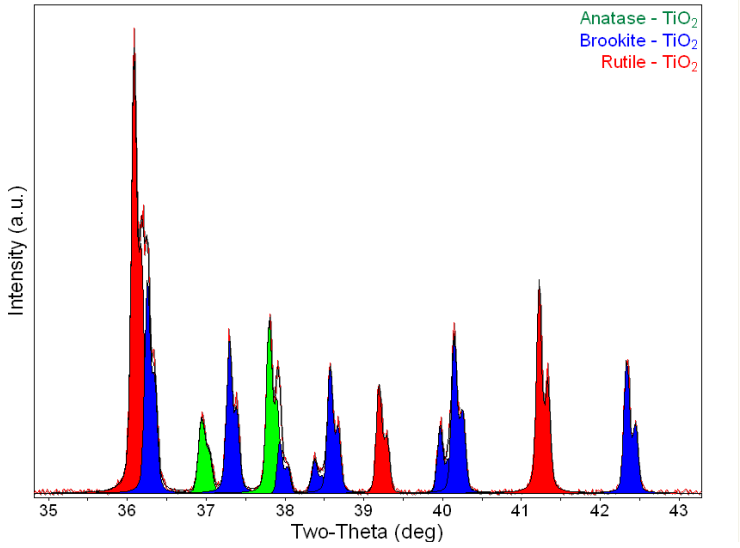
Position [°2θ]	Intensity [cts]
25.2000	372
25.2400	460
25.2800	576
25.3200	752
25.3600	1088
25.4000	1488
25.4400	1892
25.4800	2104
25.5200	1720
25.5600	1216
25.6000	732
25.6400	456
25.6800	380
25.7200	328

Reduced d-I list

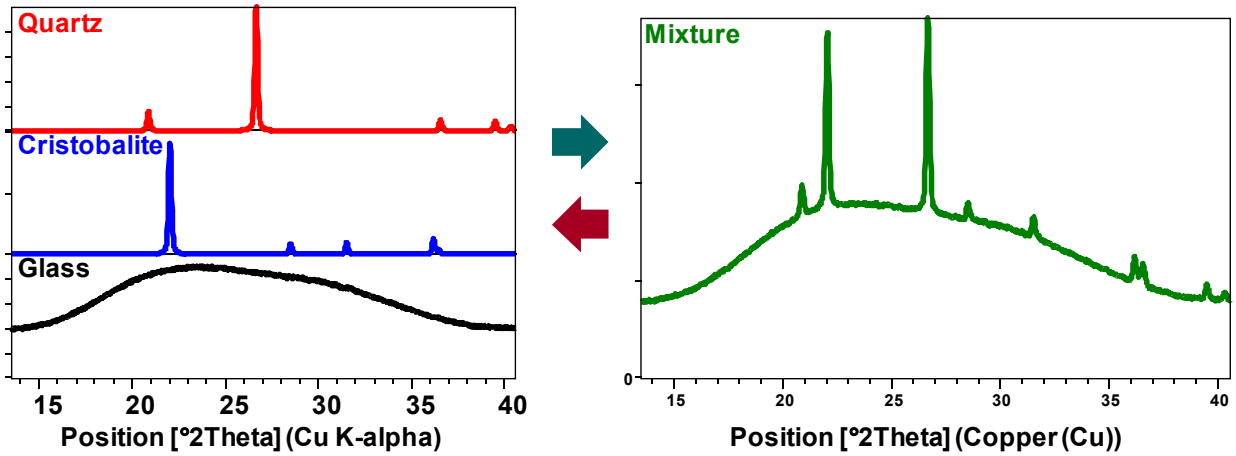
hkl	d_{hkl} (Å)	Relative Intensity (%)
{012}	3.4935	49.8
{104}	2.5583	85.8
{110}	2.3852	36.1
{006}	2.1701	1.9
{113}	2.0903	100.0
{202}	1.9680	1.4

Powder diffraction data

- Phases with the same chemical composition can have drastically different diffraction patterns.
- While every diffraction pattern is different, some can be very similar.

