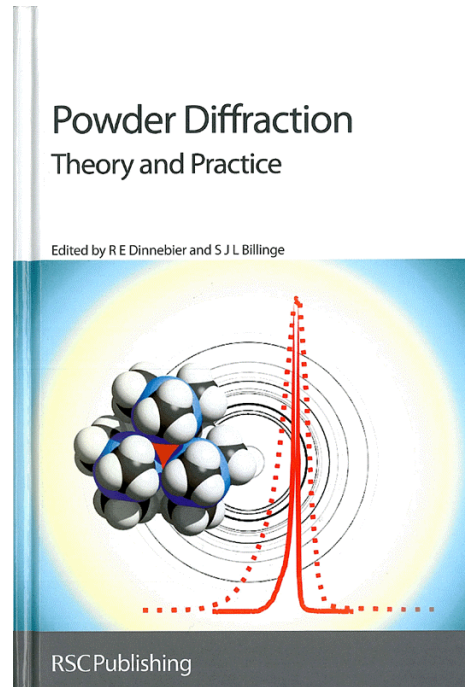


X-ray powder diffraction – a practical guide



INTERNATIONAL TABLES
for CRYSTALLOGRAPHY

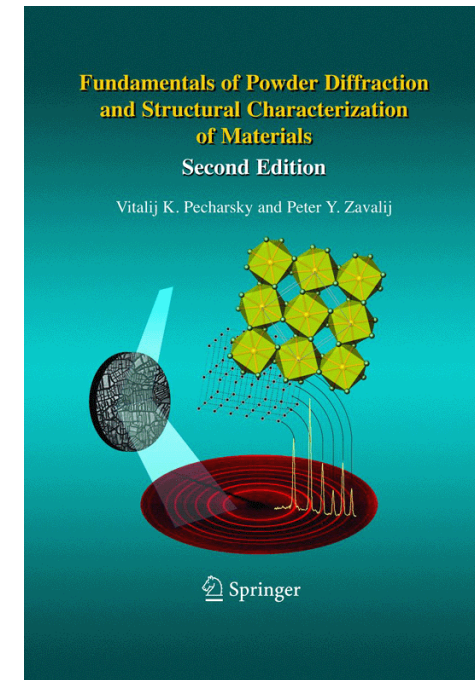
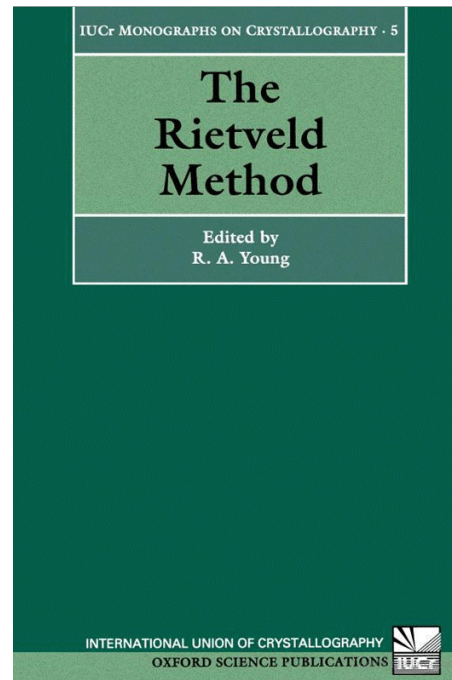
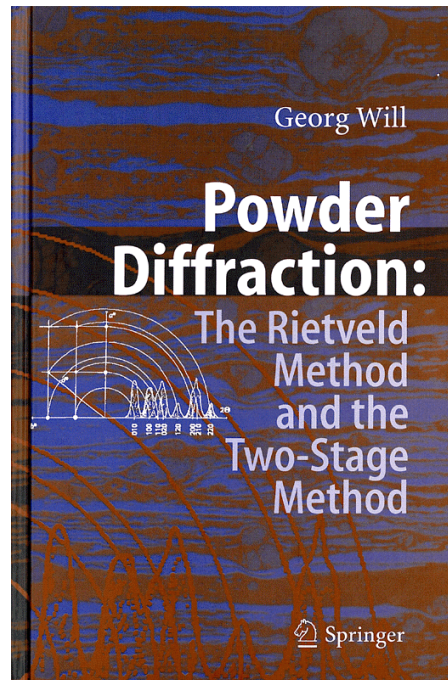
Volume

