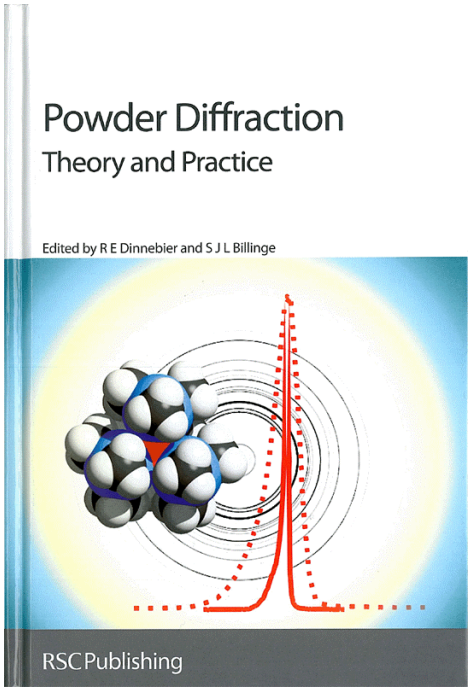
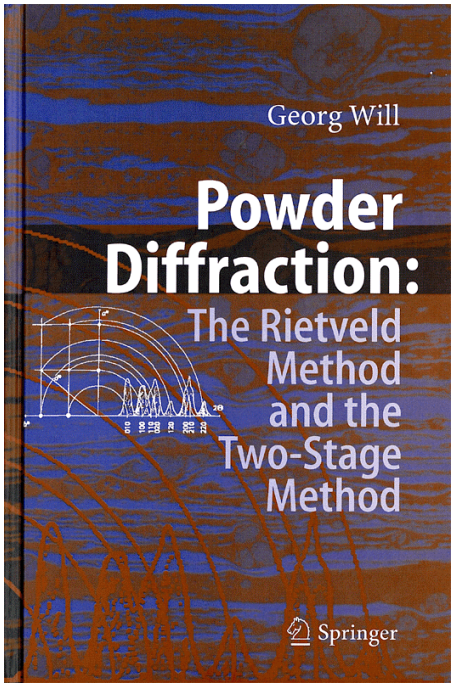
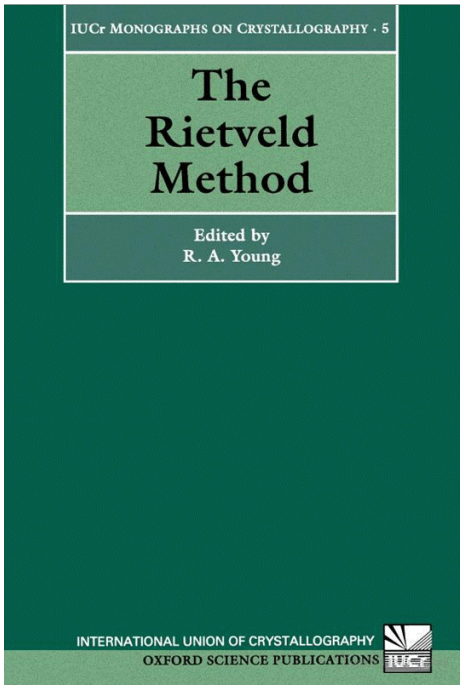
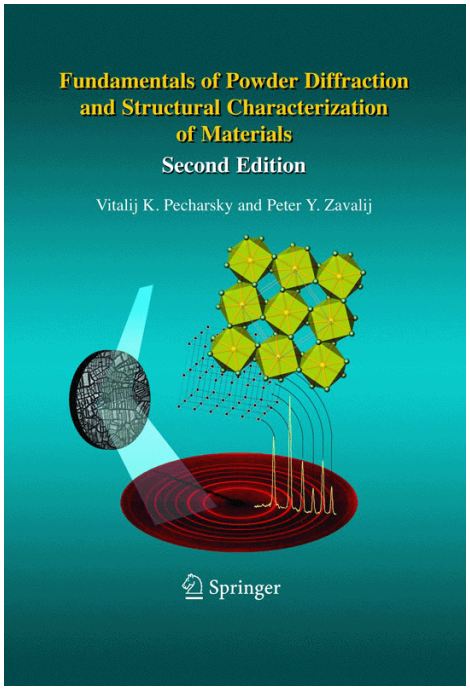
X-ray powder diffraction – a practical guide







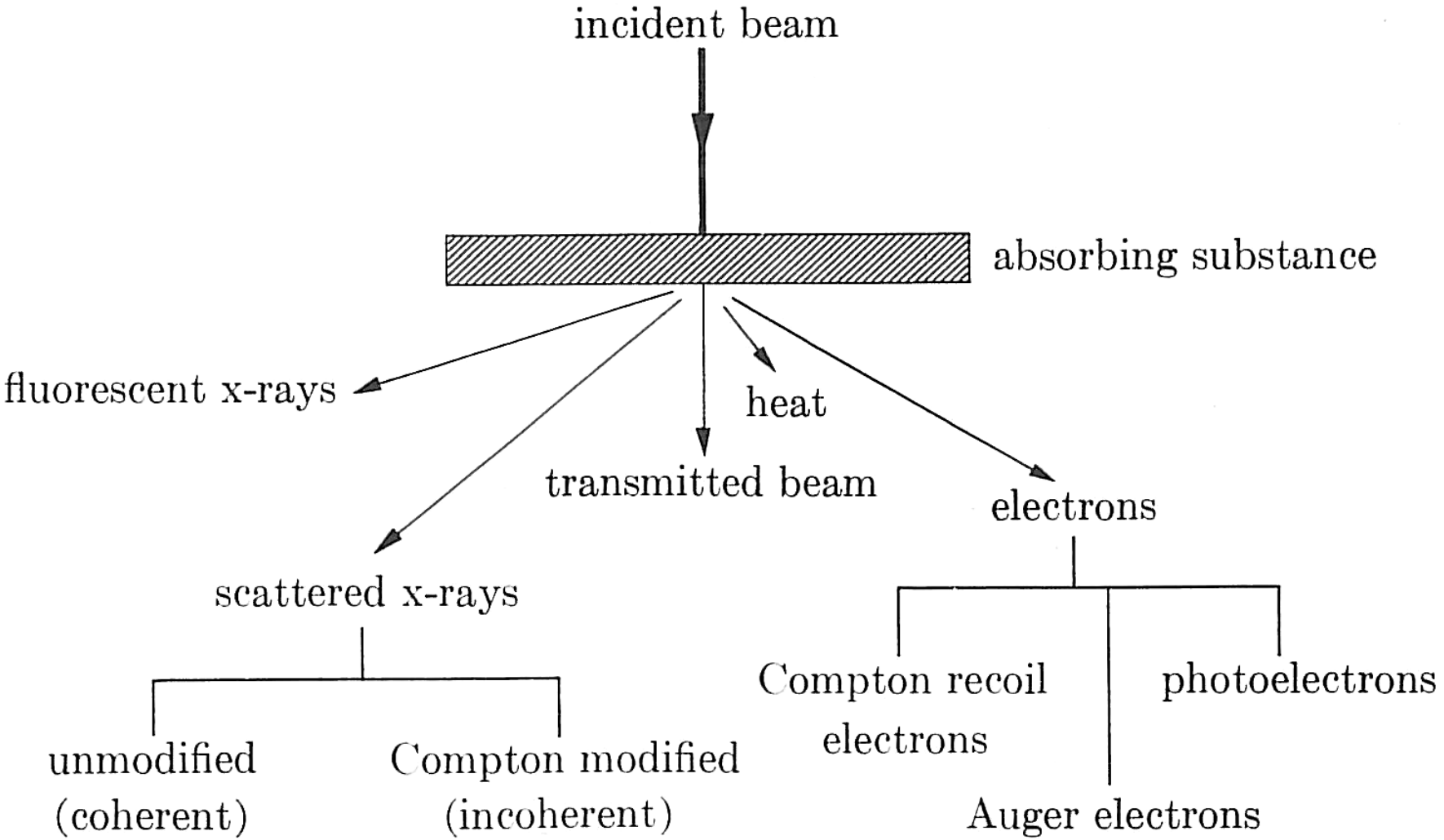


Dinnebier 0; InternationalTables 0; Will 0; Young 0; Pecharsky 0

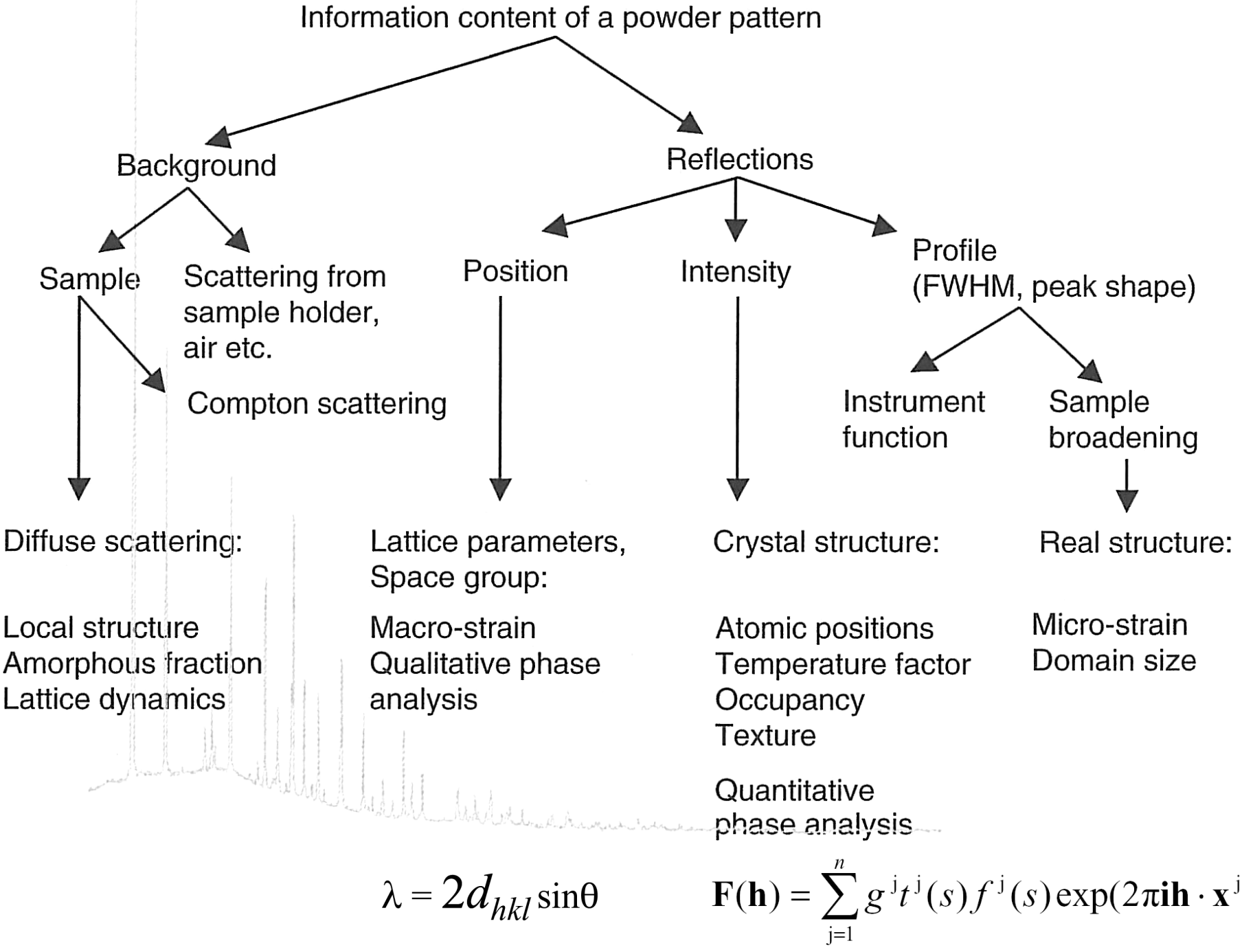
Radiation hitting condensed matter

	NEUTRONS	X-RAYS	ELECTRONS
Wavelength range	0.4 - 10 Å	0.1 - 5 Å	0 .04 - 0.2 Å
Energy range	0.001 - 0.5 eV	3000 - 100000 eV	6000 - 120000 eV
Cross-section	10^{-25} barns	10^{-25} Z^2 barns	~10^{-22} barns
Penetration depth	~ cm	~ μm	~ nm
Typical flux	10^{11} s^{-1} m^{-2}	10^{24} s^{-1} m^{-2}	10^{26} s^{-1} m^{-2}
Beam size	mm-cm	μm-mm	nm-μm
Typical sample	Any bulk sample	Small crystals, powders, surfaces	Surfaces, thin films, grains, gases
Techniques	**Diffraction** Inelastic scattering Reflectivity	Diffraction Photon absorption Photoemission Inelastic scattering	Microscopy Diffraction Emission spectroscopy EELS
Phenomena	**Magnetic/crystal structures** collective excitations (phonons, spin waves) electronic excitations (crystal-field, spin-orbit)	Crystal structures, electronic transitions (photoemission, absorption),	microstructure crystal structures electronic transitions

X-ray hitting condensed matter



X-ray hitting condensed matter

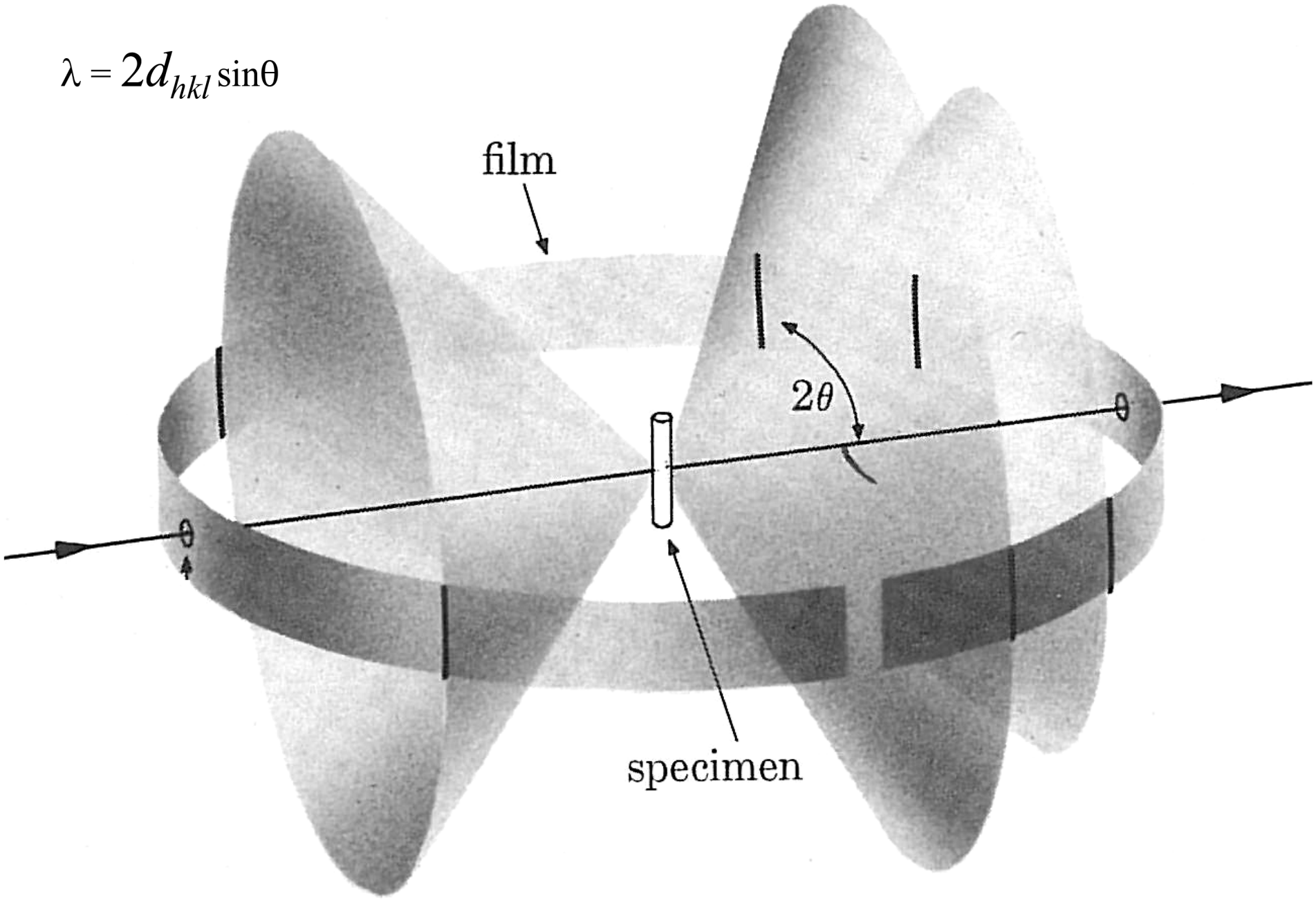


$$\lambda = 2d_{hkl}\sin\theta$$

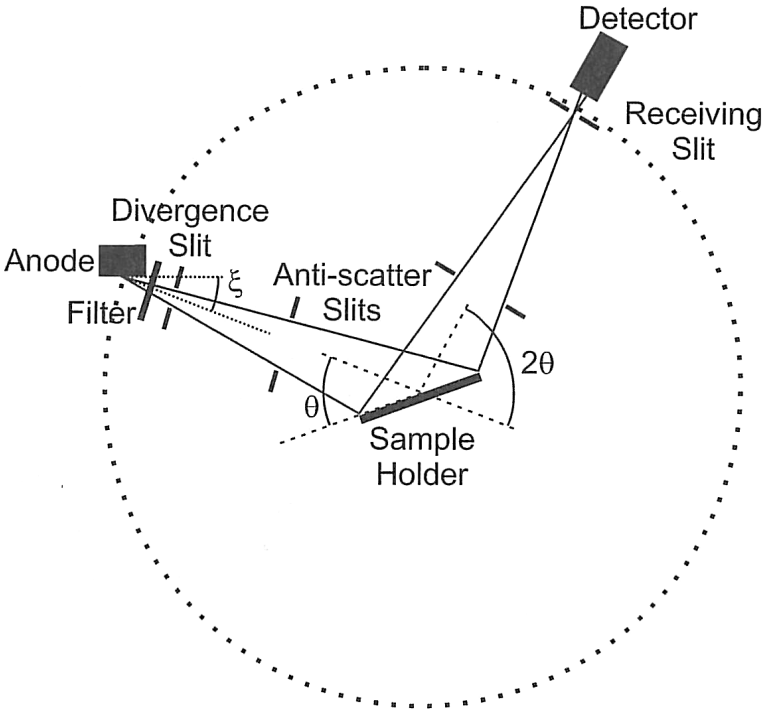
$$\mathbf{F}(\mathbf{h}) = \sum_{j=1}^{n} g^{j} t^{j}(s) f^{j}(s) \exp(2\pi \mathbf{i}\mathbf{h}\cdot\mathbf{x}^{j})$$