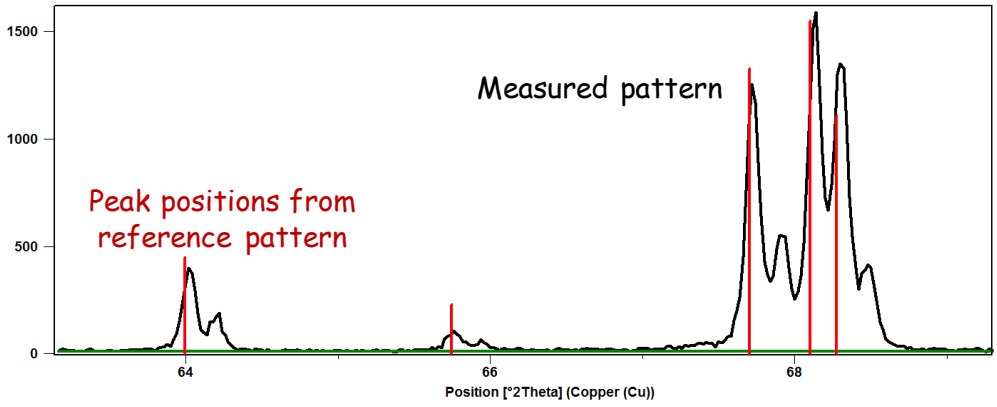


diffraction pattern of a mixture



- From the XRD pattern you can determine:
  - ✓ What crystalline phases are in a mixture (phase ID)
  - ✓ The amount of each crystalline phase in the mixture (quantitative phase analysis, QPA)
  - ✓ If any amorphous material is present in the mixture

XRD peak positions are compared with those of reference patterns



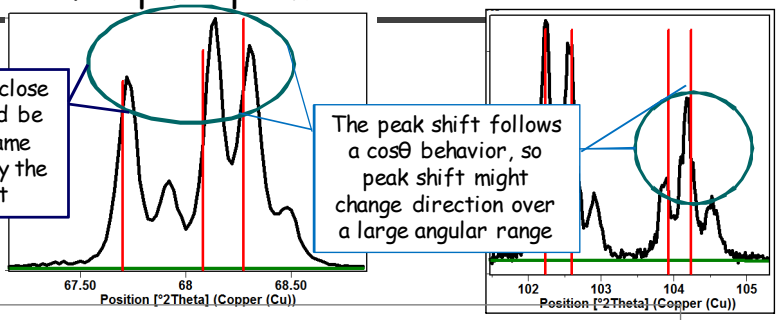
- A small amount of mismatch in peak position and intensity is acceptable experimental error

Displacement error, K-alpha1 and K-alpha2 peak doublets

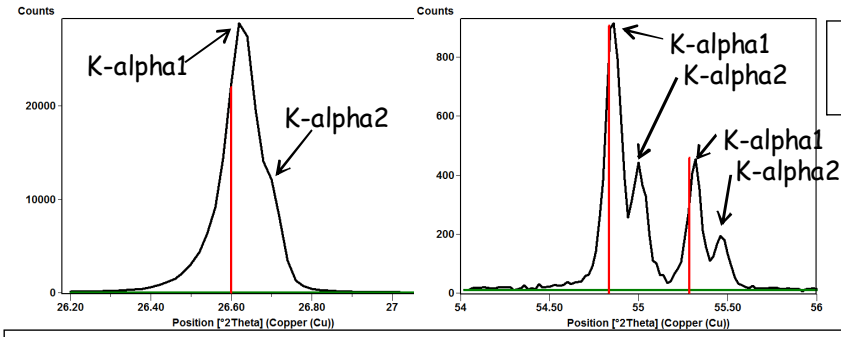
Specimen displacement

Peaks that are close together should be shifted the same direction and by the same amount

The peak shift follows a cosθ behavior, so peak shift might change direction over a large angular range



- Specimen displacement is a *systematic* peak position error due to misalignment of the sample.
- The direction and amount of peak shift will vary as $\frac{-2s\cos\theta}{R}$



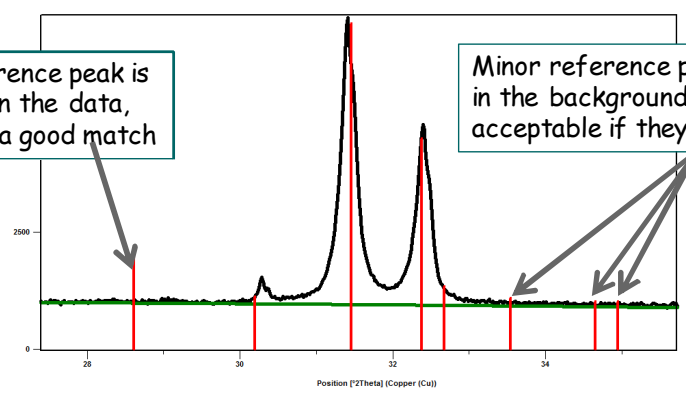
K-alpha1 and K-alpha2 peak doublets

- The k-alpha1 and k-alpha2 peak doublets are further apart at high angle 2theta
- The k-alpha1 peaks always have twice the intensity of the k-alpha2