A

Space-group symmetry

Edited by Th. Hahn

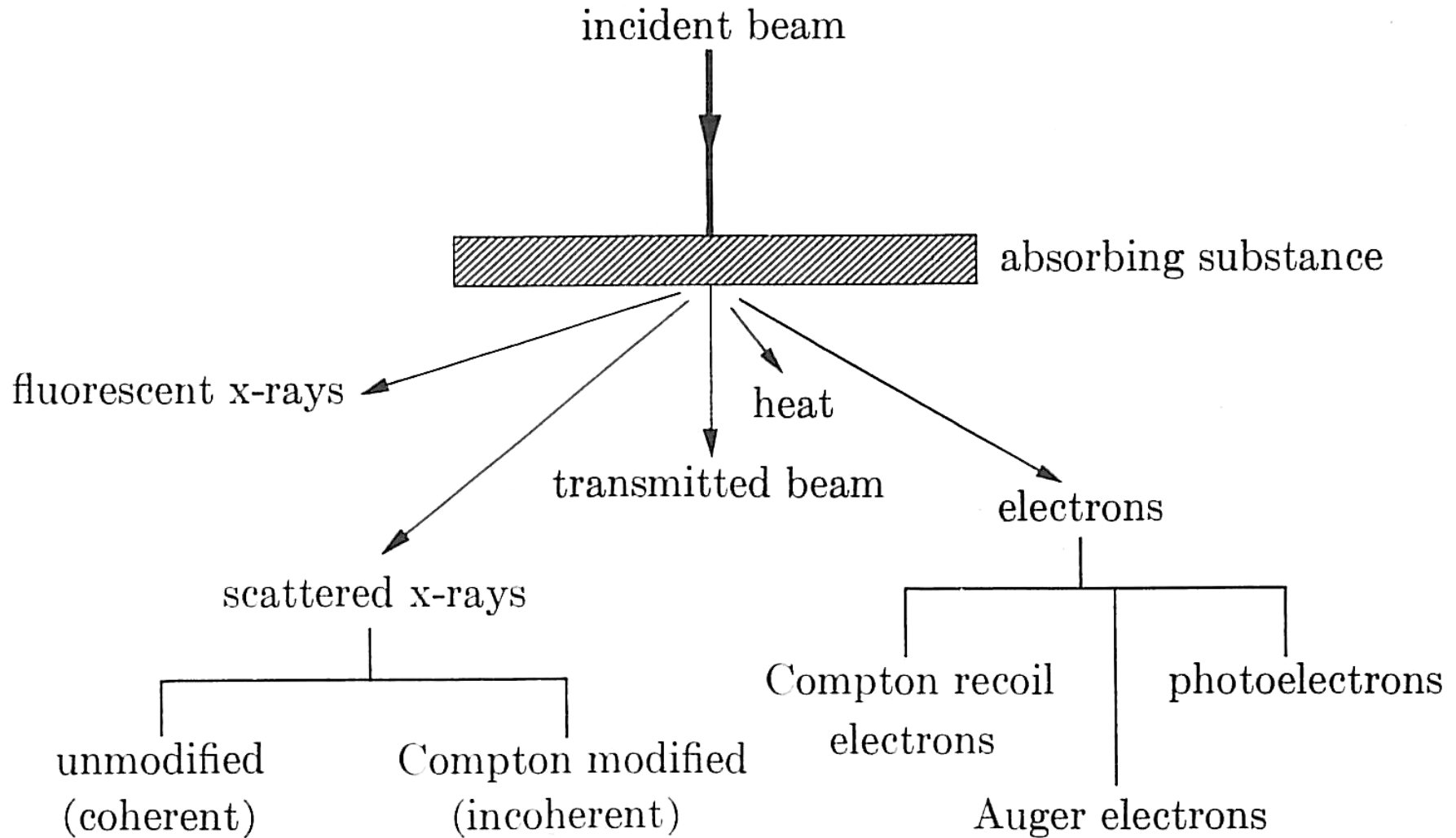
Fifth edition



Radiation hitting condensed matter

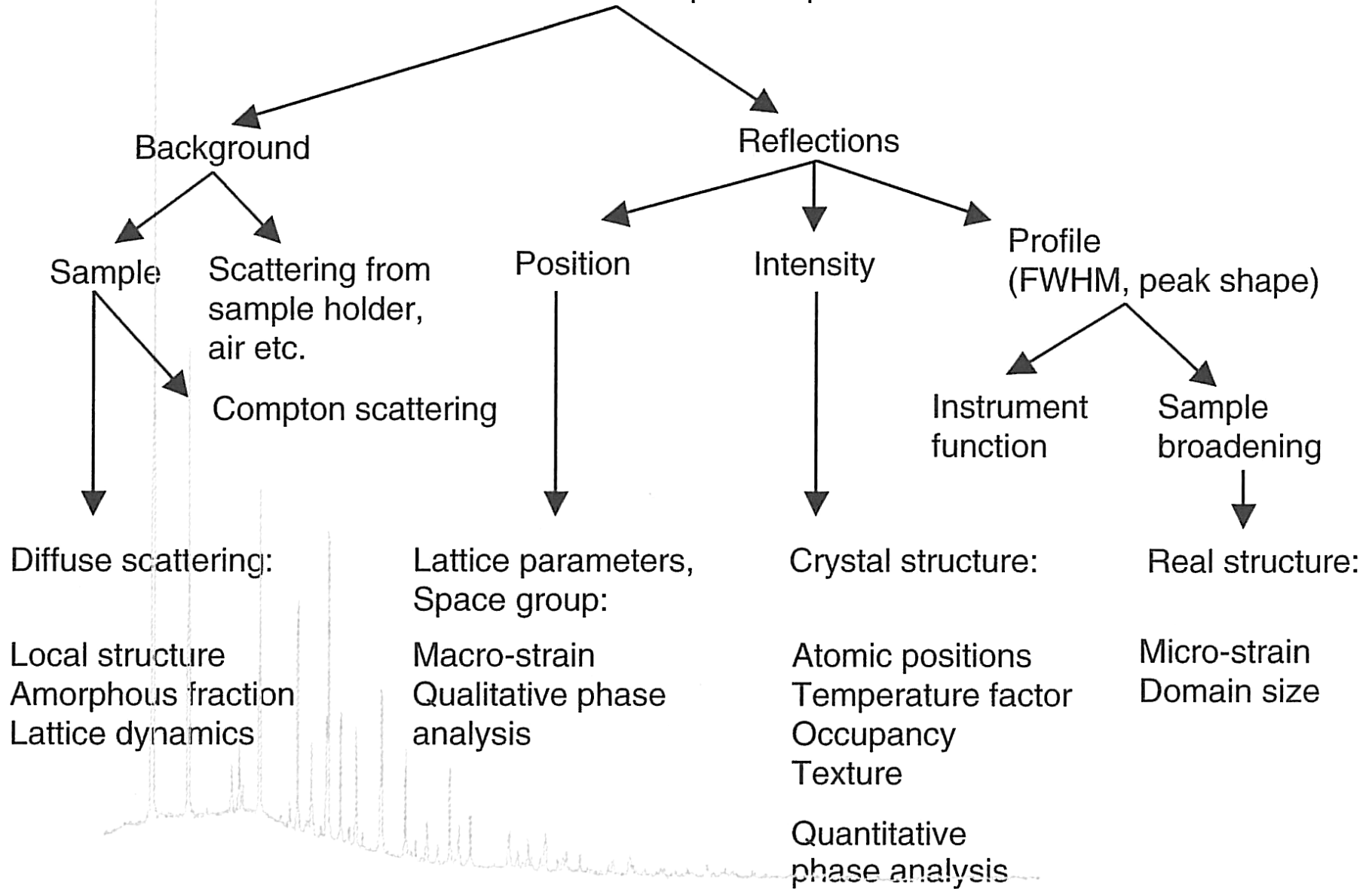
	NEUTRONS	X-RAYS	ELECTRONS
Wavelength range	0.4 - 10 Å	0.1 - 5 Å	0.04 - 0.2 Å
Energy range	0.001 - 0.5 eV	3000 - 100000 eV	6000 - 120000 eV
Cross-section	10^{-25} barns	$10^{-25} Z^2$ barns	$\sim 10^{-22}$ barns
Penetration depth	\sim cm	\sim μ m	\sim nm
Typical flux	10^{11} s ⁻¹ m ⁻²	10^{24} s ⁻¹ m ⁻²	10^{26} s ⁻¹ m ⁻²
Beam size	mm-cm	μ m-mm	nm- μ m
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