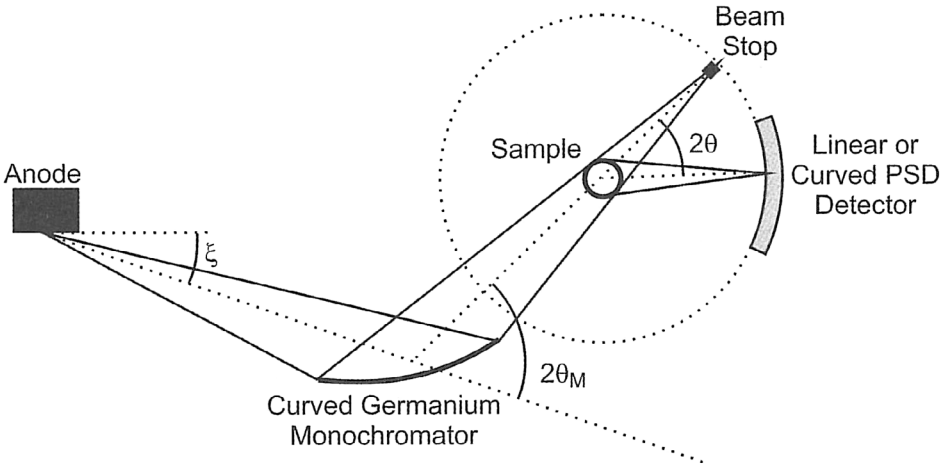
Debye-Scherrer cones from a polycrystalline sample

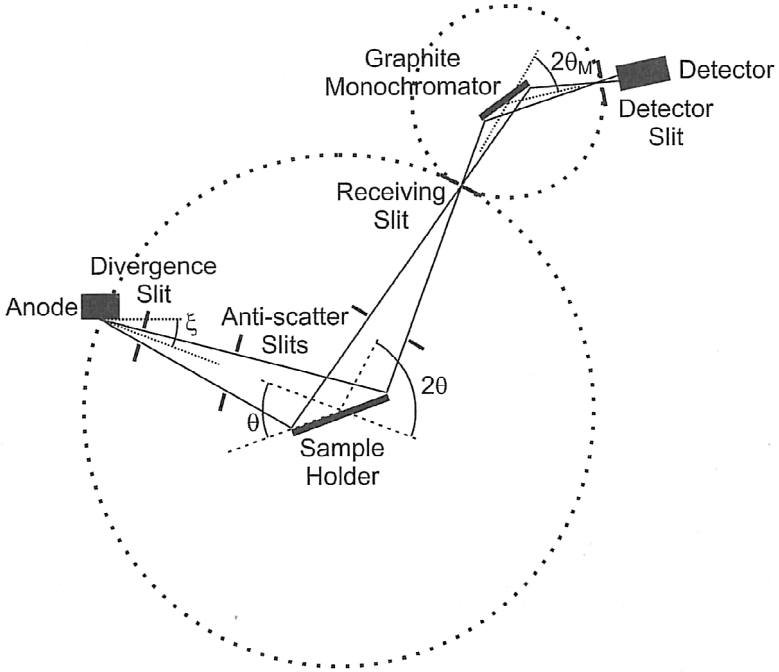
$$\lambda = 2d_{hkl}\sin\theta$$

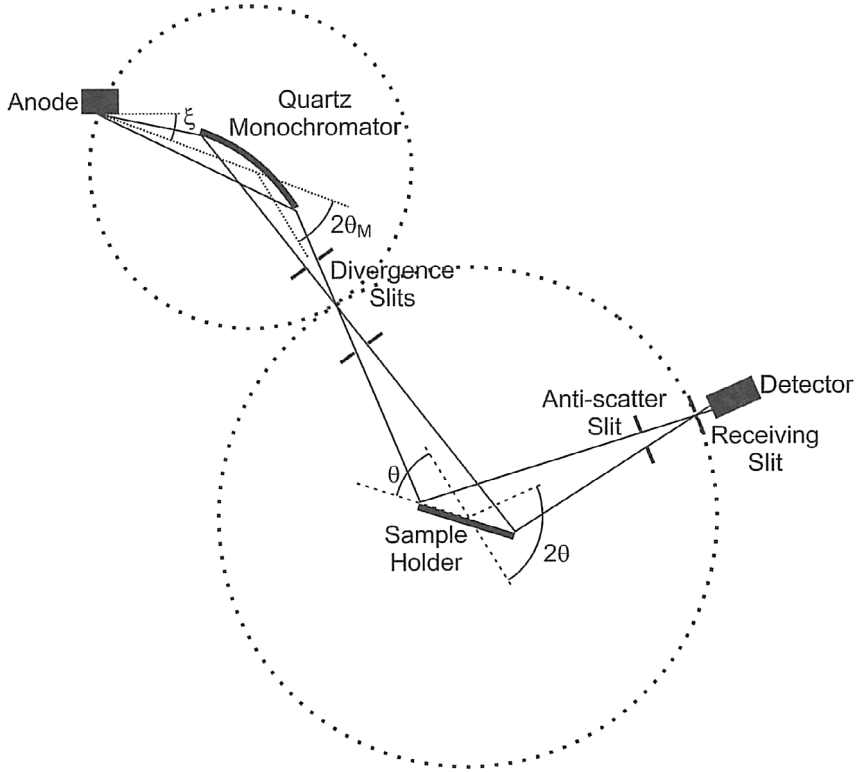


Bragg-Brentano and Guinier diffractometer

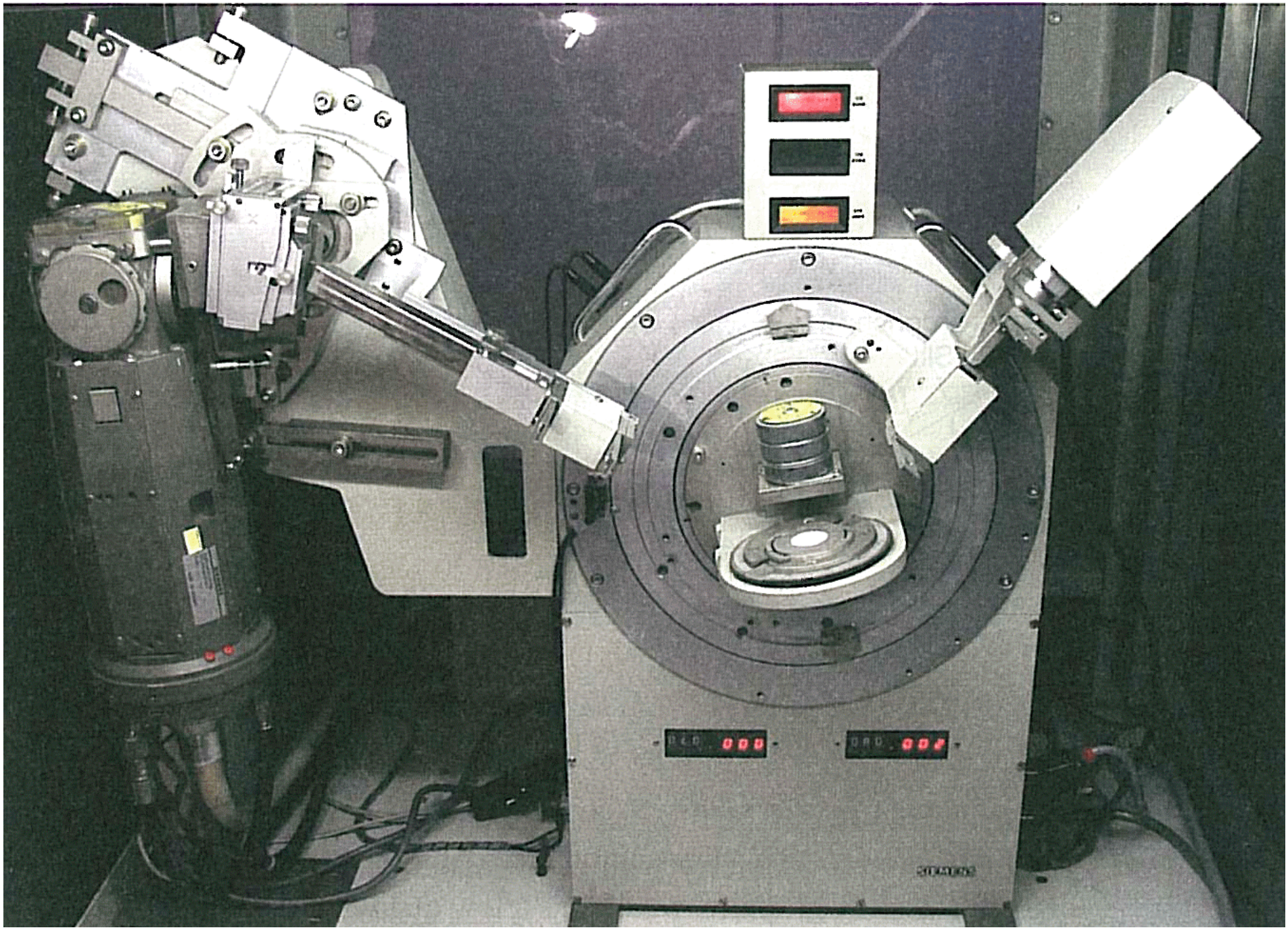




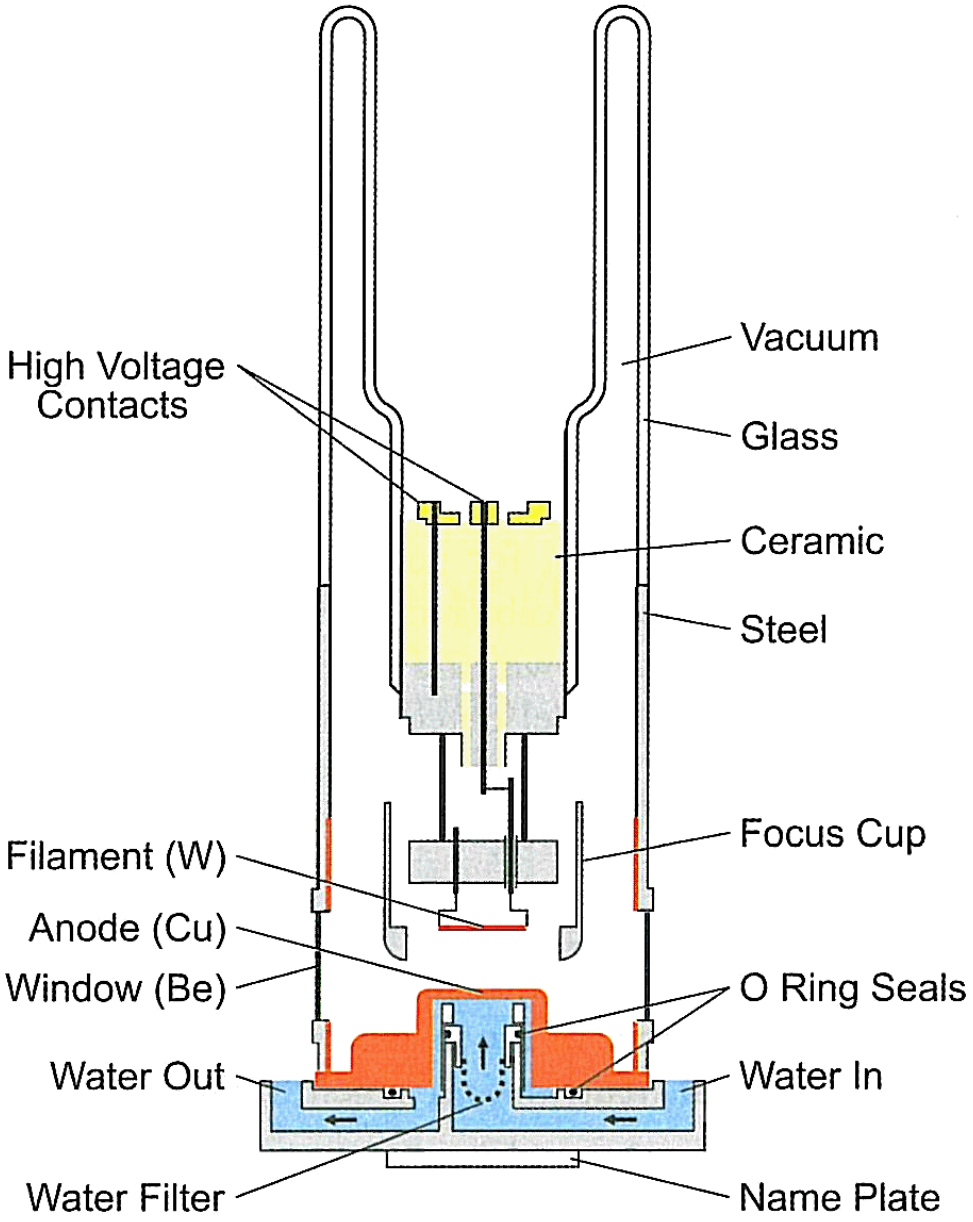




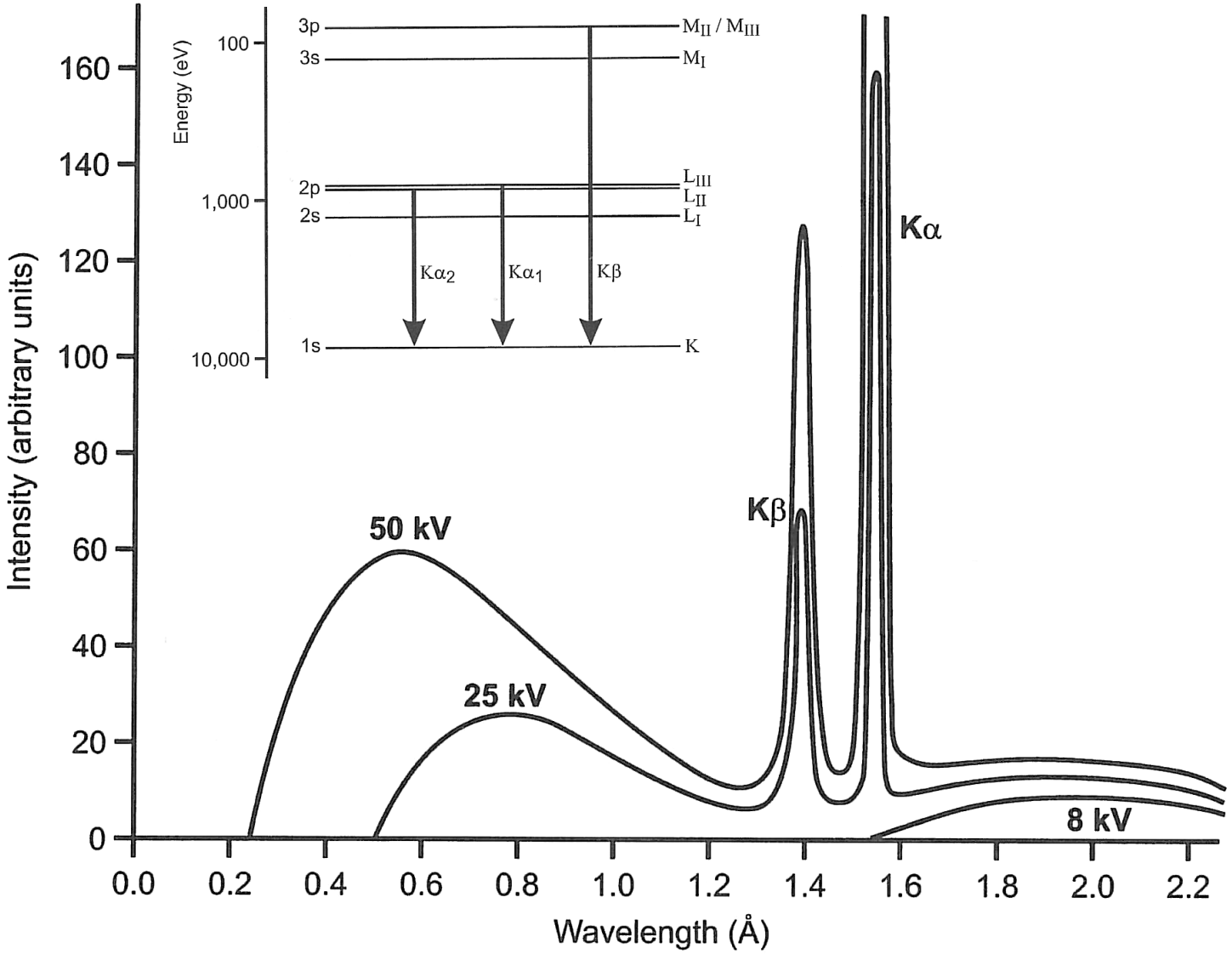
Bragg-Brentano diffractometer with monochromator



Generation of x-ray

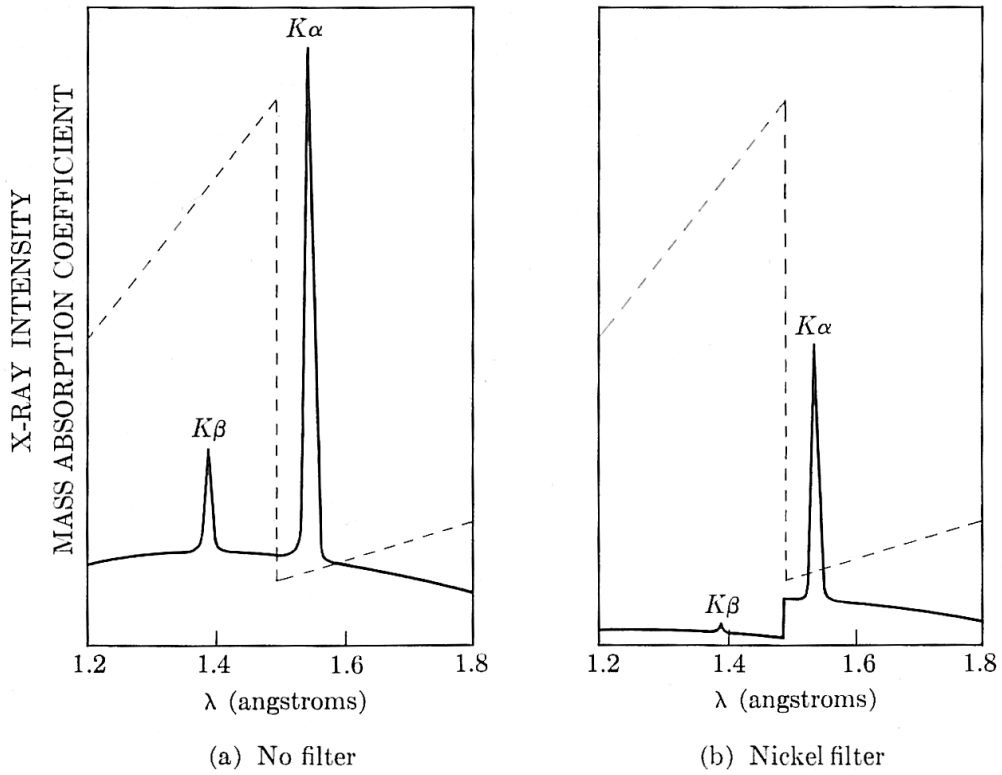


Generation of x-ray



Optimum voltage ~4 times characteristic energy (~30 kV for Cu anodes)