Diffraction pattern > peak match

If a major reference peak is not observed in the data, then that is not a good match

Minor reference peaks could be lost in the background noise, so it may be acceptable if they are not observed



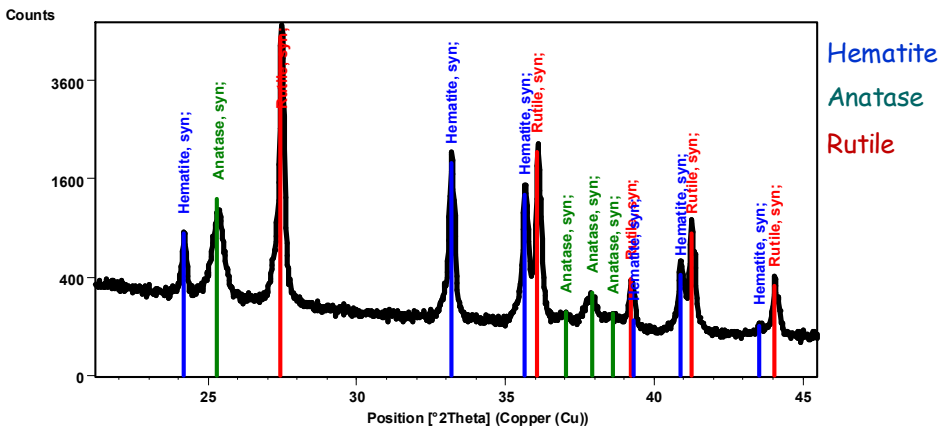


Table 12.3. Databases of Crystallographic and Structural Information

Name	Content	Center
Cambridge Structural Database (CSD)	Organic, organometallic	Cambridge, England
Inorganic Crystal Structure Database (ICSD)	Inorganic materials	Karlsruhe, Germany
NRCC Metals Data File (CRYSTMET)	Metals and alloys	Ottawa, Canada
Protein Data Bank (PDB)	Structure of macromolecules	Brookhaven, New York
NIST Crystal Data [NBS(CDF)]	Inorganic and organic unit cells	Gaithersburg, Maryland

Table 12.4. Databases for X-ray Powder Diffraction

Name	Content
Master DB	Master ICDD Database—all known powder data on a single phase, plus editorial marks and comments
PDF-2	User version of the Master DB (does not contain special editorial comments)
PDF-1	Subset of PDF-2, contains *d*'s, *I*'s and names (designed for automated search systems)
PDF-3	Contains raw data as a digitized pattern
CDF	The Crystal Data File (contains cell data, names, and references)
EISI	The Elemental and Interplanar Spacing Index (designed for electron diffraction)

PDF-4

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Errors in experimental d-values ← inadequate data treatment in locating peak position; uncertainties in the value of wavelength

Errors in experimental intensities ← preferred orientation; poor crystallinity; line broadening; partially resolved diffraction wavelength multiplets

- Successful qualitative phase analysis depends both on the accuracy of the measurement of unknown pattern and the accuracy of the PDF
- Figure of Merit F_N – quantitative criteria for evaluating powder patterns

Δ2θ & Δd

- Typical error windows
  - ✓ Debye Scherrer camera ±Δ2θ = 0.1°
  - ✓ diffractometer ±Δ2θ = 0.05°
  - ✓ diffractometer (internal standard corrected) ±Δ2θ = 0.01°
  - ✓ diffractometer (internal standard corrected & peaks profile fitted) ±Δ2θ = 0.005°
- Δ2θ – d relationship is non-linear
  - ✓ Low angle (low 2θ, large d-value) lines have large error

Table 12.2. Errors in *d*-Values Resulting from Fixed 2θ Errors

d (Å)	2θ (degrees)	±Δ2θ (degrees)	±Δ*d* (Å)	±Δ2θ (degrees)	±Δ*d* (Å)
5	17.73	0.1	0.04	0.05	0.014
4	22.20	0.1	0.02	0.05	0.008
3	29.76	0.1	0.01	0.05	0.005
2	45.30	0.1	0.004	0.05	0.002
1.5	61.80	0.1	0.002	0.05	0.0011
1.0	100.76	0.1	0.0007	0.05	0.0004