Information content of a powder pattern

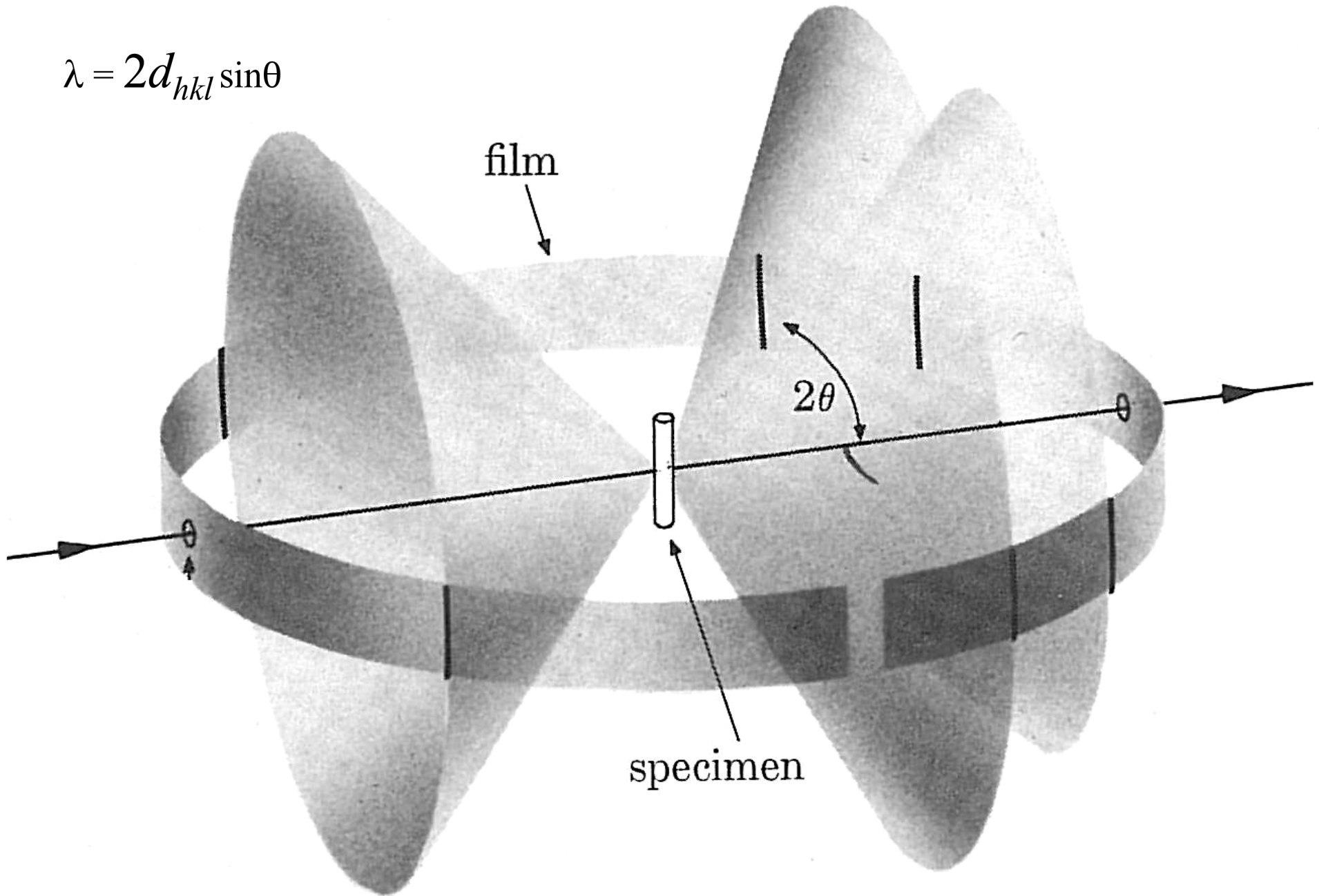


$$\lambda = 2d_{hkl} \sin\theta$$