Generation of x-ray

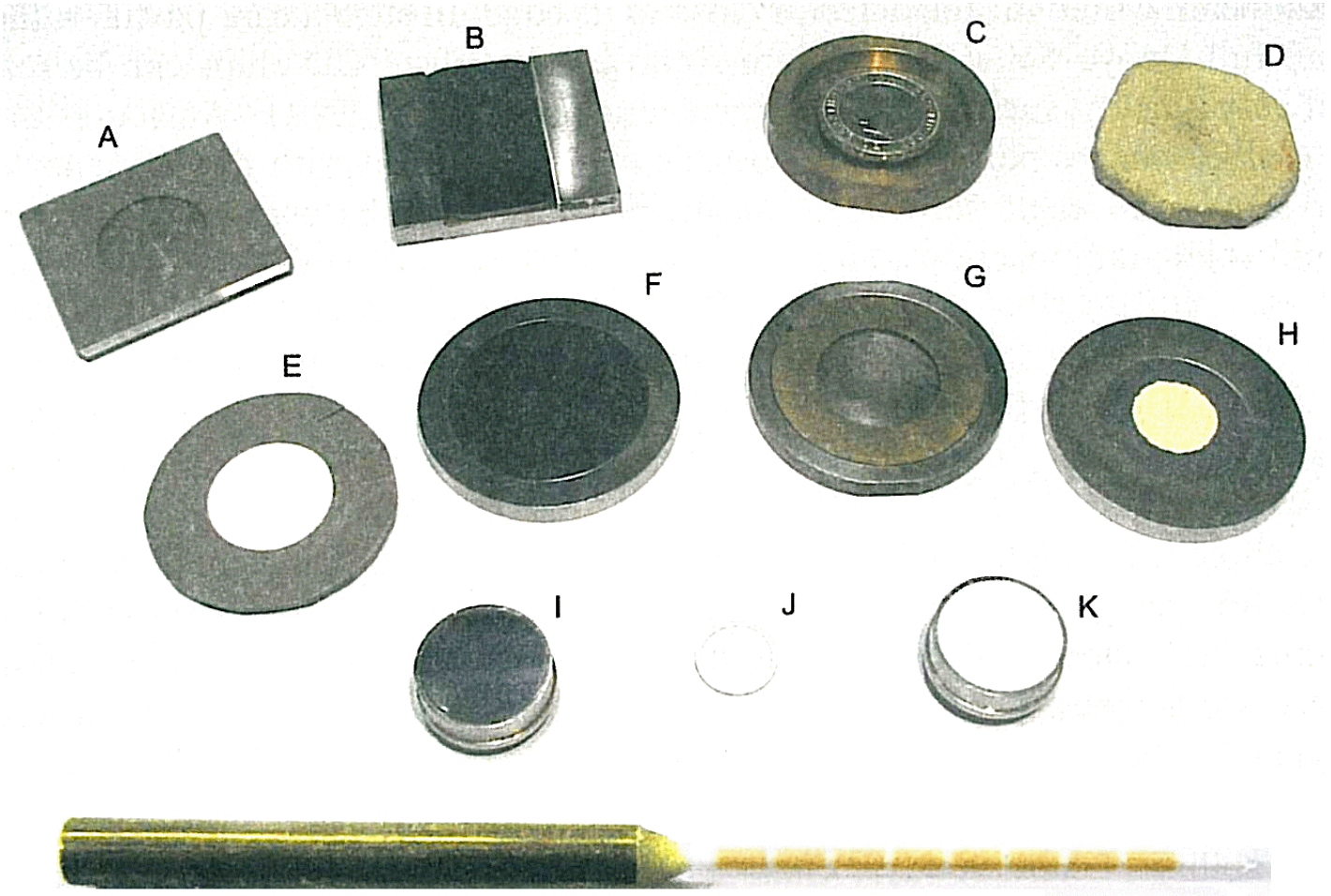


Target	Filter	Incident beam* $\frac{I(K\alpha)}{I(K\beta)}$	Filter thickness for $\frac{I(K\alpha)}{I(K\beta)} = \frac{500}{1}$ in trans. beam		$\frac{I(K\alpha)\text{ trans.}}{I(K\alpha)\text{ incident}}$
			mg/cm²	in.	
Mo	Zr	5.4	77	0.0046	0.29
Cu	Ni	7.5	18	0.0008	0.42
Co	Fe	9.4	14	0.0007	0.46
Fe	Mn	9.0	12	0.0007	0.48
Cr	V	8.5	10	0.0006	0.49

* This is the intensity ratio *at the target* [G.11, Vol. 3, p. 71]. This ratio outside the x-ray tube will be changed somewhat by the differential absorption of $K\alpha$ and $K\beta$ by the tube window, typically beryllium, 0.01 inch (0.25 mm) thick.

Suppression of $K\beta$ radiation by filter with lighter neighbor element in periodic table

Samples for x-ray powder diffraction



Well prepared samples at the right sample holder is the key for success!!!

Samples for x-ray powder diffraction

Hygiene in preparing the powder is the second key for success!!!

Samples for x-ray powder diffraction

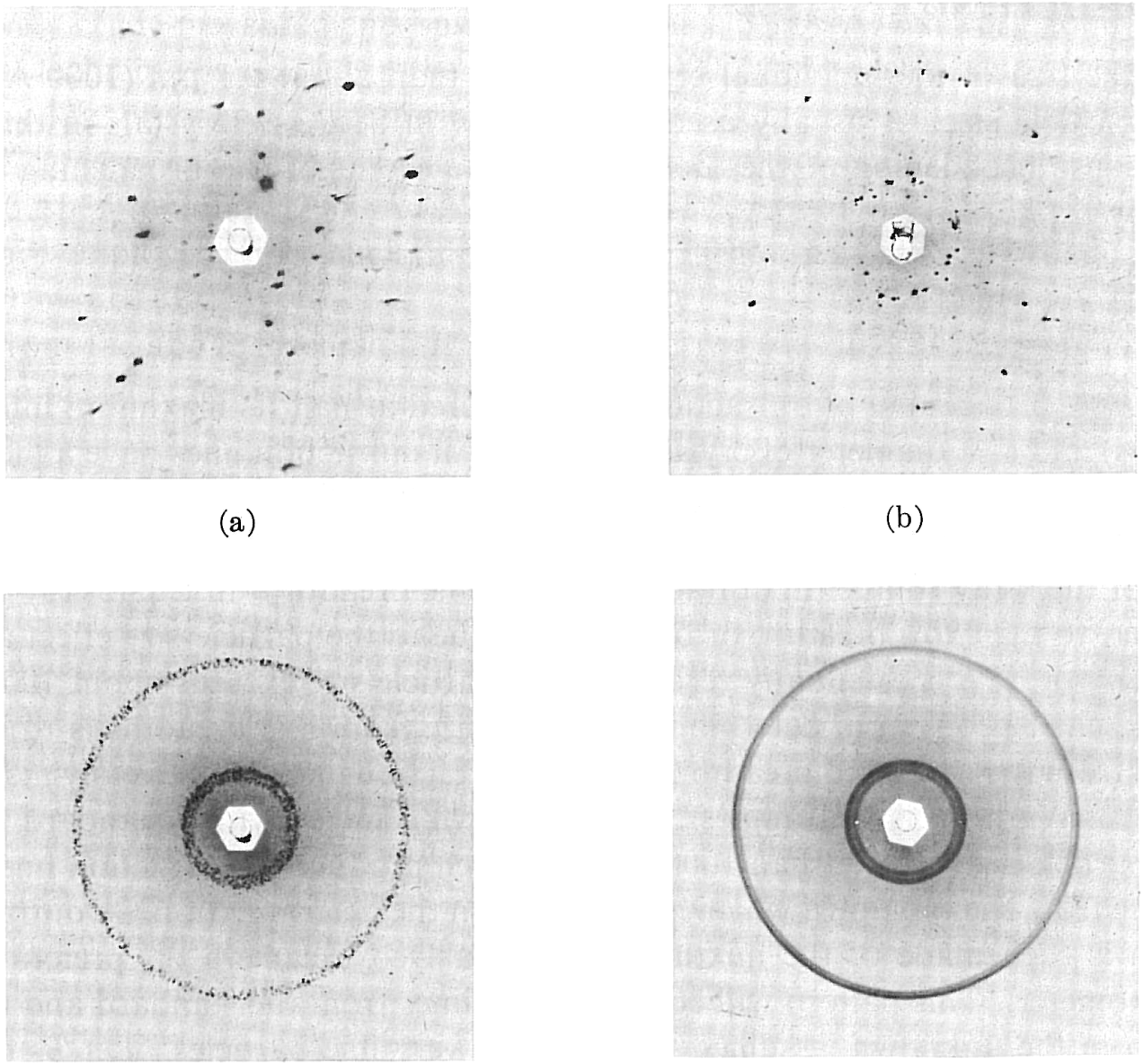
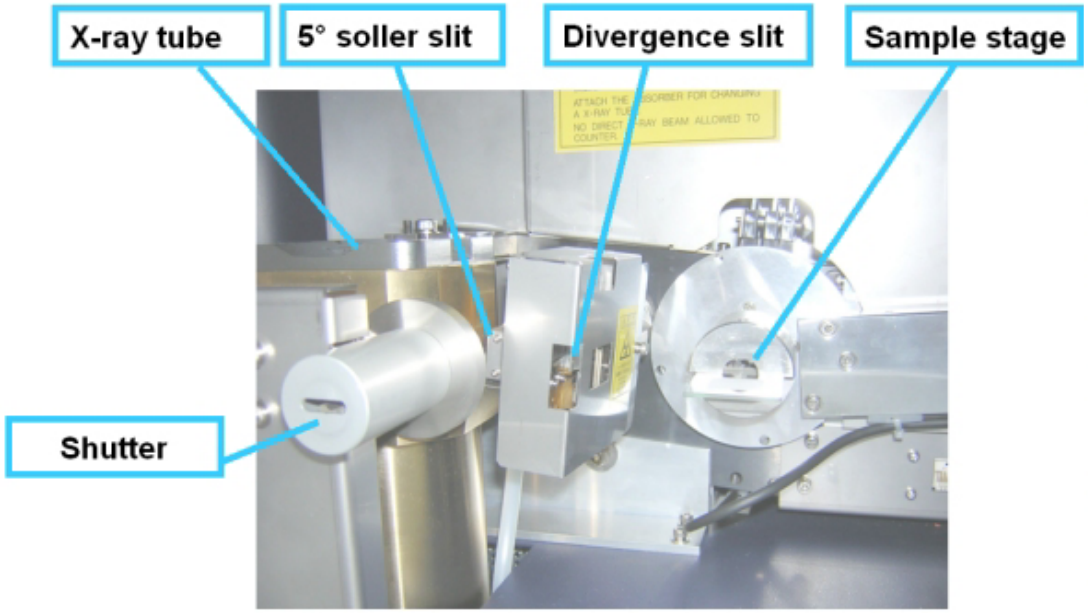


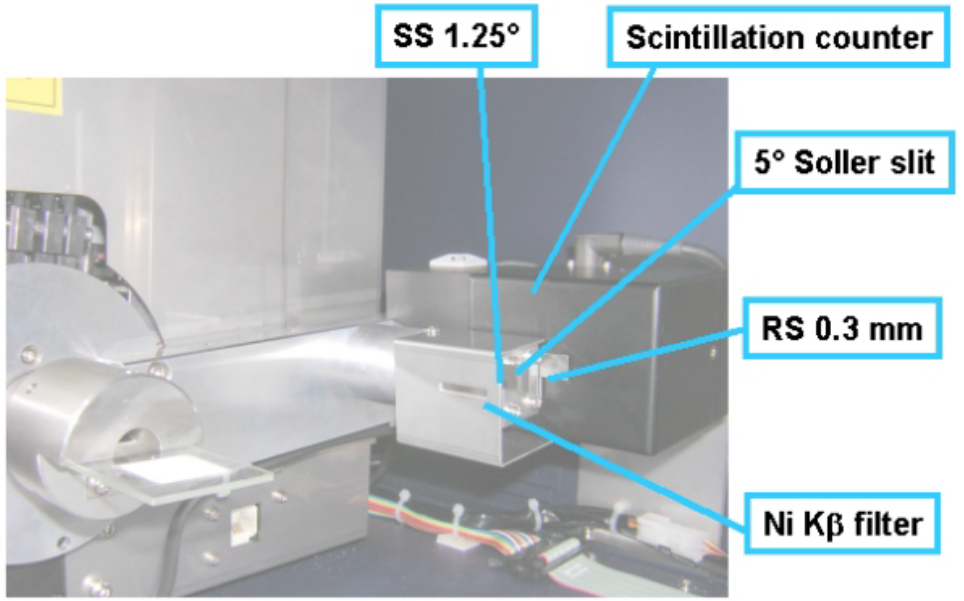
Fig. 9–1 Back-reflection pinhole patterns of recrystallized aluminum specimens; grain size decreases in the order (a), (b), (c), (d). Filtered copper radiation.

Bragg-Brentano diffractometer for the desk

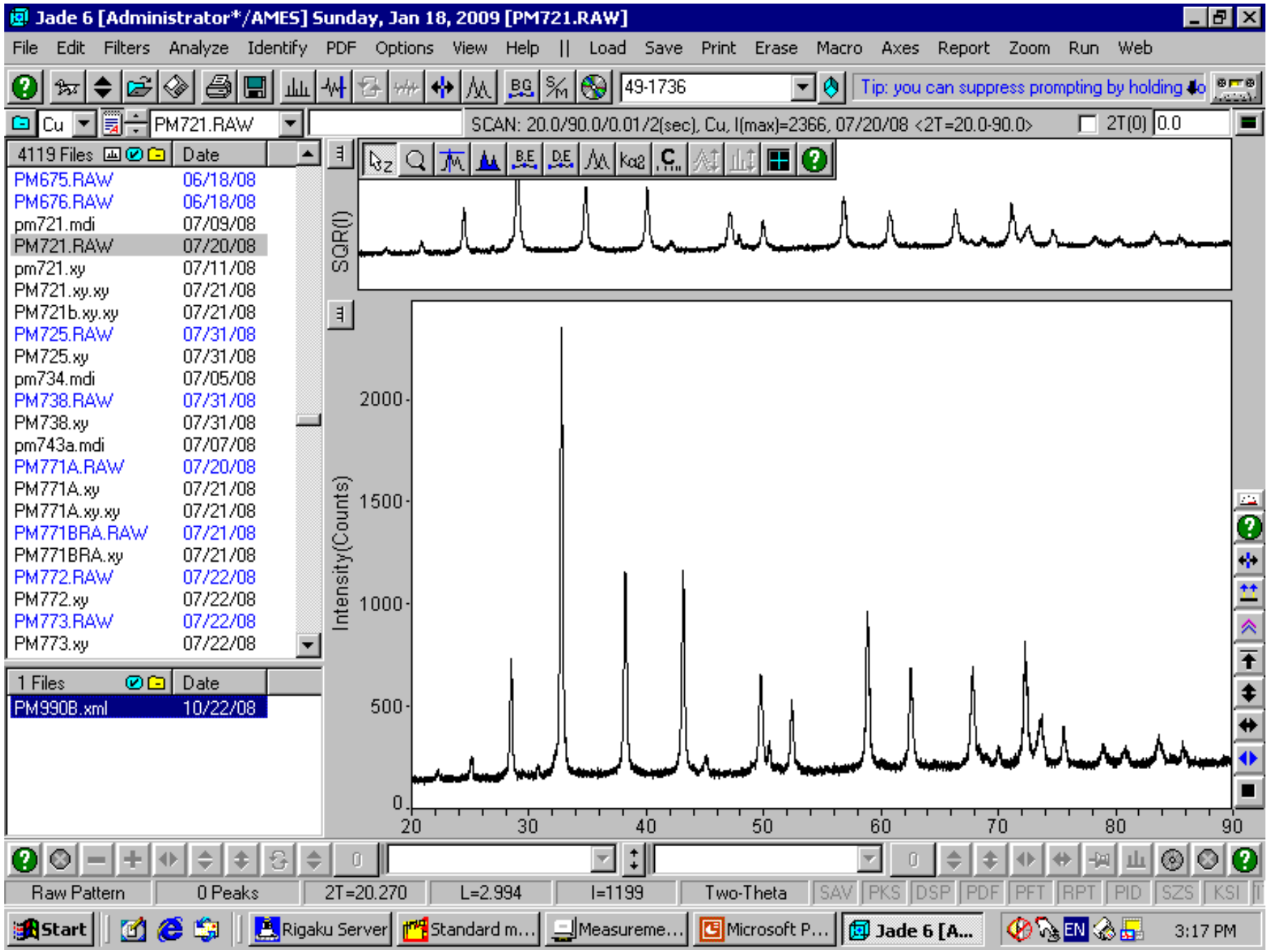
Goniometer & optics (incident)



Goniometer & optics (receiving)



Example: growth of PrAuSi out of Sn flux



Which phases are present?

Phase analysis with the PDF database

POWDER DIFFRACTION FILE

Sets 1-5 (Revised)

Inorganic Volume, No. PD1S-5iRB

Published by the
JOINT COMMITTEE ON POWDER DIFFRACTION STANDARDS
1601 Park Lane, Swarthmore, Pennsylvania 19081
U.S.A.

1-0024 MAJOR CORRECTION

0068 d 1-0024	12.8	3.60	6.9	12.8	$ZrOCl_2.8H_2O$
I/I_1 1-0024	100	83	67	100	ZIRCONIUM OXYCHLORIDE OCTA HYDRATE

Rad. MoKα λ 0.709 Filter ZrO_2
Dia. 16 INCHES Cut off Coll.
I/I_1 CALIBRATED STRIPS d corr. abs.? No
Ref. H

Sys. TETRAGONAL S.G.
a_o 12.9 b_o c_o 10.6 A C
α β γ Z
Ref. B.P. (COMPUTED FROM POWDER DATA)

ε α nωβ 1.552 εγ 1.563 Sign +
2V D mp Color
Ref. WA

d Å	I/I_1	hkl	d Å	I/I_1	hkl
12.8	100	100	2.07	13	
10.6	27	001	2.00	7	
7.9	20	101	1.91	13	
6.9	67	111	1.81	13	
4.80	13	102	1.71	13	
4.12	27	221	1.62	13	
3.82	20	212,311	1.57	7	
3.60	83	320	1.51	7	
3.24	40	400	1.46	7	
2.96	7	213	1.42	7	
2.74	7	402			
2.55	7	430,104			
2.39	7	520			
2.22	13	304,441			
2.15	20	600			
		INDEXED BY B.P.			

33-1161 33-1162

d	3.34	4.26	1.82	4.26	SiO_2 ★
I/I_1	100	22	14	22	Silicon Oxide Quartz, low

Rad. $CuK\alpha_1$ λ 1.540598 Filter Mono. Dia.
Cut off I/I_1 Diffractometer I/I_1 cor.
Ref. Nat. Bur. Stand. (U.S.) Monogr. 25, Sec. 18 (1981)

Sys. Hexagonal S.G. $P3_121$ (152)
a_0 4.9133(2) b_0 c_0 5.4053(4) A C 1.1001
α β γ Z 3 Dx 2.649
Ref. Ibid.

ε α nωβ 1.544 εγ 1.553 Sign +
2V D 2.656 mp Color Colorless
Ref. Ibid.