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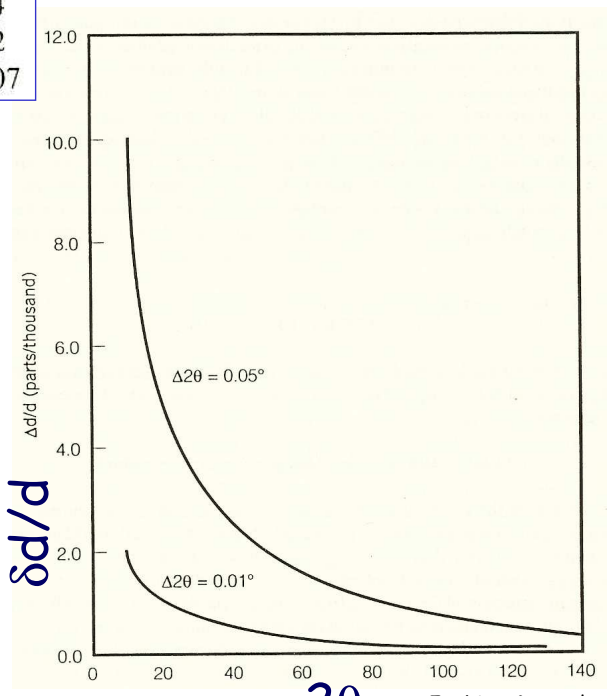
Δ2θ & Δd

d (Å)	2θ (degrees)	±Δ2θ (degrees)	±Δ*d* (Å)
5	17.73	0.1	0.04
4	22.20	0.1	0.02
3	29.76	0.1	0.01
2	45.30	0.1	0.004
1.5	61.80	0.1	0.002
1.0	100.76	0.1	0.0007

$$\delta d/d = -\Delta\theta \cot\theta$$



Jenkins & Snyder

- Process of qualitative phase ID = **search/match/identify**
  - ✓ Search – index
  - ✓ Match – file (PDF)

- Alphabetical index; chemistry-based index using only elemental information
- Hanawalt index; intensity-driven index, use only the strongest lines
- Fink index; D-spacing-driven index, mainly use the largest d-values

Table 12.7. Types of PDF Data-Searching Indexes

Index	Entry Method	Search Parameters
Alphabetic	Chemistry	Permuted elemental symbols
Hanawalt	*I*/*d*	Three strongest lines
Fink	*d*/*I*	First eight lines
EISI[a]	Chemistry/*d*	Low high *Z* elements; *d*-spacing
Boolean	Various	*d*-Spacings, chemistry, strong lines, CODEN, physical properties, functional groups, etc.

[a]Elemental and Interplanar Spacing Index.

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QM	Chemical Name	Chemical Formula	Reflections	PDF#
	Chloride : Palladium	$PdCl_2$	5.30_x 2.39_8 1.64_4	1- 228
★	Chloride : Potassium/**Sylvite, syn**	KCl	3.15_x 2.23_4 1.82_1	41-1476
i	Chloride : Praseodymium	$PrCl_3$	2.57_x 2.11_8 3.56_7	12- 787
★	Chloride : Rubidium	RbCl	3.29_x 2.33_7 3.80_3	6- 289†
★	Chloride : Samarium	$SmCl_3$	2.54_x 2.09_9 3.49_8	12- 789
★	Chloride : Silver/**Chlorargyrite, syn**	AgCl	2.77_x 3.20_5 1.96_5	31-1238
→★	Chloride : Sodium/**Halite, syn**	NaCl	2.82_x 1.99_6 1.63_2	5- 628†
	Chloride : Sodium Platinum	Na_2PtCl_6	8.00_x 5.60_x 6.50_7	1- 83
★	Chloride : Strontium	$SrCl_2$	2.47_x 4.03_6 2.10_5	6- 537
	Chloride : Tin	$SnCl_2$	4.62_x 2.30_5 2.21_4	32-1359
i	Chloride : Uranyl	UO_2Cl_2	4.78_x 3.16_4 6.05_4	20-1331
i	Chloride : Uranyl	$(UO_2)_2Cl_3$	4.69_x 5.08_6 3.94_6	34- 215
	Chloride : Zinc	$ZnCl_2$	3.08_x 4.79_7 1.87_5	15- 452
★	Chromium :/**Chromium, syn**	Cr	2.04_x 1.18_3 1.44_2	6- 694†
C	Chromium : Aluminum	Al_8Cr_5	2.15_x 6.44_9 2.12_8	29- 15