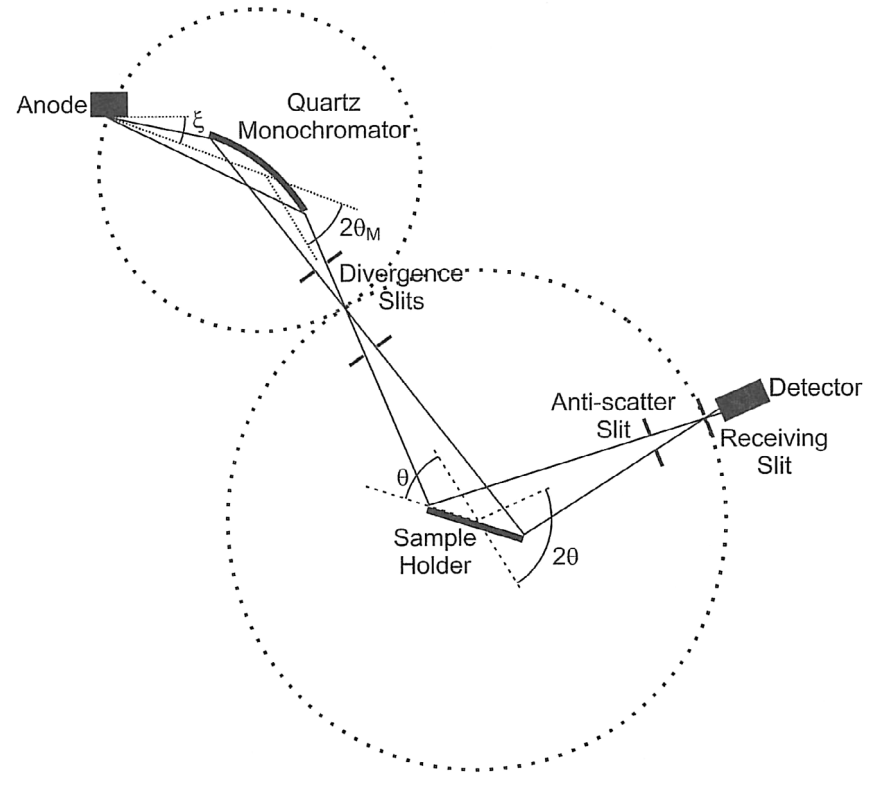
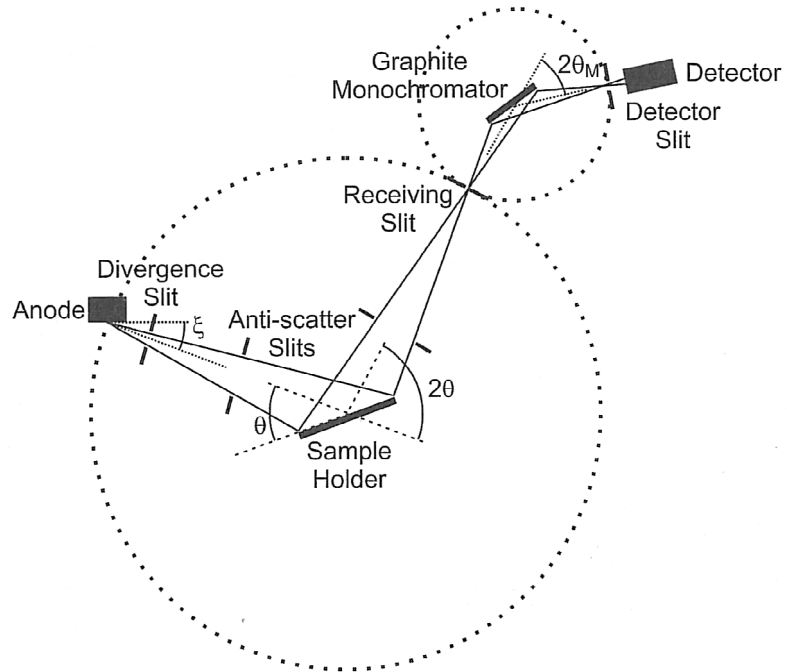
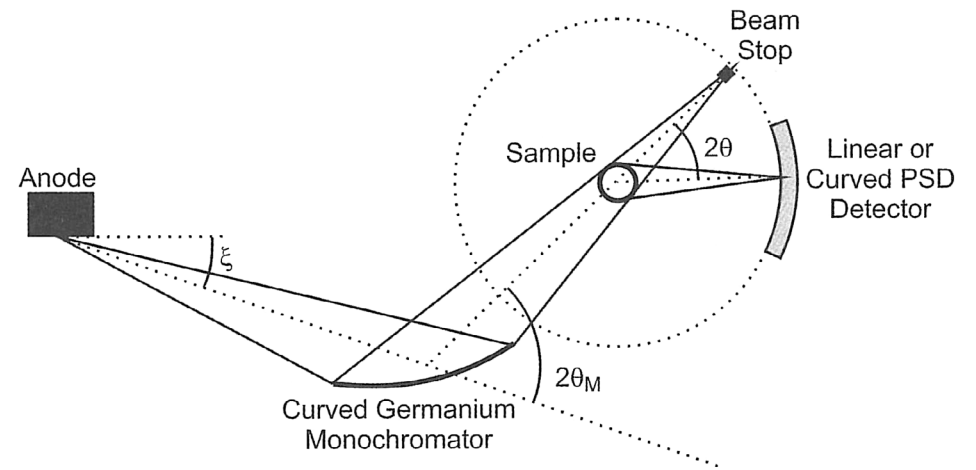
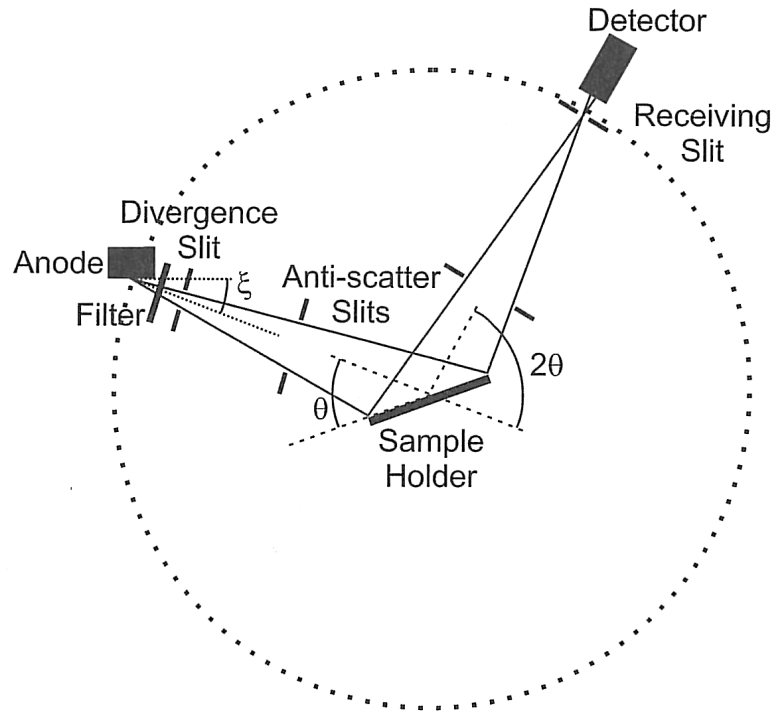
$$\mathbf{F}(\mathbf{h}) = \sum_{j=1}^n g^j t^j(s) f^j(s) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}^j)$$