Sample from the Glass Section at the National Bureau of Standards; ground single crystals of optical quality, locality unknown. Pattern at 25°C.
Silicon (a_0=5.43088Å) used as internal standard.
F_{30} = 76.6(0.0126,31). Quartz group.
To replace 5-490.

d A	I/I_1	hkl	d A	I/I_1	hkl
4.257	22	100	1.2285	1	220
3.342	100	101	1.1999	2	213
2.457	8	110	1.1978	1	221
2.282	8	102	1.1843	3	114
2.237	4	111	1.1804	3	310
2.127	6	200	1.1532	1	311
1.9792	4	201	1.1405	<1	204
1.8179	14	112	1.1143	<1	303
1.8021	<1	003	1.0813	2	312
1.6719	4	202	1.0635	<1	400
1.6591	2	103	1.0476	1	105
1.6082	<1	210	1.0438	<1	401
1.5418	9	211	1.0347	<1	214
1.4536	1	113	1.0150	1	223
1.4189	<1	300	0.9898	1	402
1.3820	6	212	.9873	1	313
1.3752	7	203	.9783	<1	304
1.3718	8	301	.9762	1	320
1.2880	2	104	.9636	<1	205
1.2558	2	302	6 reflections		to 0.9089

1-0378 MAJOR CORRECTION

0831 d 1-0363	4.30	3.81	4.08	4.30	SiO_2 SiO_2
I/I_1 1-0378	100	67	33	100	SILICON DI OXIDE TRIDYMITE (LOW FORM)

Rad. MoKα λ 0.709 Filter ZrO_2
Dia. 16 INCHES Cut off Coll.
I/I_1 CALIBRATED STRIPS d corr. abs.? No
Ref. H_1

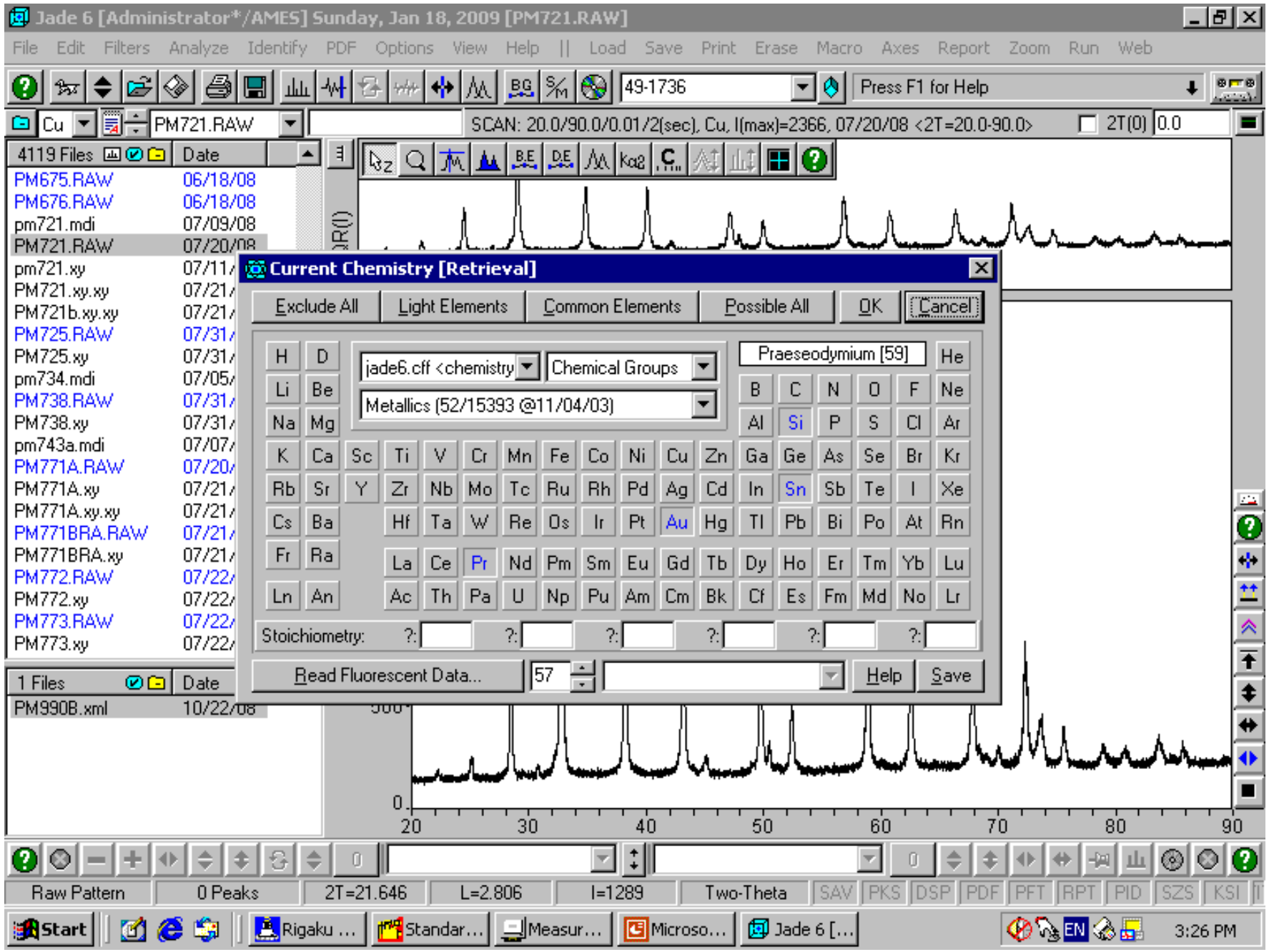
Sys. ORTHORHOMBIC S.G.
a_o 9.88 b_o 17.1 c_o 16.3 A 0.578 C 0.954
α β γ Z 64 ?
Ref. WY (FOR ONLY ONE TYPE OF TRIDYMITE)

ε α 1.478 nωβ 1.479 εγ 1.481 Sign +
2V 35° D 2.26 mp Color COLORLESS
Ref. WN, C.C. (FOR ONLY ONE TYPE OF TRIDYMITE)

T.P. TO β_1 (LOWER HIGH-TRIDYMITE) AT 117°C
T.P. TO β_2 (UPPER HIGH-TRIDYMITE) AT 163°C
SPECIMEN WAS HAWS REFRACTORY BRICK
LOW TRIDYMITE OCCURS IN MANY POLYTYPIC FORMS, THE PATTERNS OF WHICH ARE CHARACTERIZED BY THE SAME STRONG REFLECTIONS AND DIFFERENT WEAK ONES (SEE ALSO OTHER TRIDYMITE CARDS). SEE FLORKE, BER. DEUT. KERAM. GES. 32,369-82(1955) FOR REPRODUCTIONS OF POWDER PHOTOGRAPHS.

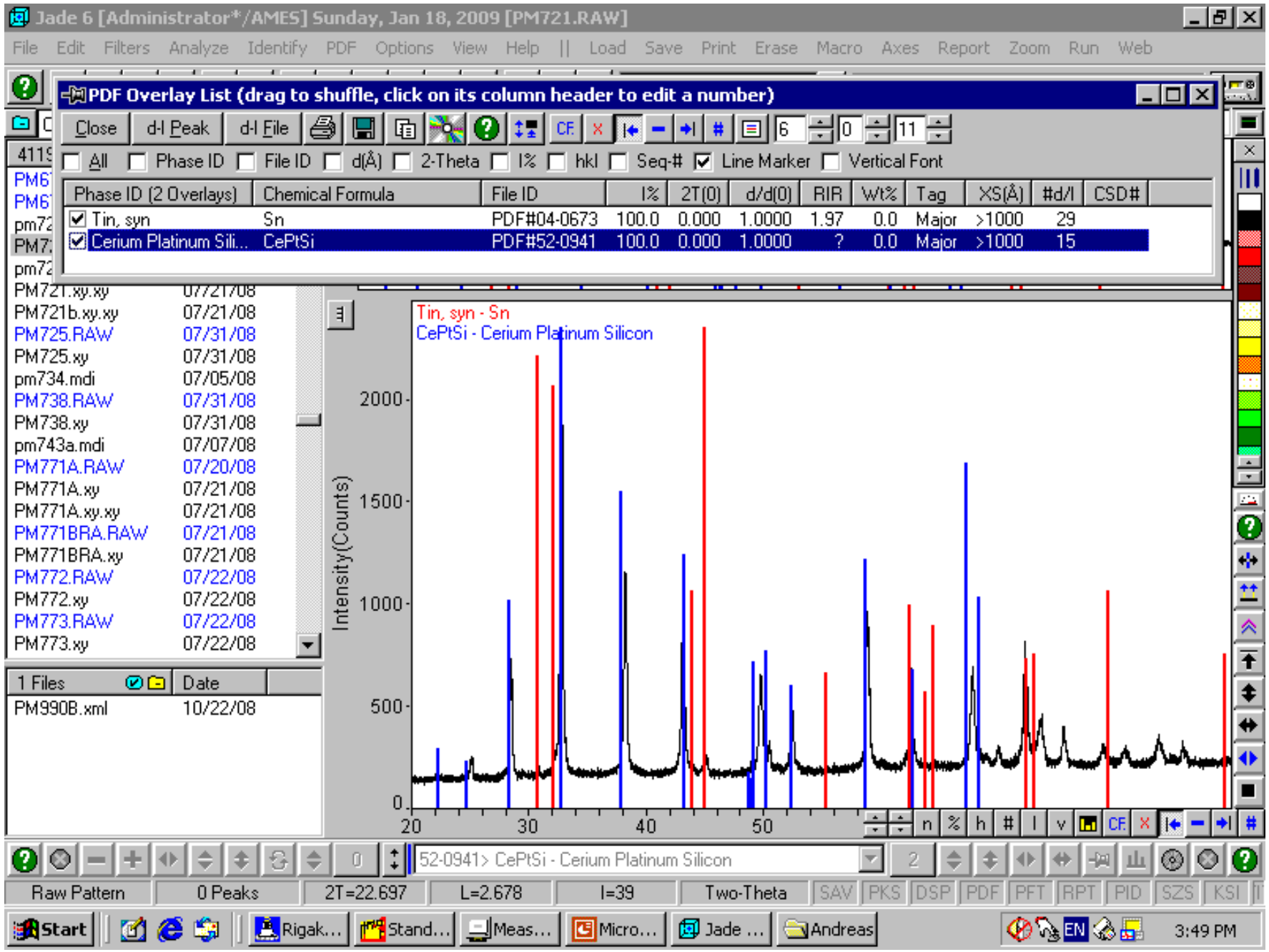
d Å	I/I_1	hkl	d Å	I/I_1	hkl
4.30	100		1.44	3	
4.08	33		1.40	7	
3.81	67		1.36	3	
3.43	1		1.31	4	
3.21	1		1.25	3	
2.96	17		1.19	5	
2.80	3		1.15	3	
2.49	27		1.10	1	
2.31	11				
2.08	5				
1.84	3				
1.69	8				
1.64	4				
1.60	4				
1.53	5				

Example: growth of PrAuSi out of Sn flux



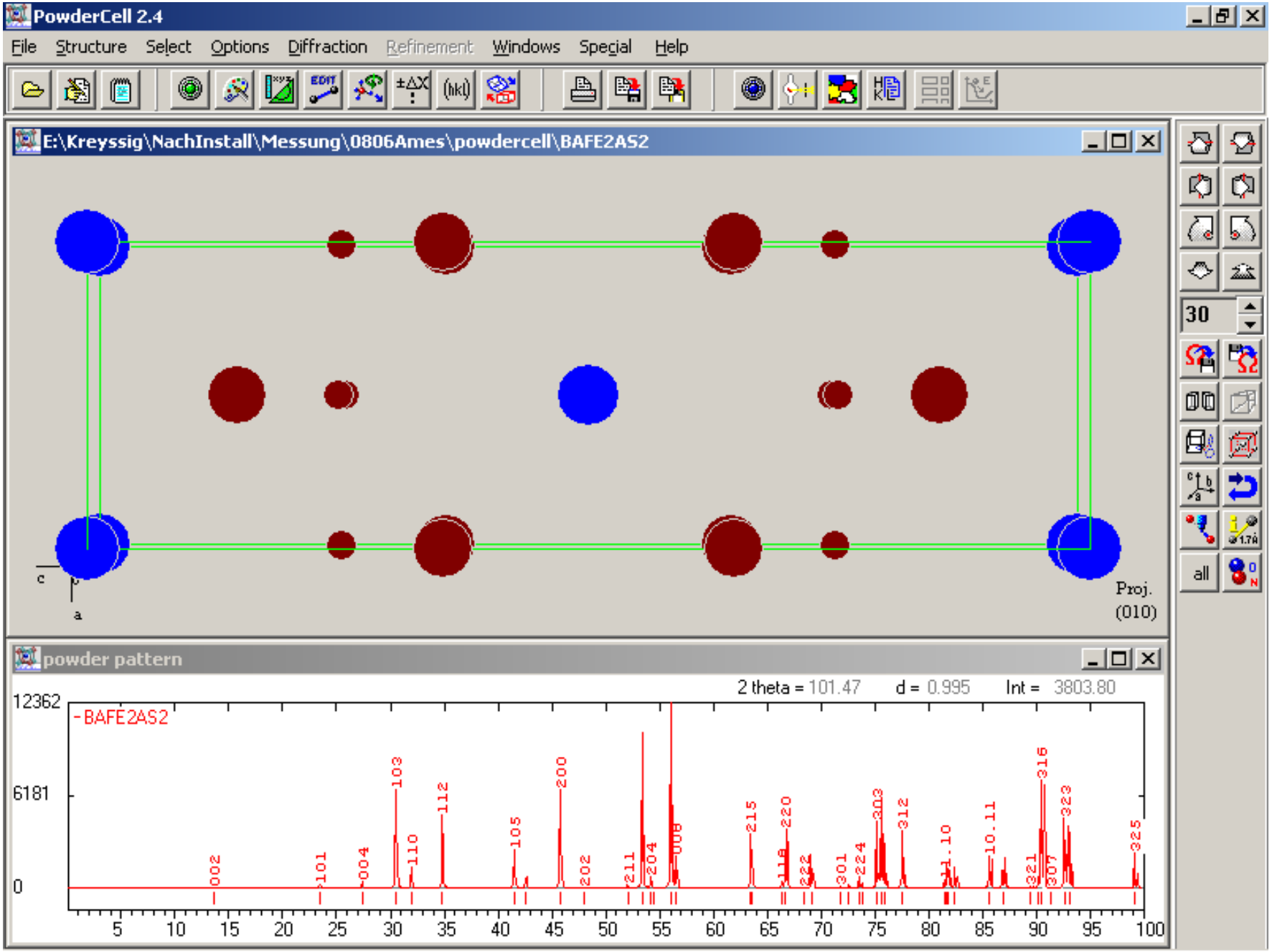
Which elements can/must be present?

Example: growth of PrAuSi out of Sn flux



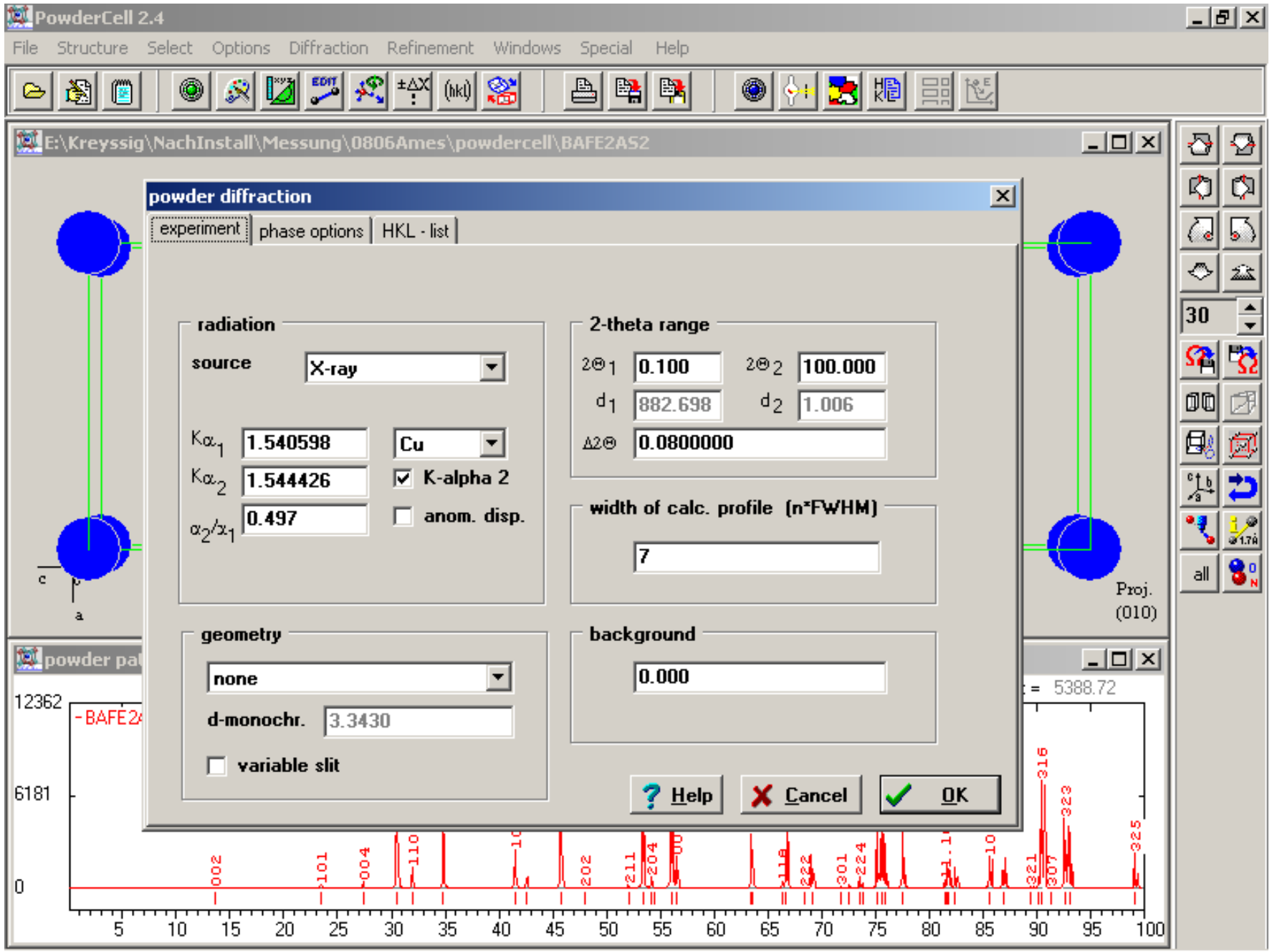
If your phase is not in the database – search for isostructural compounds...