QM	Chemical Name	Chemical Formula	Reflections	PDF#
→★	Sodium Chloride :/**Halite, syn**	NaCl	2.82_x 1.99_6 1.63_2	5- 628†
★	Sodium Chromium Oxide :	β-$Na_2Cr_2O_7$	4.67_x 4.46_9 3.24_9	30-1178
★	Sodium Chromium Oxide :	Na_2CrO_4	2.90_x 2.73_7 4.07_7	22-1365†
	Sodium Chromium Oxide :	Na_3CrO_4	2.68_x 4.37_9 3.78_4	29-1199
★	Sodium Chromium Oxide :	$NaCrO_2$	2.16_x 5.32_7 2.45_4	25- 819†
★	Sodium Cyanide :	NaCN	2.94_x 2.08_3 1.70_1	37-1490
★	Sodium Fluoride :/**Villiaumite, syn**	NaF	2.32_x 1.64_4 1.34_1	36-1455
i	Sodium Germanium Oxide :	Na_4GeO_4	6.89_x 3.88_x 5.11_8	36- 62
★	Sodium Hydrogen Carbonate :/**Nahcolite, syn**	$NaHCO_3$	2.94_x 2.60_x 2.96_7	15- 700†
	Sodium Hydrogen Phosphate :	$Na_2H(PO_3)_3$	5.03_x 3.11_9 3.21_8	9- 101
i	Sodium Hydrogen Phosphate :	NaH_2PO_4	3.20_x 3.94_7 3.30_6	11- 659
i	Sodium Hydrogen Phosphate :	$Na_2H_2P_2O_7$	2.93_x 3.09_7 3.43_6	10- 192
i	Sodium Hydrogen Sulfate :	$Na_3H(SO_4)_2$	3.95_x 2.89_x 2.73_x	32-1090
★	Sodium Hydrogen Sulfate :	β-$NaHSO_4$	3.59_x 3.74_9 2.94_9	26- 960
★	Sodium Hydrogen Sulfate :	$NaHSO_4$	3.39_x 4.48_5 3.43_5	25- 833

FIGURE 8.3. Alphabetical search index entries for NaCl. (From the ICDD Powder Diffraction File.)

Krawitz

Alphabetical index

- End of proper name :
  - ✓ Chloride: Sodium
  - ✓ Sodium Chloride:
- 2.82_x – X stands for 100 (intensity)
- 1.99_6 – 6 stands for 60 (intensity)

→ ★	Sodium Chloride :/**Halite, syn**	NaCl	2.82_x	1.99_6 1.63_2	5- 628†
★	Sodium Chromium Oxide :	β-$Na_2Cr_2O_7$	4.67_x	4.46_9 3.24_9	30-1178
★	Chloride : Silver/**Chlorargyrite, sy**	AgCl	2.77_x	3.20_5 1.96_5	31-1238
→★	Chloride : Sodium/**Halite, syn**	NaCl	2.82_x	1.99_6 1.63_2	5- 628†

Hanawalt index

Hanawalt group

2.84 – 2.80 (± .01)

QM	Strongest Reflections								PSC	Chemical Formula	Mineral Name;Common Name or Chemical Name	PDF#	I/I$_c$
★	2.81_8	2.30_x	2.04_x	5.13_9	3.36_6	1.68_5	3.14_5	4.44_1	cI232	$Ca_3Al_2(OH)_{12}$	**Katoite, syn**	24- 217	
★	2.81_x	2.23_9	4.56_8	2.30_7	6.20_7	2.85_6	3.36_6	2.47_5	oP16	$Sr(OH)_2{\cdot}H_2O$		28-1222	0.80
→ ★	2.82_x	1.99_6	1.63_2	3.26_1	1.26_1	1.15_1	1.41_1	0.89_1	cF8	NaCl	**Halite, syn**	5- 628	4.40
i	2.83_x	1.97_3	2.89_2	1.77_2	1.76_2	2.60_1	2.43_1	1.99_1	hR20	$MgCa(CO_3)_4$	**Huntite**	11- 489	
★	2.81_x	1.90_8	3.05_7	2.72_5	1.74_4	1.56_4	3.22_3	1.57_2	hP12	CuS	**Covellite, syn**	6- 464	
	2.81_x	1.62_8	4.15_7	3.05_6	3.09_5	1.53_5	6.04_4	2.48_4	h**	$CrBr_3$		43- 937	
★	2.84_x	1.75_3	3.06_2	2.43_2	3.71_2	2.39_1	2.41_1	2.29_1	tP24	$Ca_2Al_2SiO_7$	**Gehlenite, syn**	35- 755	
★	2.84_x	1.74_8	1.48_3	4.02_3	2.10_3	1.93_2	2.46_2	1.45_1	cI80	Sc_2O_3		5- 629	
★	2.80_x	1.73_4	1.74_3	3.59_3	2.35_2	2.13_2	1.97_2	1.51_1	hR10	$FeCO_3$	**Siderite**	29- 696	
	2.83_x	1.71_8	1.09_6	2.00_5	2.54_4	2.32_4	1.00_4	1.57_3	cP12	NiS_2	**Vaesite**	11- 99	
i	2.85_x	1.67_9	2.37_8	1.82_7	3.35_6	0.97_5	1.23_3	1.18_3	cF56	Ni_3S_4	**Polydymite**	43-1469	
	2.85_x	1.67_9	2.36_8	1.82_7	3.34_6	0.96_5	0.91_4	1.23_3	cF56	Co_3S_4	**Linnaeite**	42-1448	
★	2.82_x	1.67_9	2.25_8	2.87_5	2.50_5	2.08_5	1.30_3	1.89_2	hR7	Al_4C_3		35- 799	
	2.85_8	1.58_x	2.55_8	1.10_x	1.08_x	1.03_x	1.47_6	1.25_6	cI40	U_2C_3		6- 709	