Powdercell



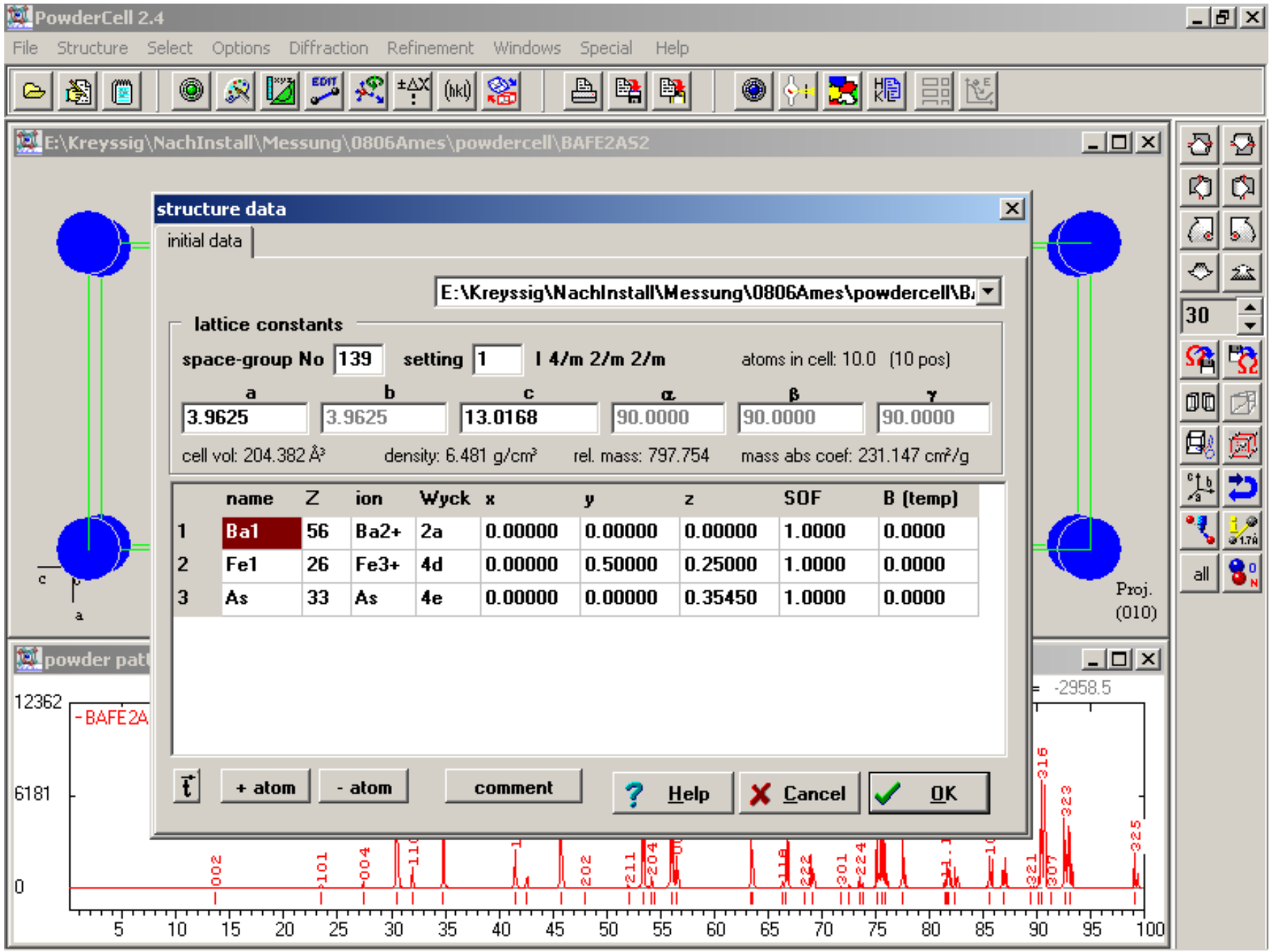
The best tool to calculate diffraction pattern, to verify structure data and more...

Powdercell



The best tool to calculate diffraction pattern, to verify structure data and more...

Powdercell



The best tool to calculate diffraction pattern, to verify structure data and more...

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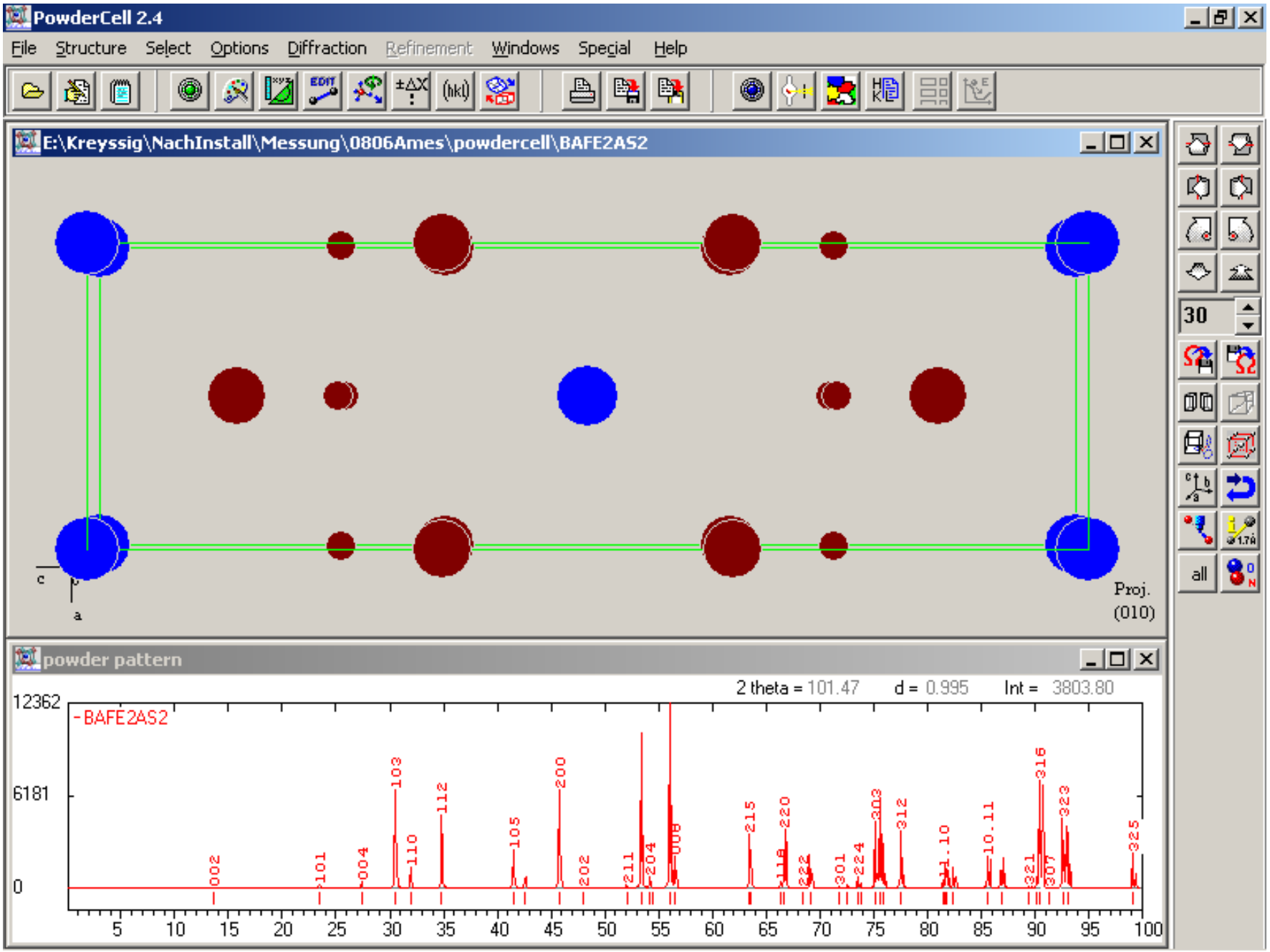
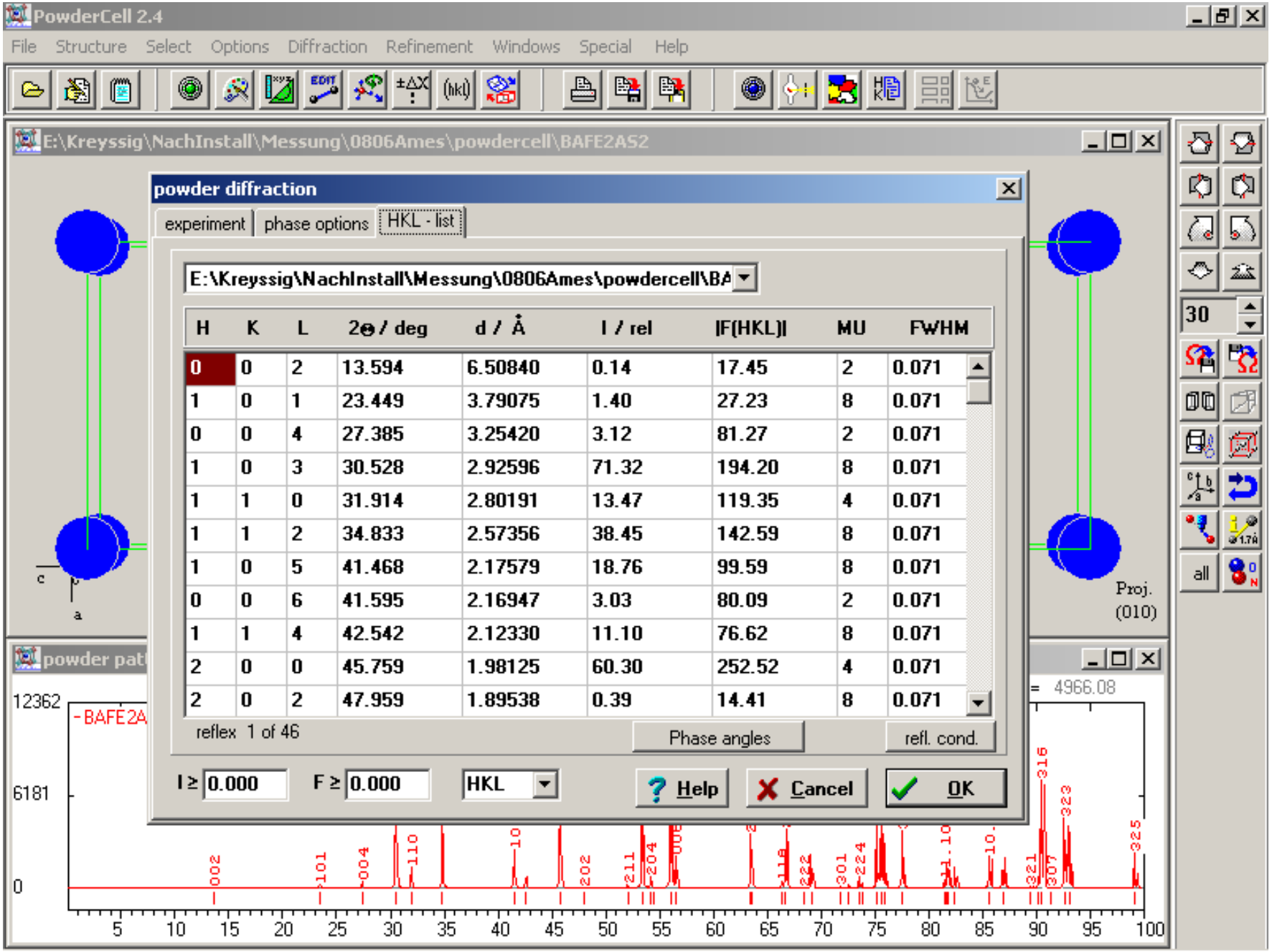


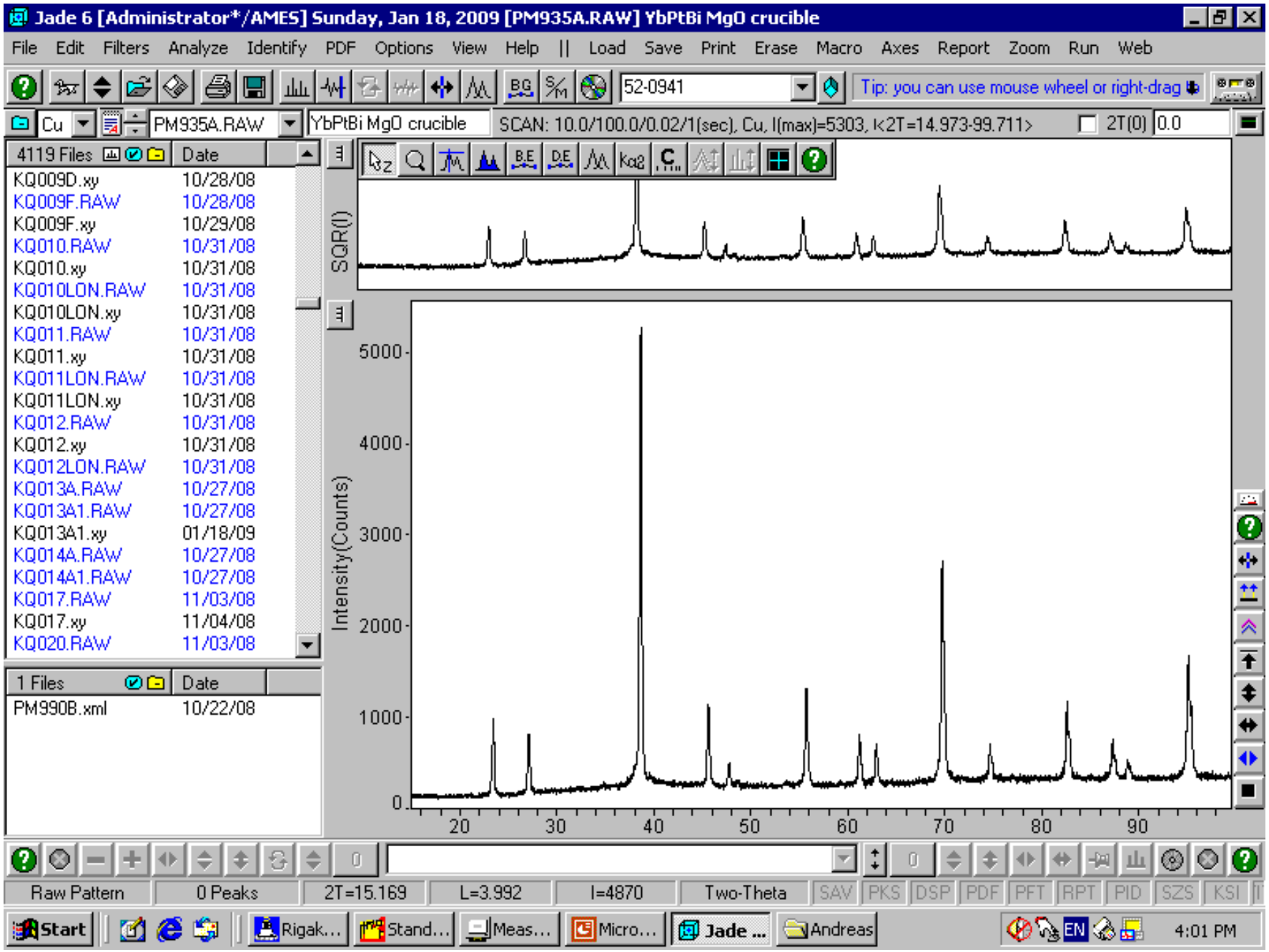
Verify the structure data visually and via plausible bonding length!!!

Powdercell



Extract the reflection list: (hkl) – position - intensity

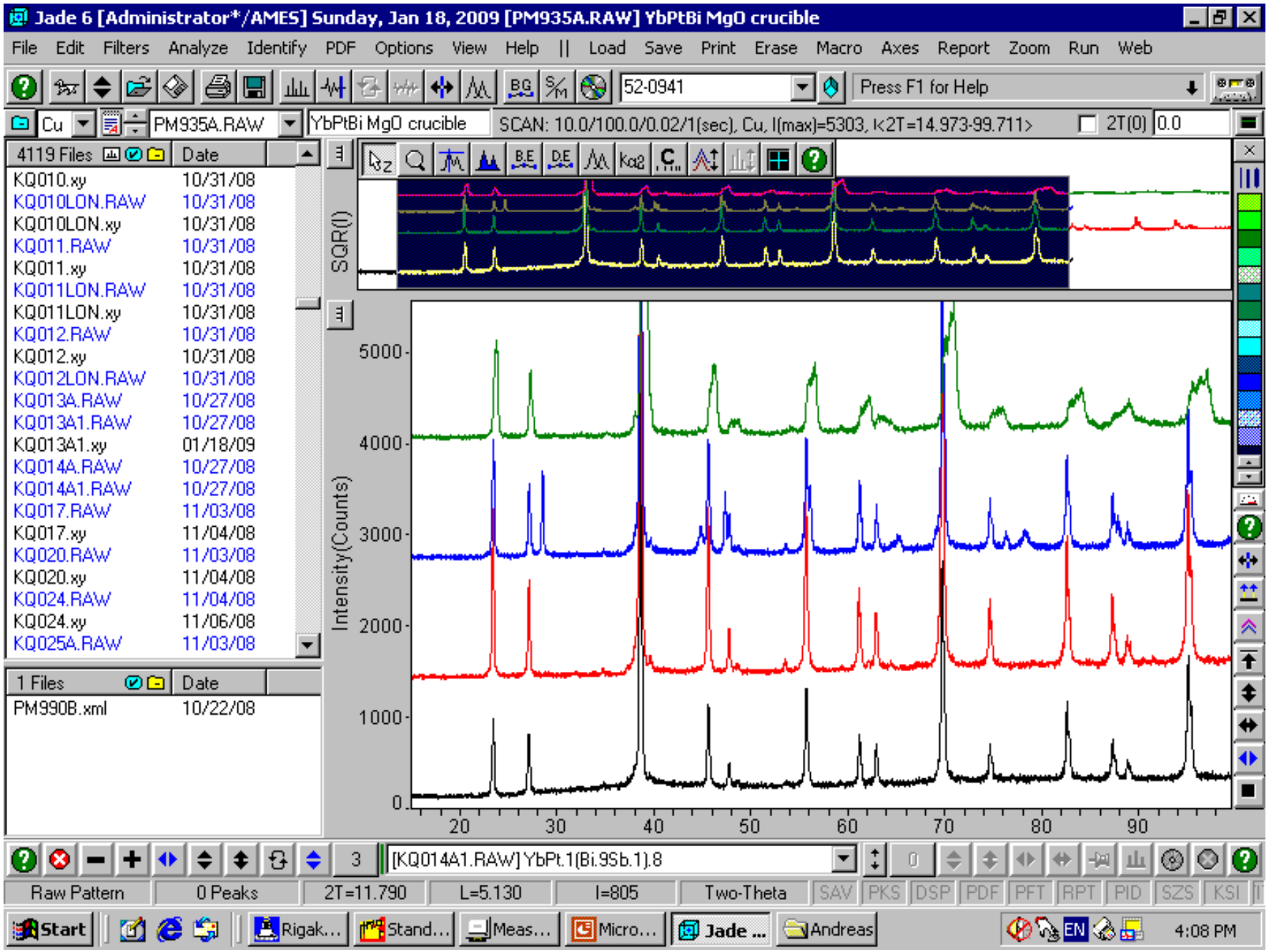
Example: growth of YbPtBi with partial element substitution



YbPtBi

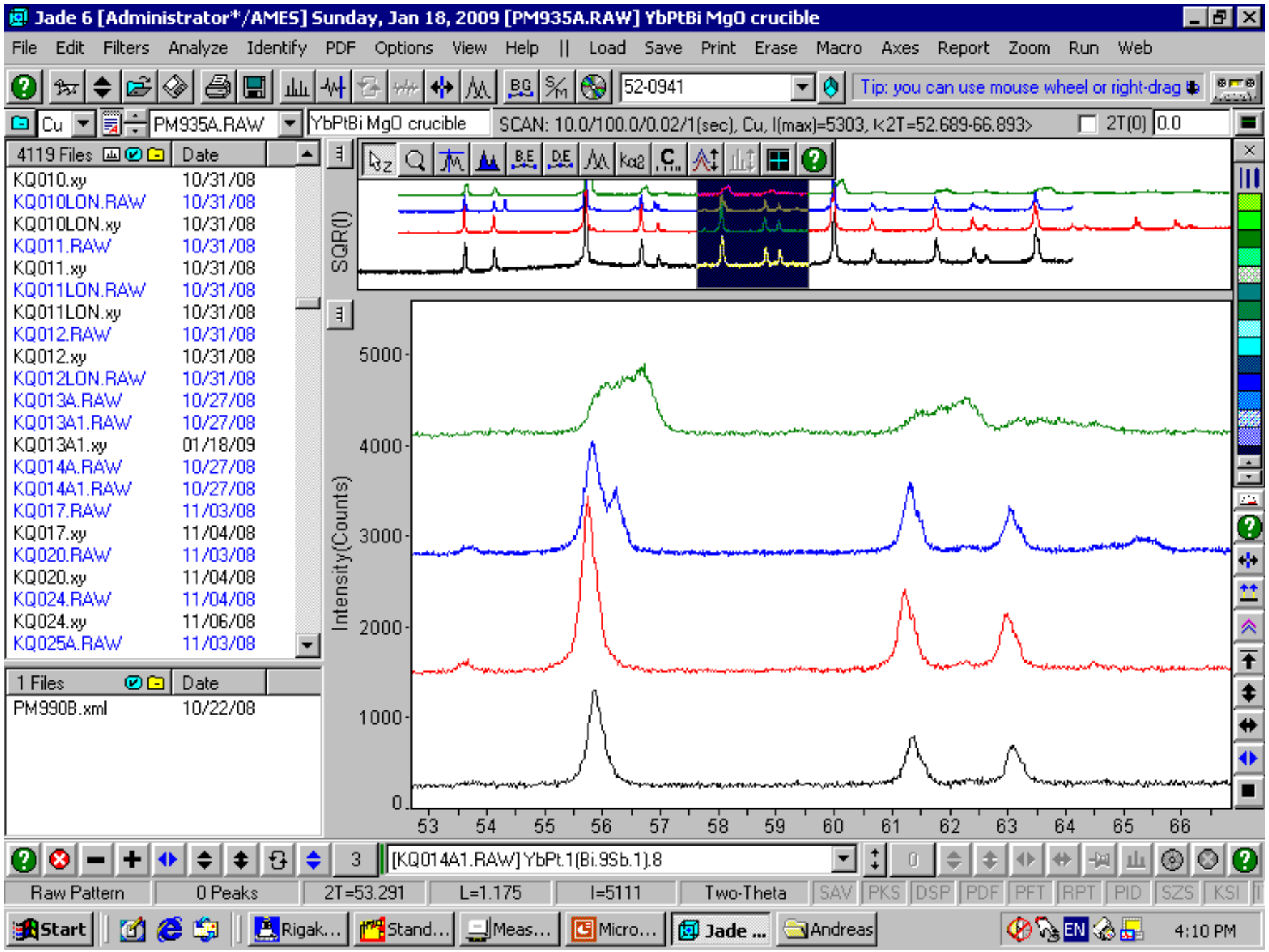
Nice crystals of parent compound

Example: growth of YbPtBi with partial element substitution



Which phases were grown successfully?

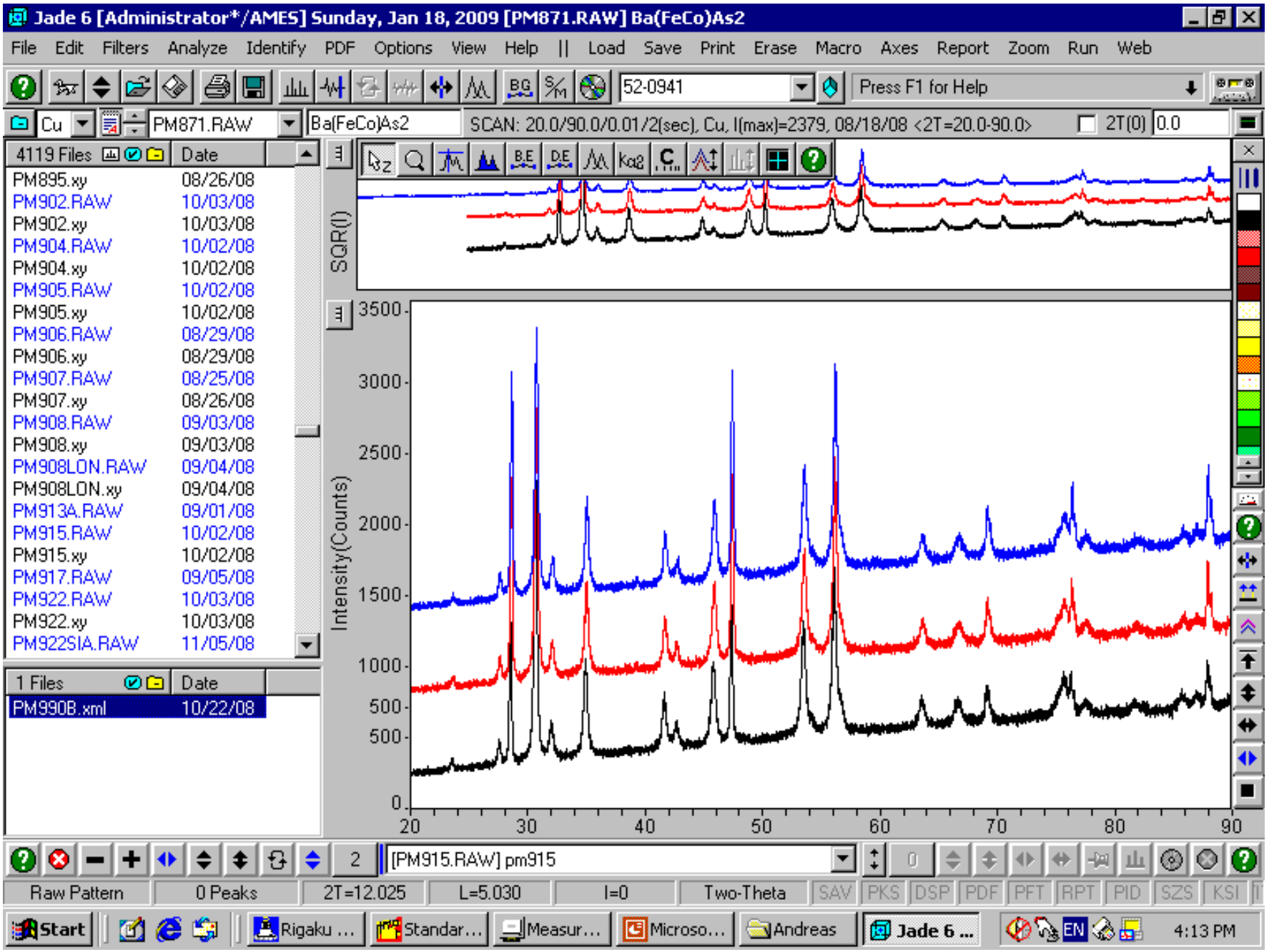
Example: growth of YbPtBi with partial element substitution



Only $YbPt_{0.9}Au_{0.1}Bi$ was grown successfully.

E. D. Mun: PM935-Ex2c

Example: growth of $Ba(Fe_{1-x}Co_x)_2As_2$



x = 0.10

PM915

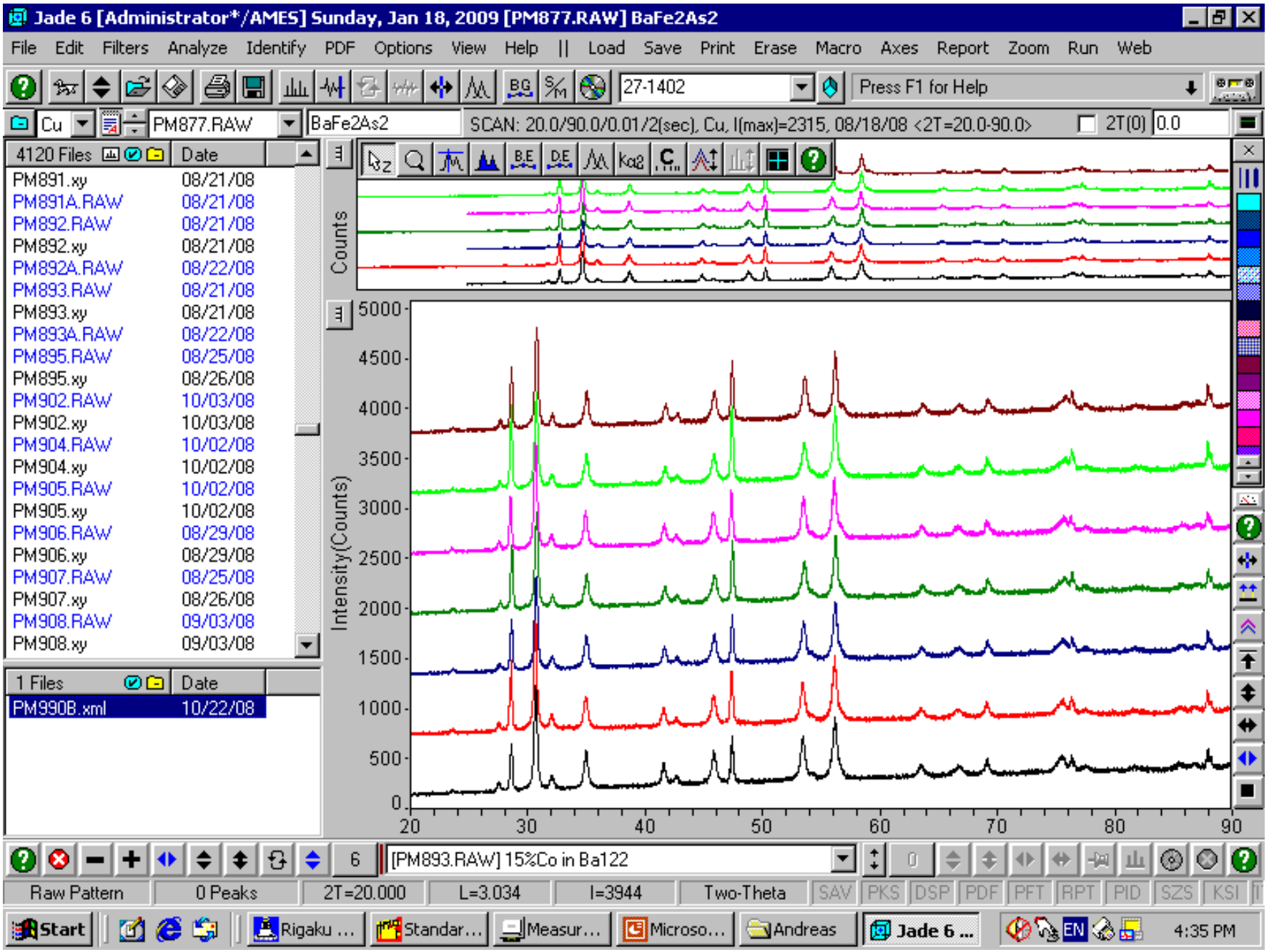
PM892

PM871

Preparation of samples with same stoichiometry is reproducible.

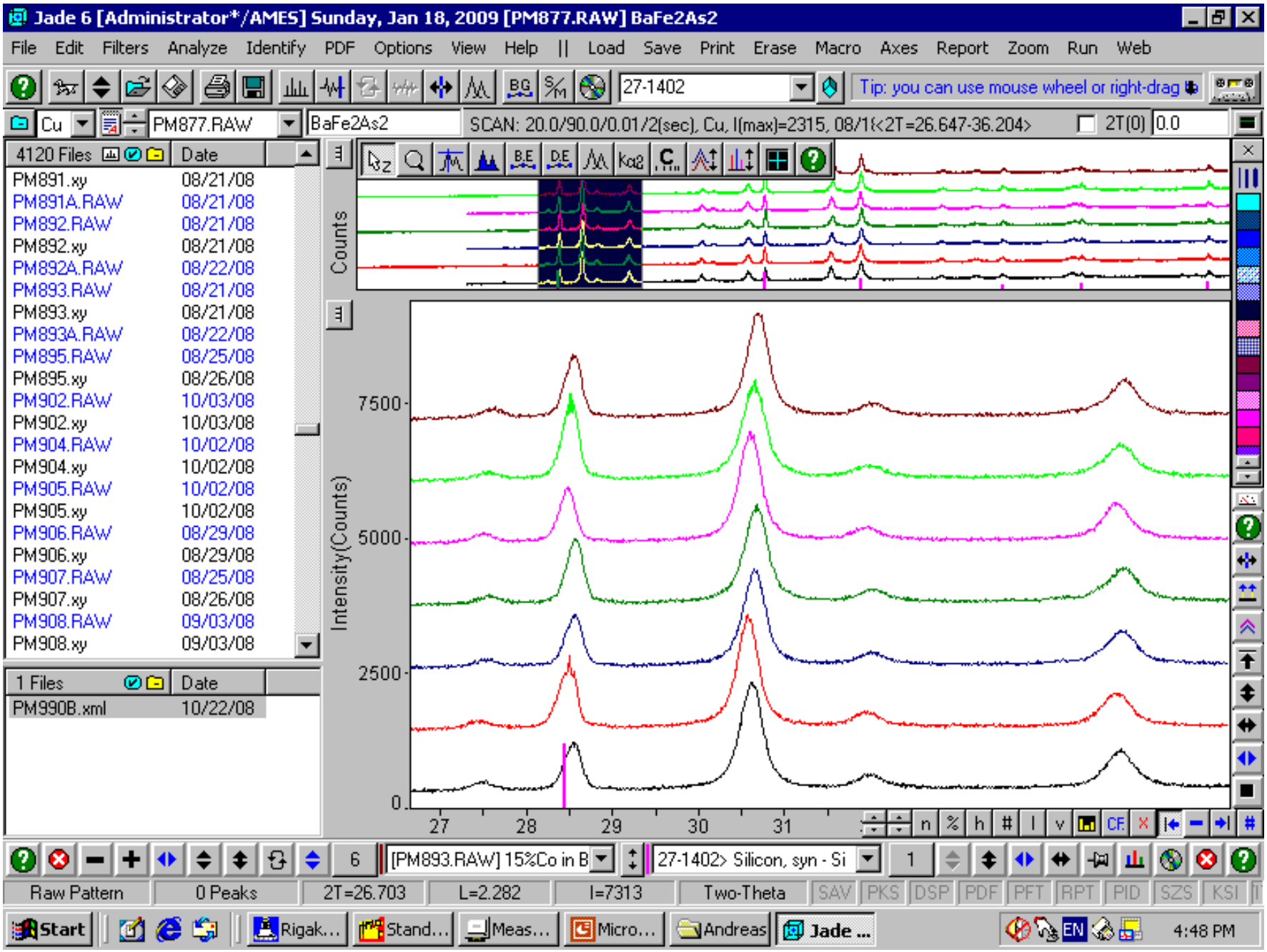
N. Ni: PM871-Ex3a

Example: growth of $Ba(Fe_{1-x}Co_x)_2As_2$



Preparation of samples with varying stoichiometry seems also successful.

Example: growth of $Ba(Fe_{1-x}Co_x)_2As_2$



Use of “inner” standard a MUST.

N. Ni: PM871-Ex3e

Position of Bragg reflections in powder pattern

$$\lambda = 2d_{hkl}\sin\theta$$

$$\frac{1}{d^2} = \frac{1}{V^2}\left(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{13}hl + 2S_{23}kl\right)$$

$$V = abc\sqrt{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma}$$

$$S_{11} = b^2c^2\sin^2\alpha$$
$$S_{22} = a^2c^2\sin^2\beta$$
$$S_{33} = a^2b^2\sin^2\gamma$$
$$S_{12} = abc^2(\cos\alpha\cos\beta-\cos\gamma)$$
$$S_{13} = ab^2c(\cos\gamma\cos\alpha-\cos\beta)$$
$$S_{23} = a^2bc(\cos\beta\cos\gamma-\cos\alpha)$$

Factors affecting peak positions:

$$\Delta 2\theta = \frac{p_1}{\tan 2\theta} + \frac{p_2}{\sin 2\theta} + \frac{p_3}{\tan\theta} + p_4\sin 2\theta + p_5\cos\theta + p_6$$

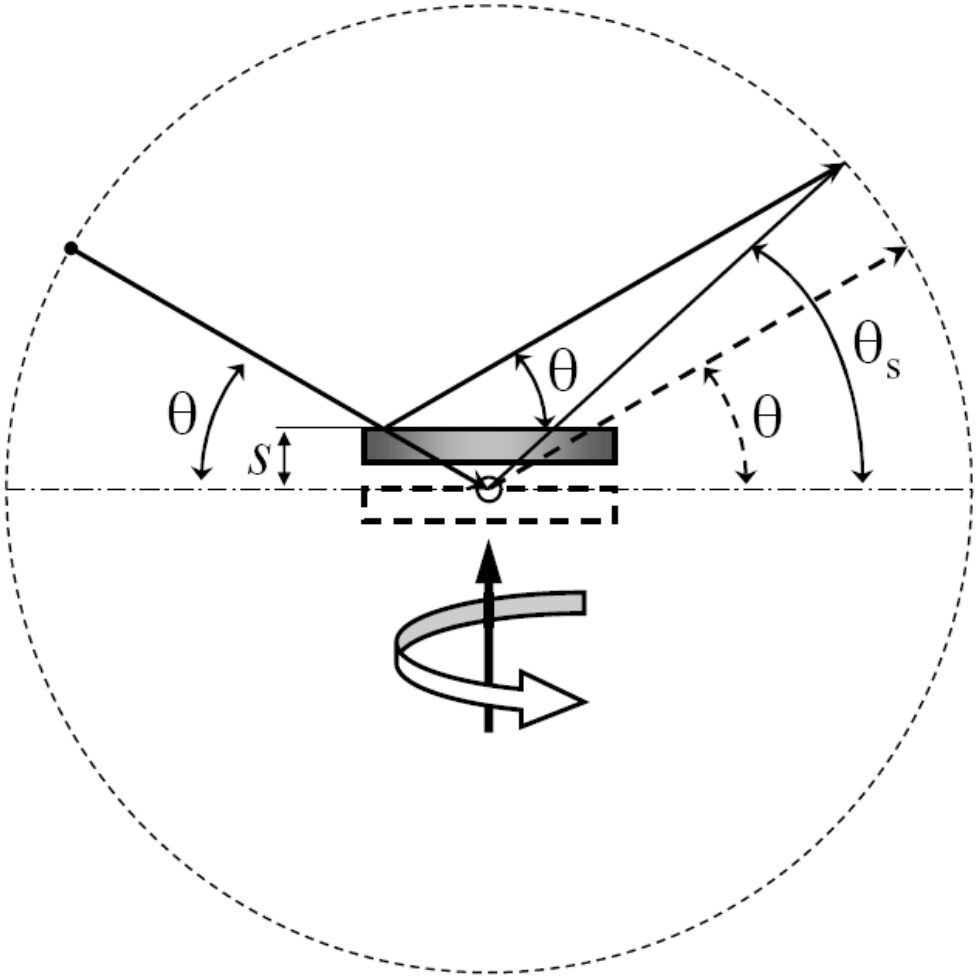
Asymmetry: $p_1 = -\frac{h^2K_1}{3R^2}$; $p_2 = -\frac{h^2K_2}{3R^2}$