FIGURE 8.4. Hanawalt search index entry for NaCl. Since the ratio $I_2/I_1 < 0.75$, this is the only entry. (From the ICDD Powder Diffraction File.)

- 8 most intense lines are listed
- d's of three strongest lines
- 2 listings if $I_2/I_1 > 0.75$, $I_3/I_1 < 0.75$; d_1, d_2 & d_2, d_1
- 3 listings if $I_3/I_1 > 0.75$, $I_4/I_1 < 0.75$; d_1, d_2 & d_2, d_1 & d_3, d_1
- ---
- In case of NaCl, one listing ← $I_2/I_1 < 0.75$
- Multiple listing ← to minimize problems of preferred orientation

Groups of Hanawalt index & Fink index

Table 8.3. *d*-Spacing Groups for the Hanawalt and Fink Search Indexes

d-Spacing Group (Å)	*d*-Spacing Group (Å)
999.99–10.00 (Fink only)	3.04–3.00
999.99–8.00 (Hanawalt only)	2.99–2.95
9.99–8.00 (Fink only)	2.94–2.90
7.99–7.00	2.89–2.85
6.99–6.00	2.84–2.80
5.99–5.50	2.79–2.75
5.49–5.00	2.74–2.70
4.99–4.60	2.69–2.65
4.59–4.30	2.64–2.58
4.29–4.10	2.57–2.51
4.09–3.90	2.50–2.44
3.89–3.75	2.43–2.37
3.74–3.60	2.36–2.30
3.59–3.50	2.29–2.23
3.49–3.40	2.22–2.16
3.39–3.32	2.15–2.09
3.31–3.25	2.08–2.02
3.24–3.20	2.01–1.86
3.19–3.15	1.85–1.68
3.14–3.10	1.67–1.38
3.09–3.05	1.37–0.00

Fink index

3.31 – 3.25

QM	Strongest Reflections								PSC	Chemical Formula	Mineral Name;Common Name or Chemical Name	PDF#	I/I$_c$
*	3.30$_6$	2.82$_4$	2.75$_5$	2.66$_1$	5.48$_6$	4.73$_x$	3.99$_x$	3.71$_9$	aP42	$CuSO_4$*$5H_2O$	**Chalcanthite, syn**	11- 646	
	3.29$_x$	2.82$_x$	2.77$_5$	2.71$_5$	2.42$_4$	1.82$_4$	1.81$_4$	1.64$_4$		Sn_3O_4		16- 737	
*	3.26$_x$	2.82$_7$	6.79$_1$	5.17$_7$	4.84$_7$	4.11$_1$	4.05$_2$	3.95$_3$	oP84	$C_6H_6O_5$*$2H_2O$	Phloroglucinol dihydrate	40-1632	
*	3.26$_7$	2.82$_x$	2.00$_5$	1.70$_3$	1.63$_1$	1.41$_1$	1.30$_1$	1.26$_1$	cF8	RbF		22- 886	
*	3.26$_1$	2.82$_x$	1.99$_8$	1.63$_7$	1.41$_1$	1.26$_1$	1.15$_1$	0.89$_1$	cF8	NaCl	**Halite, syn**	5- 628	4.40