In-plane divergence: $p_3 = -\frac{\alpha^2}{K_3}$

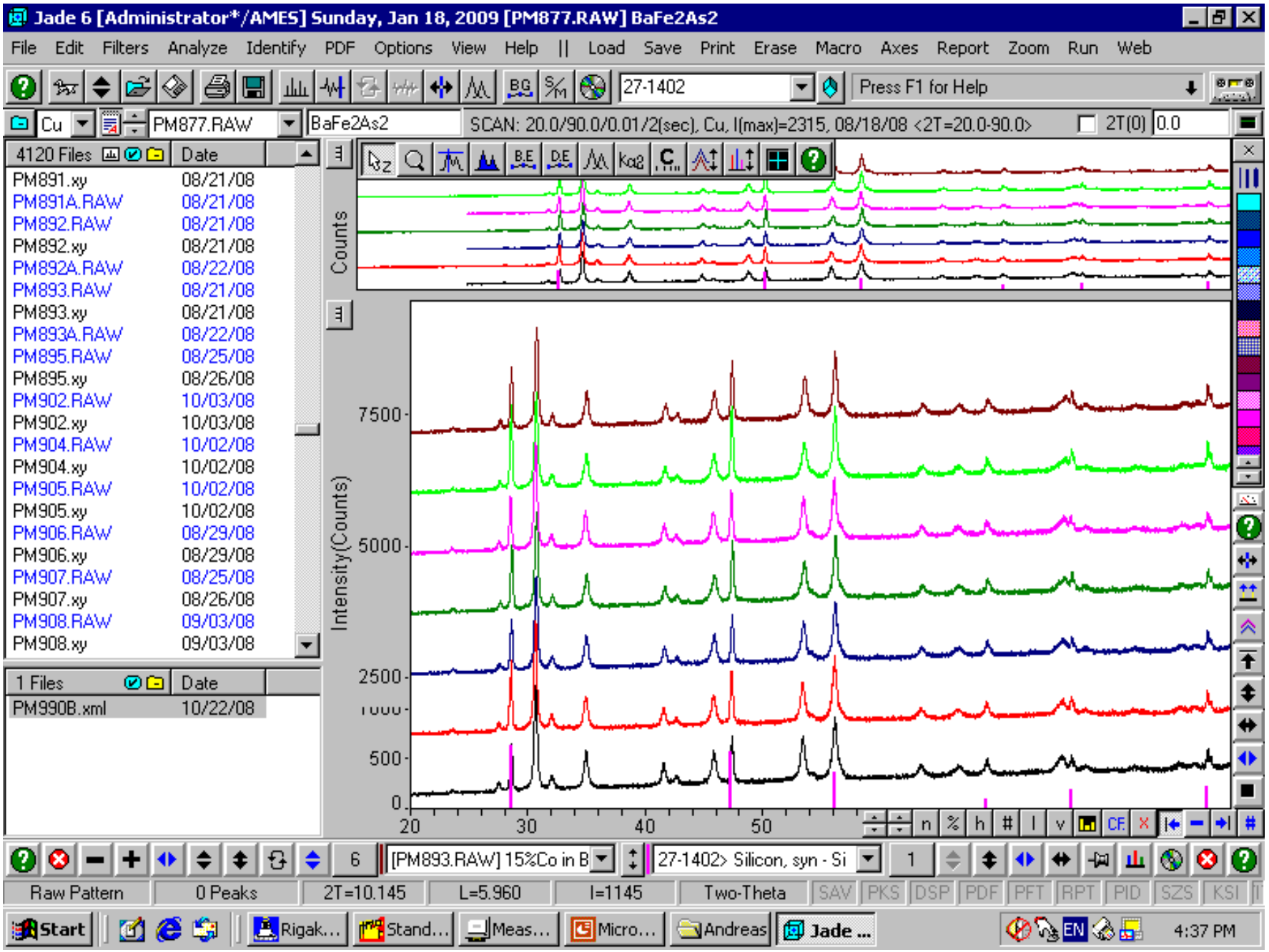
Transparency: $p_4 = \frac{1}{2\mu_{eff}R}$

Sample displacement: $p_5 = -\frac{2s}{R}$

Zero shift: p_6

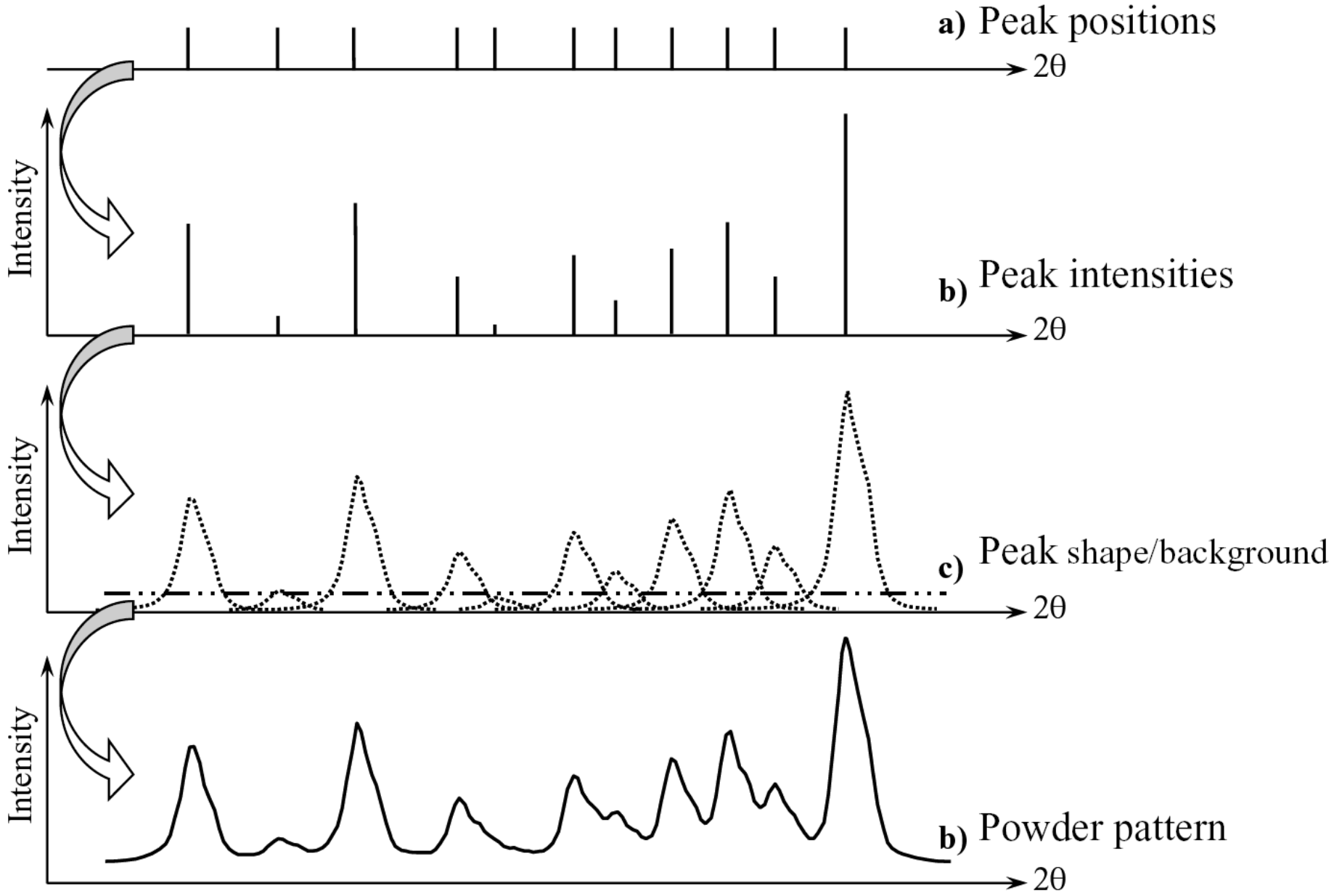


Example: growth of $Ba(Fe_{1-x}Co_x)_2As_2$



Combined analysis of series of Bragg reflections (main phase + standard) necessary.

Combined fitting of Bragg reflections



Example: growth of $Ba(Fe_{1-x}Co_x)_2As_2$

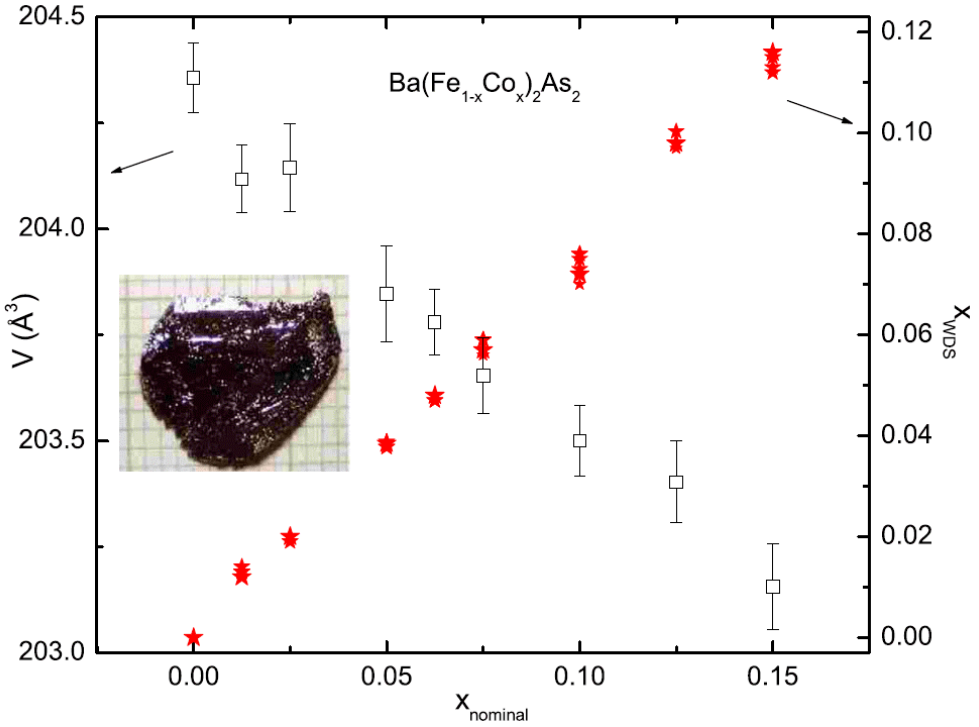


FIG. 2. (Color online) Unit-cell volume and Co concentration determined from WDS measurement as a function of nominal Co concentration. Multiple WDS data points were collected for each nominal x and are each plotted, giving a sense of measured variation in Co concentration. Inset: picture of a representative single crystal over a millimeter grid.

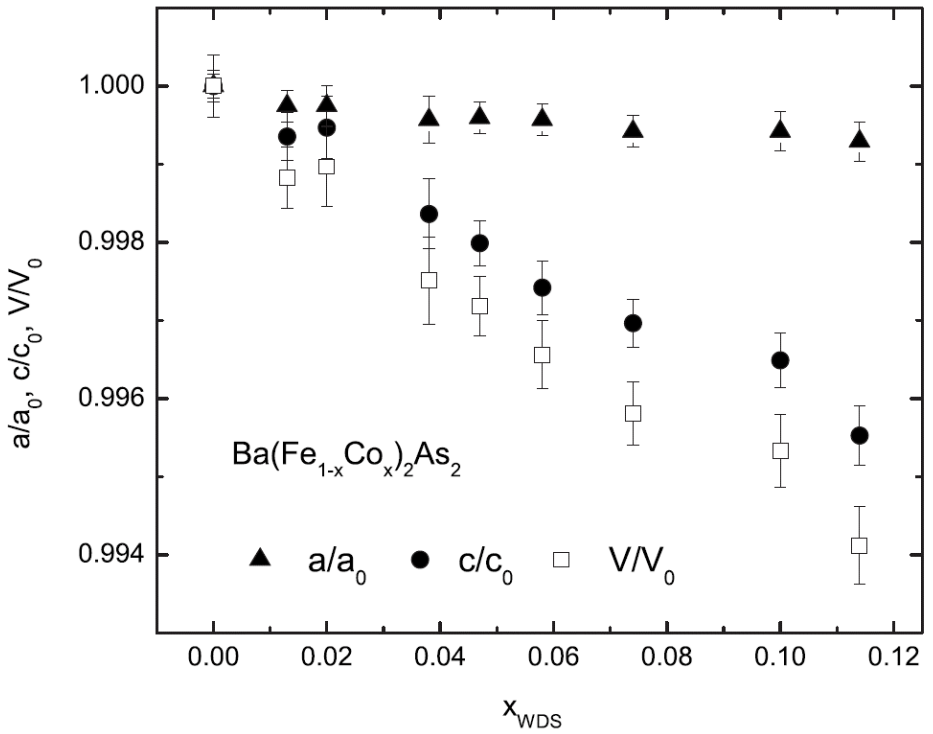
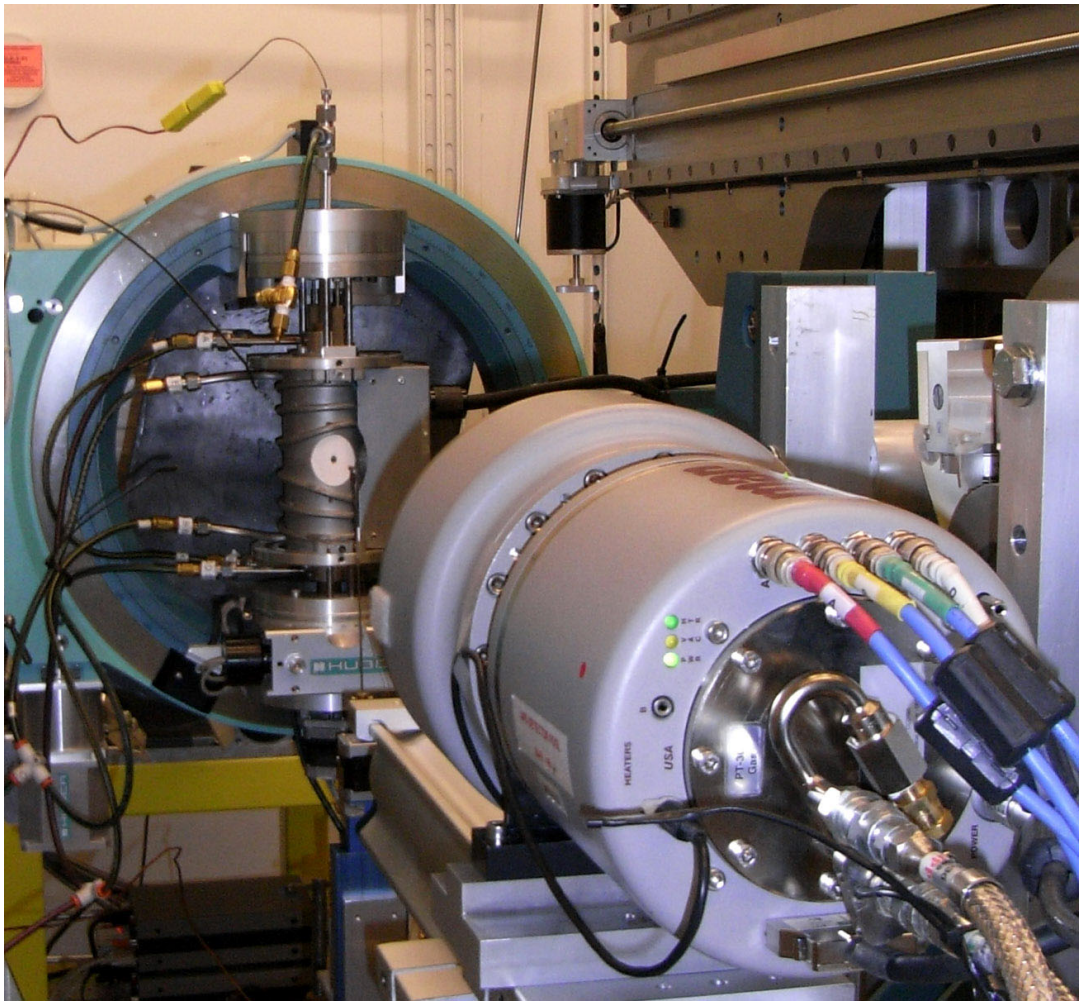


FIG. 3. Unit cell parameters, a and c, as well as unit-cell volume, V, normalized to a_0=3.9621 Å, c_0=13.0178 Å, and V_0 =204.3565 Å^3 of undoped $BaFe_2As_2$ as a function of measured concentration of Co, x_{WDS}.

Realized stoichiometry by WDS study; Vegard's law for lattice parameter

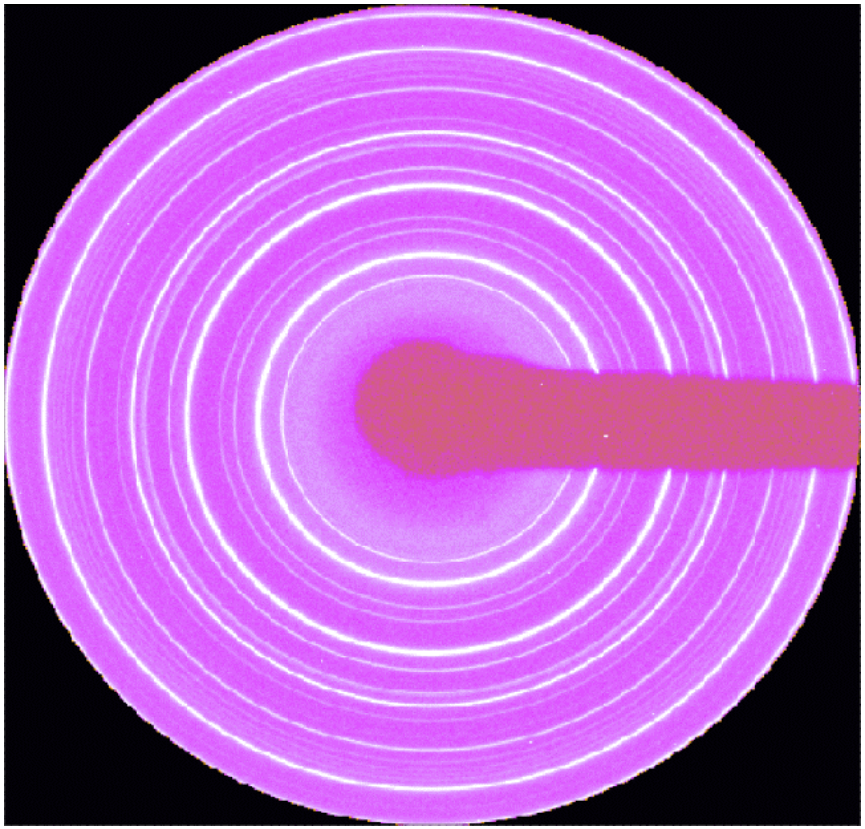
Example: preparation of *R*FeAs(O/F)

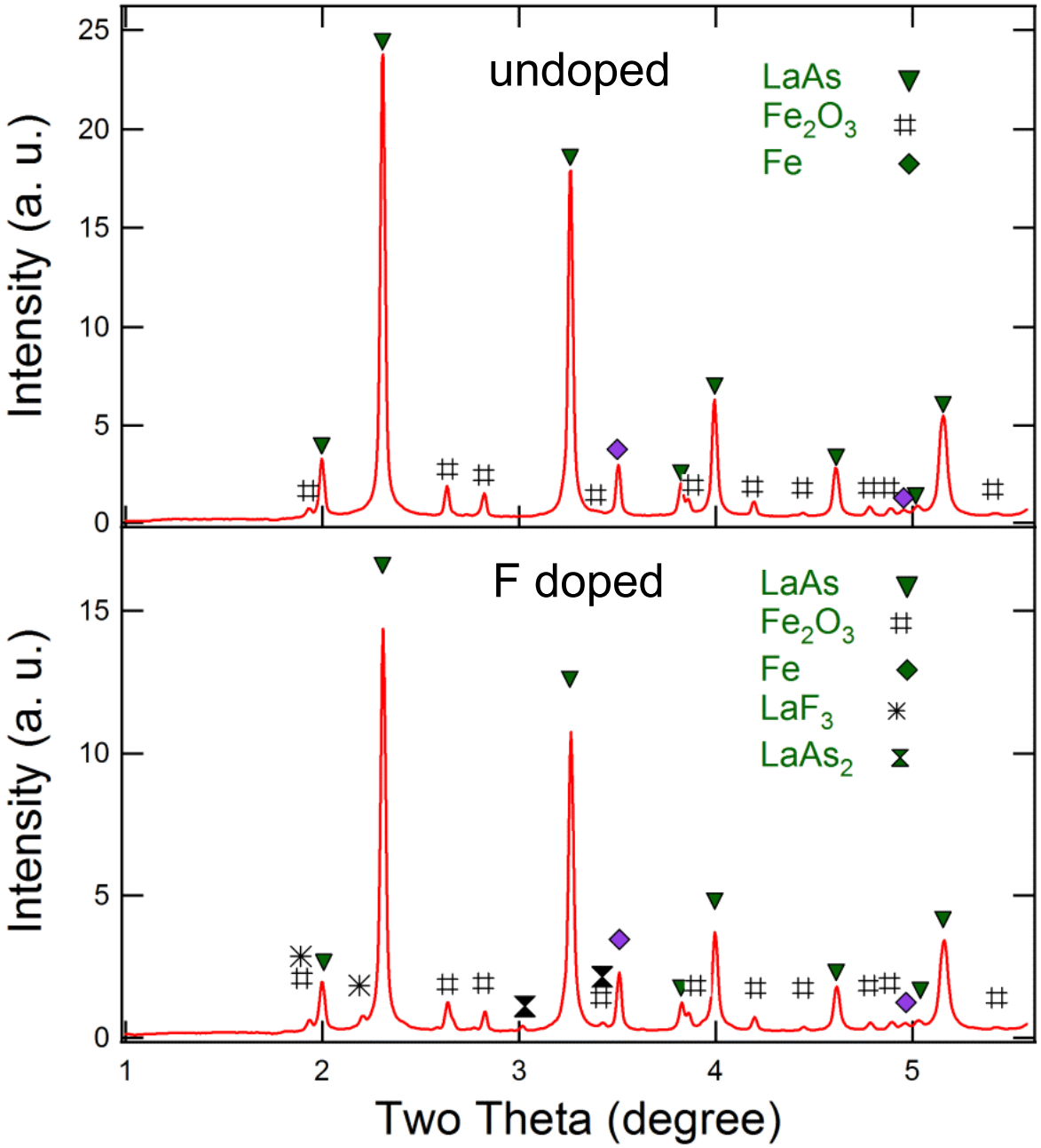


High-temperature x-ray diffraction with 2-dimensional detector

Rimg3307; 3318

Example: preparation of *R*FeAs(O/F)



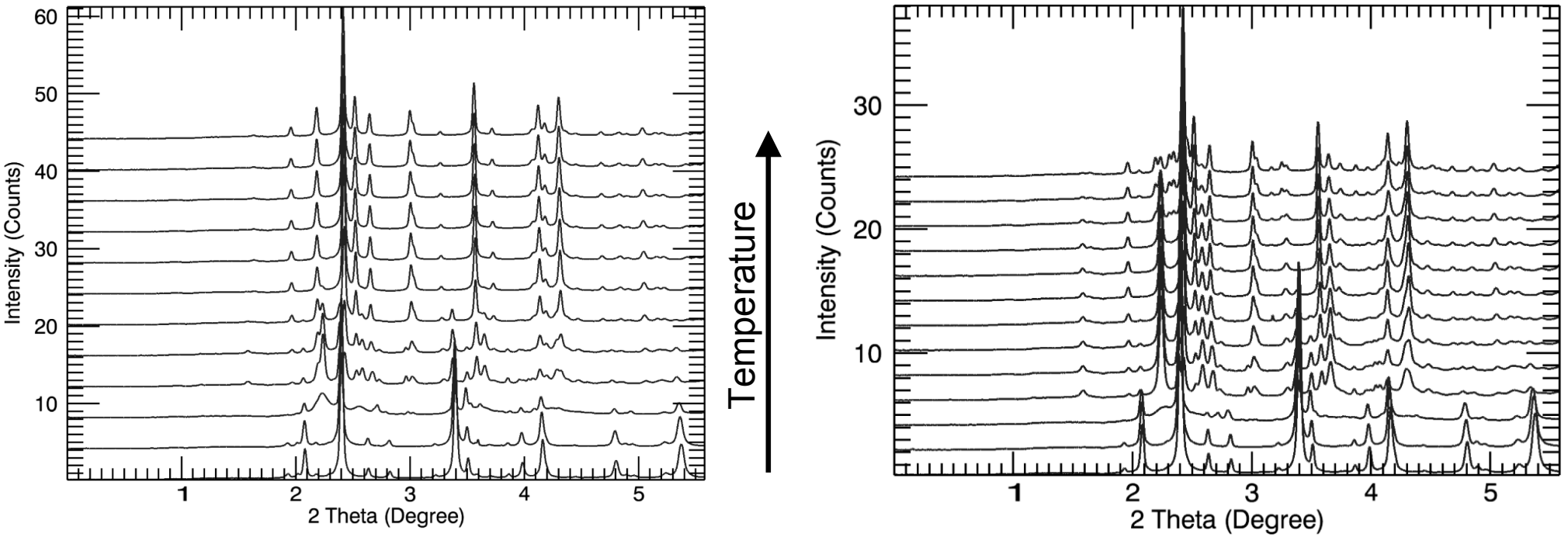


High-temperature x-ray diffraction with 2-dimensional detector

Example: preparation of *R*FeAs(O/F)

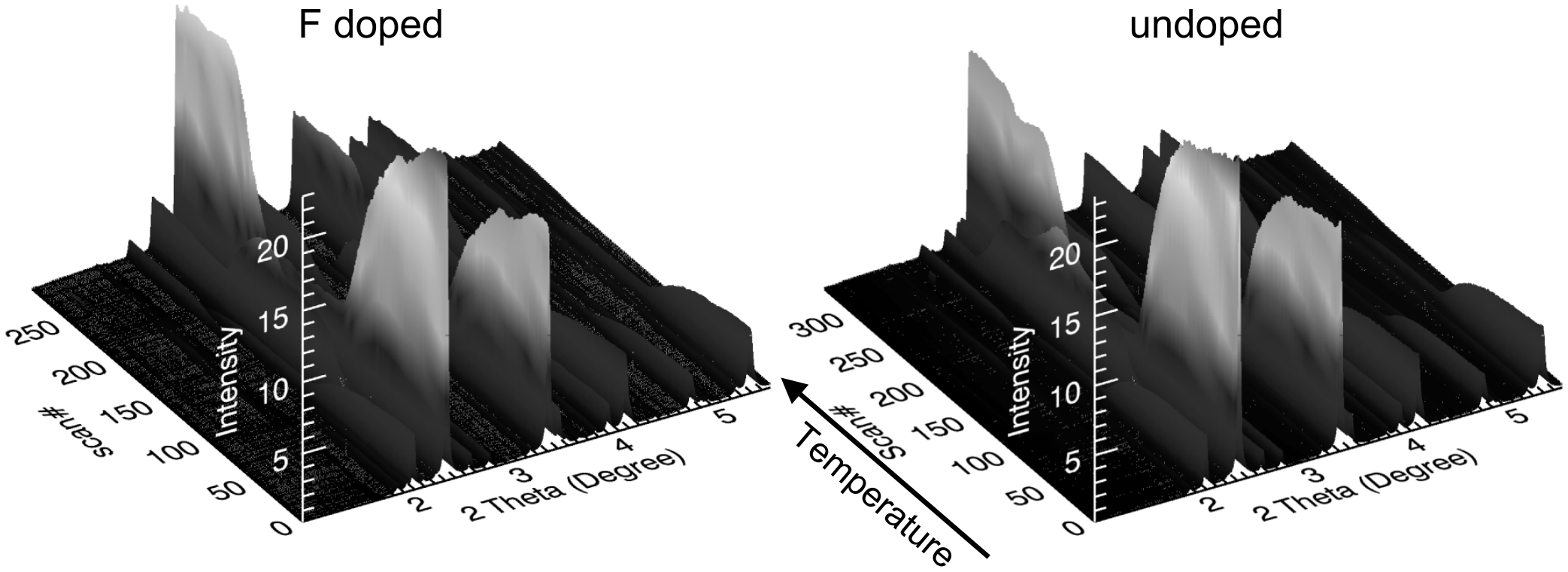
F doped

undoped



Temperature-dependent x-ray diffraction (20 sec. pattern)

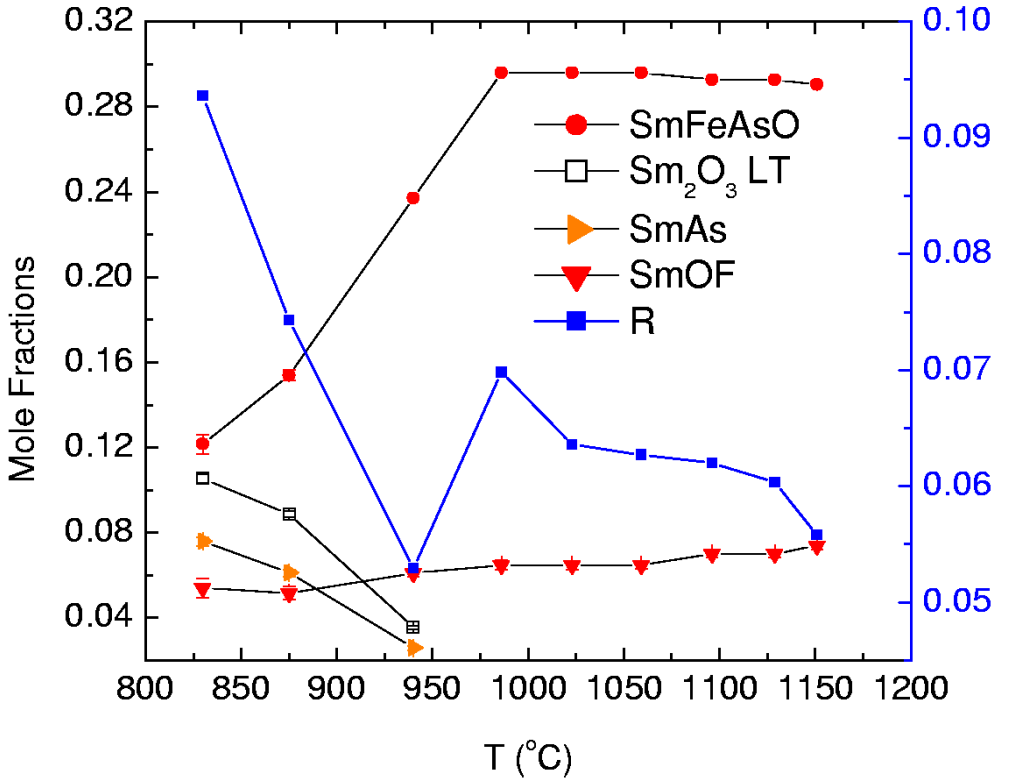
Example: preparation of *R*FeAs(O/F)



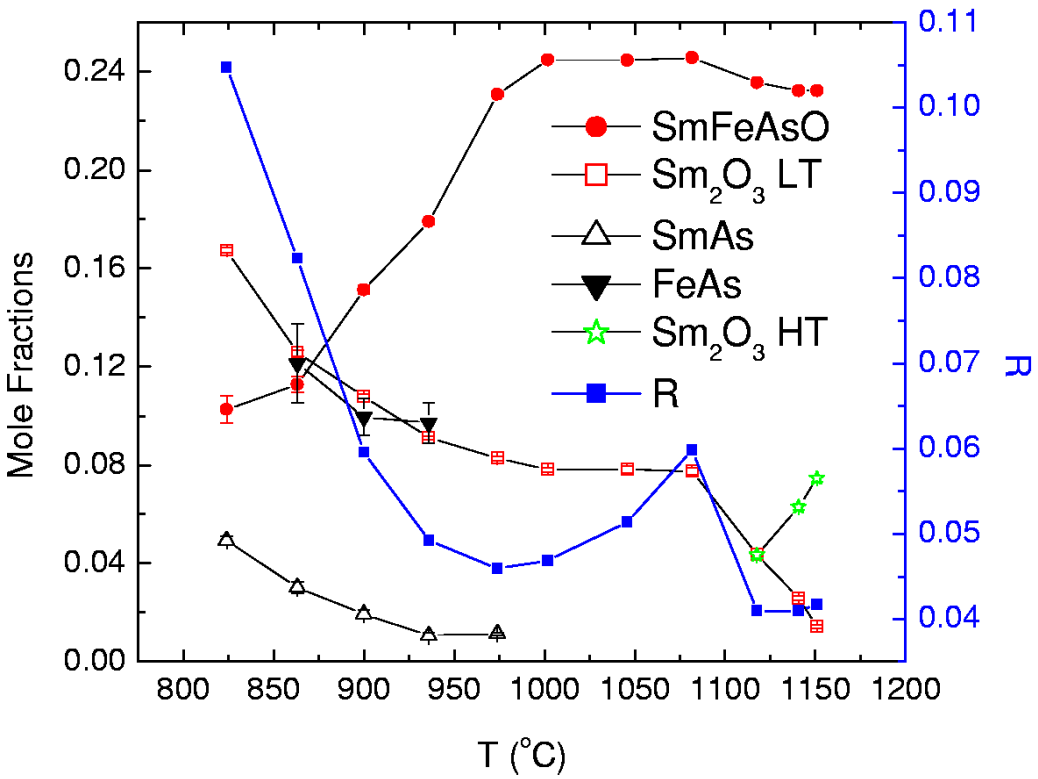
Temperature-dependent x-ray diffraction (20 sec. pattern)

Example: preparation of *R*FeAs(O/F)

F doped

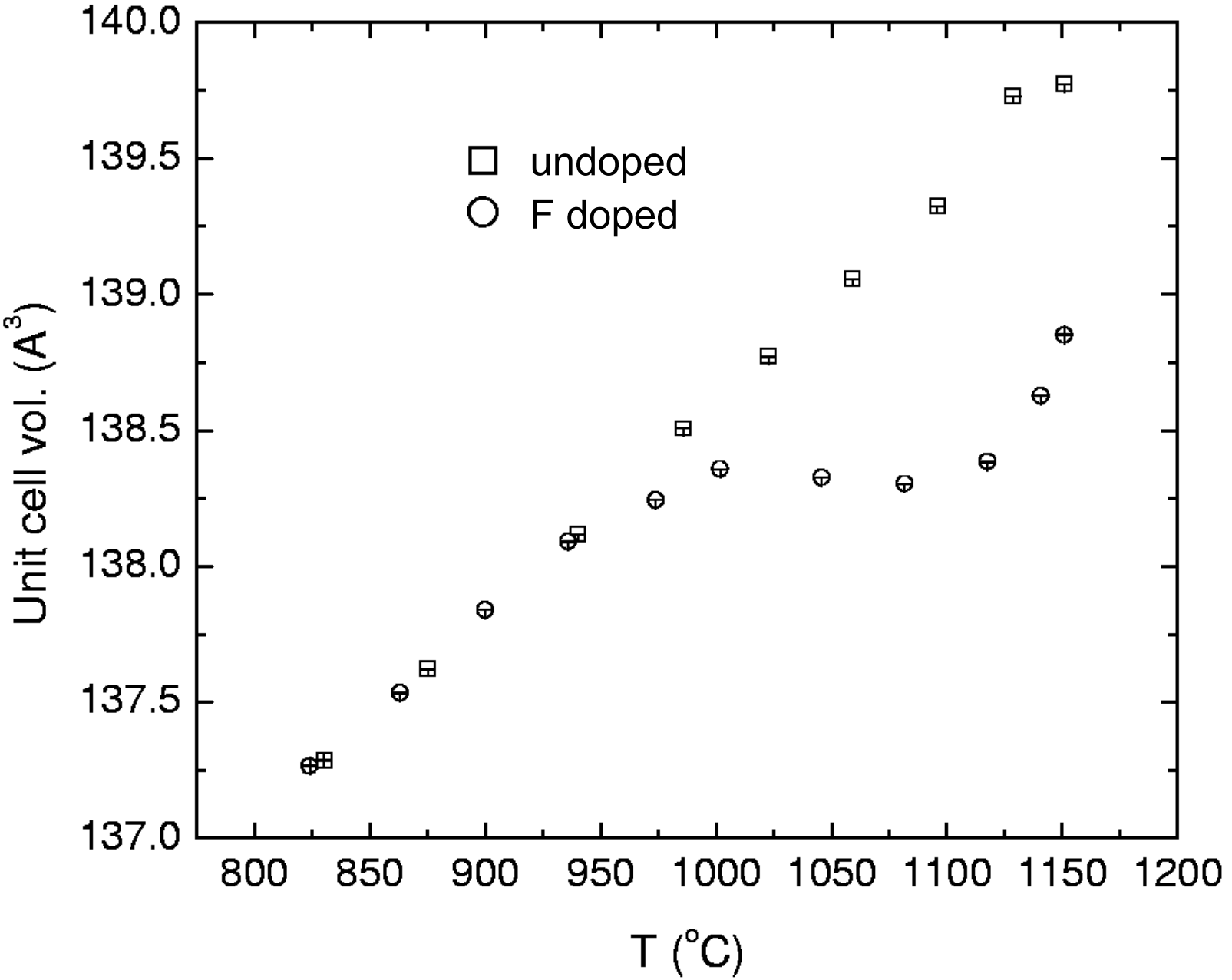


undoped



Crystalline phase fraction determined by Rietveld analysis

Example: preparation of *R*FeAs(O/F)



Unit-cell volume of *R*FeAs(O/F) phase determined by Rietveld analysis