2.84 – 2.80

QM	Strongest Reflections								PSC	Chemical Formula	Mineral Name;Common Name or Chemical Name	PDF#	I/I$_c$
i	2.82$_4$	2.00$_2$	1.84$_4$	11.3$_8$	5.48$_3$	3.53$_2$	3.08$_x$	2.98$_7$	oC172	$Ca_5(OH)_2Si_6O_{16}$*$4H_2O$	**Tobermorite-11A, syn**	19-1364	
*	2.82$_x$	2.00$_8$	1.70$_3$	1.63$_1$	1.41$_1$	1.30$_1$	1.26$_1$	3.26$_7$	cF8	RbF		22- 886	
i	2.81$_7$	2.00$_2$	1.84$_2$	11.3$_x$	5.45$_4$	3.51$_3$	3.08$_9$	2.97$_7$	oC176	$Ca_5Si_6O_{16}OH_2$*$5H_2O$	**Tobermorite-*O*, 11A**	45-1480	
*	2.82$_7$	1.99$_8$	1.63$_7$	1.41$_1$	1.26$_1$	1.15$_1$	0.89$_1$	3.26$_1$	cF8	NaCl	**Halite, syn**	5- 628	
*	2.80$_4$	1.98$_x$	1.69$_x$	1.28$_4$	1.14$_7$	1.08$_7$	0.95$_7$	3.23$_x$	cF12	ThO_2	**Thorianite, syn**;thoria	4- 556	

2.01 – 1.94

QM	Strongest Reflections								PSC	Chemical Formula	Mineral Name;Common Name or Chemical Name	PDF#	I/I$_c$
i	1.98$_5$	1.65$_5$	7.15$_x$	4.12$_7$	3.80$_6$	3.58$_x$	2.51$_5$	2.33$_9$	mC68	$Al_2Si_2O_5(OH)_4$	**Dickite-2*M*$_1$**	10- 446	
	1.94$_4$	1.65$_1$	1.58$_1$	1.37$_1$	1.26$_1$	1.23$_1$	5.70$_1$	2.75$_x$		$Na_4Fe(CN)_6$		1-1026	
	1.94$_1$	1.65$_1$	1.49$_2$	1.40$_2$	1.38$_2$	2.85$_2$	2.63$_4$	2.52$_4$	hP2	Sc		17- 714	
	1.94$_4$	1.65$_x$	1.26$_7$	1.23$_7$	1.12$_7$	1.06$_8$	3.16$_x$	2.74$_7$	cF4	Yb		2-1367	
*	1.99$_8$	1.63$_2$	1.41$_1$	1.26$_1$	1.15$_1$	0.89$_1$	3.26$_1$	2.82$_x$	cF8	NaCl	**Halite, syn**	5- 628	4.40

1.67 – 1.58

QM	Strongest Reflections								PSC	Chemical Formula	Mineral Name;Common Name or Chemical Name	PDF#	I/I$_c$
*	1.58$_1$	1.42$_1$	4.36$_2$	3.45$_x$	2.52$_1$	2.36$_1$	2.18$_1$	1.88$_1$	hP18	$FePO_4$		29- 715	
*	1.63$_1$	1.41$_1$	1.30$_1$	1.26$_1$	3.26$_7$	2.82$_x$	2.00$_5$	1.70$_3$	cF8	RbF		22- 886	
*	1.63$_7$	1.41$_1$	1.26$_1$	1.15$_1$	0.89$_1$	3.26$_7$	2.82$_x$	1.99$_8$	cF8	NaCl	**Halite, syn**	5- 628	4.40
*	1.64$_4$	1.40$_1$	1.34$_1$	1.16$_1$	1.04$_1$	0.95$_1$	2.68$_1$	2.32$_x$	cF8	NaF	**Villiaumite, syn**	36-1455	
i	1.60$_x$	1.40$_3$	1.37$_5$	3.48$_x$	2.55$_9$	2.38$_4$	2.09$_x$	1.74$_5$	hR10	Al_2O_3	**Corundum, syn**;alumina	10- 173	1.00

FIGURE 8.5. Fink search index entries for NaCl. Short segments of eight entries containing NaCl (halite) are shown. (From the ICDD Powder Diffraction File.)

- 8 listings
- Useful when I information is not reliable ← oriented grains, overlapping multiphase patterns

Factors affecting PDF search

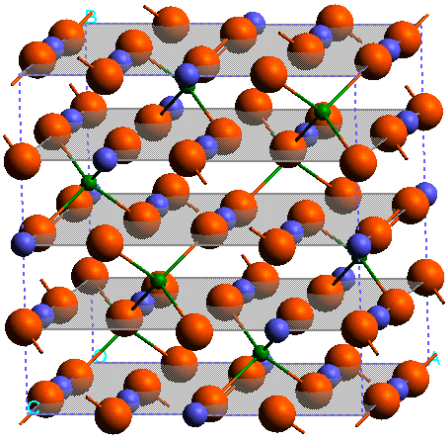
- Preferred orientation - I
- solid solution – d (mostly)
- Impurities – d (mostly)
- Defect – d, I
- Site occupancy – d, I; e.g. spinel
- Order/disorder
- Knowledge of possible elements present → elemental analysis

Site occupancy in spinel

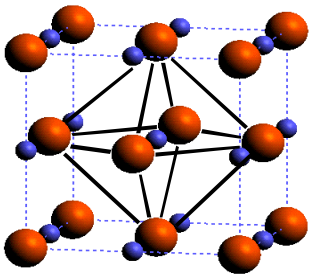
- Spinel AB_2O_4; $MgAl_2O_4$, $MgFe_2O_4$, Fe_3O_4
- Cubic close packed anion
- 2x2x2 ccp cells = 1 unit cell
  - ✓ Z (# formula units per unit cell) = 8
- 1 unit cell; 32 anions, 16 cations in octahedral sites, 8 cations in tetrahedral sites
  - ✓ ½ octahedal sites & 1/8 tetrahedral sites occupied
- $MgFe_2O_4$; Fe – octa, Mg – tetra → normal spinel
- $MgFe_2O_4$; Mg/Fe – octa, Fe – tetra → inverse spinel

Octahedral & Tetrahedral interstices in CCP lattice

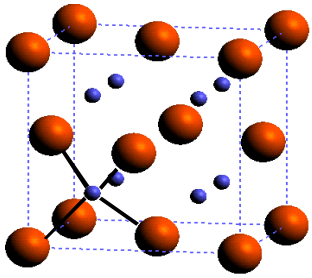
Spinel



($MgAl_2O_4$; $ZnFe_2O_4$; $MnFe_2O_4$)



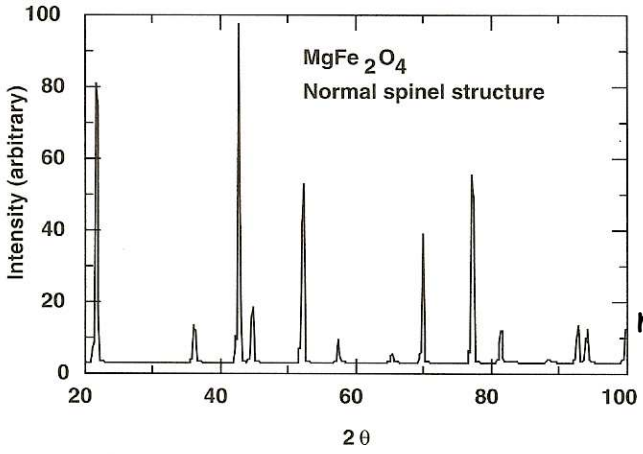
4 octahedral sites
4 x 8 = 32



8 tetrahedral sites
8 x 8 = 64

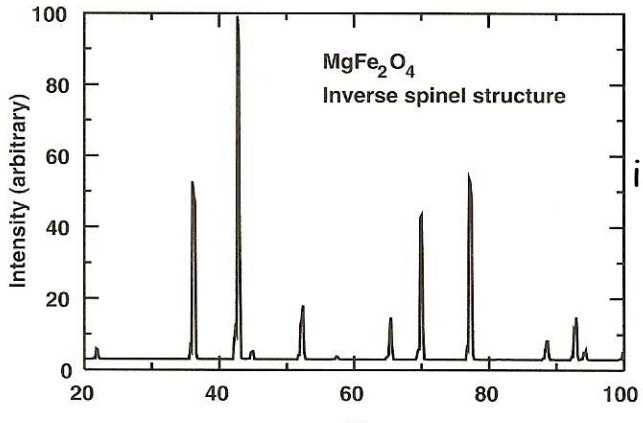
- 1 unit cell of spinel
  - ✓ 32 anions
  - ✓ 16 cations in octahedral sites, 8 cations in tetrahedral sites
  - ✓ ½ octahedral sites & 1/8 tetrahedral sites occupied

Spinel



$MgFe_2O_4$
normal spinel

Same peak positions
Different peak intensities



$MgFe_2O_4$
inverse spinel