Debye-Scherrer cones from a polycrystalline sample

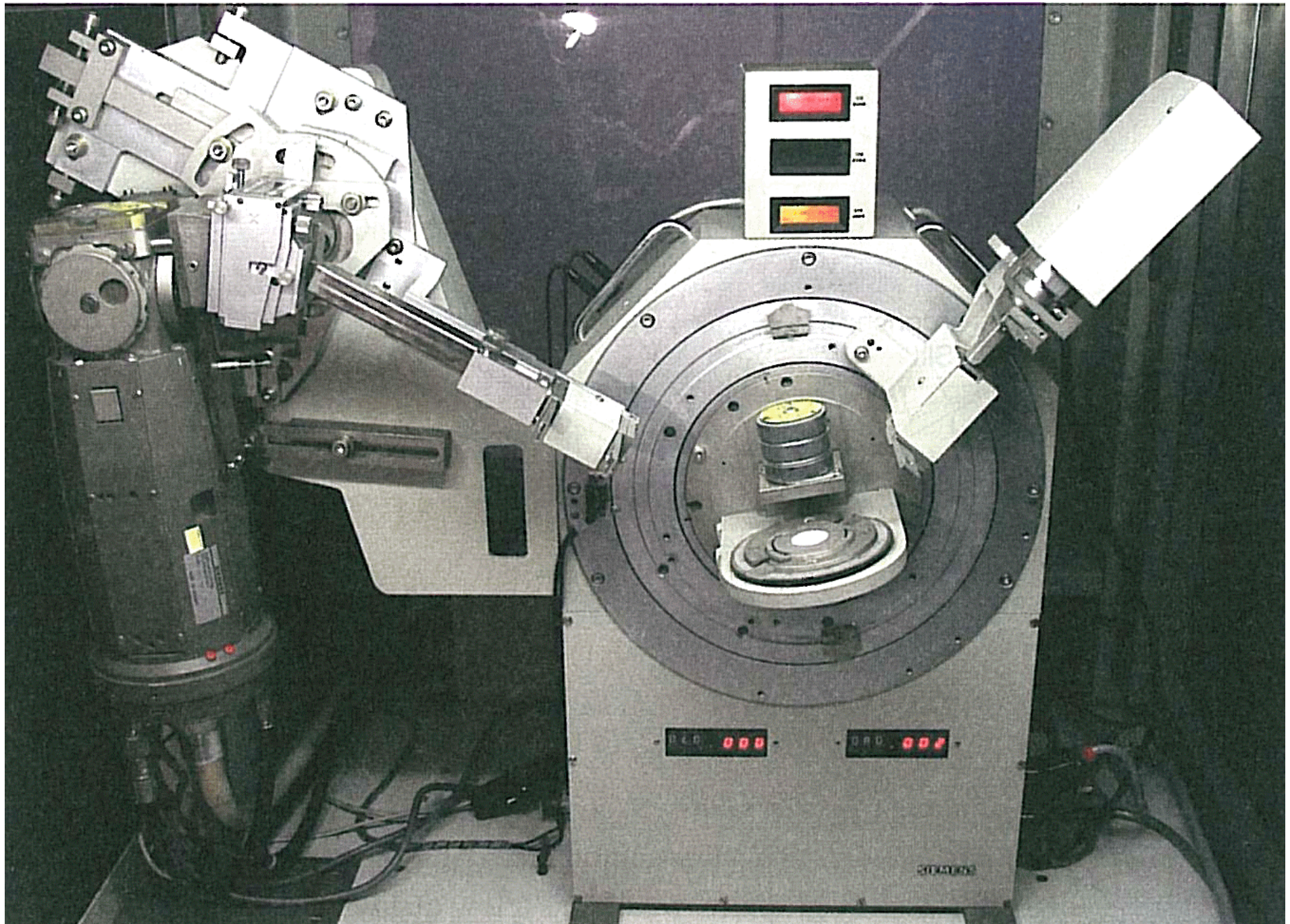
$$\lambda = 2d_{hkl} \sin\theta$$



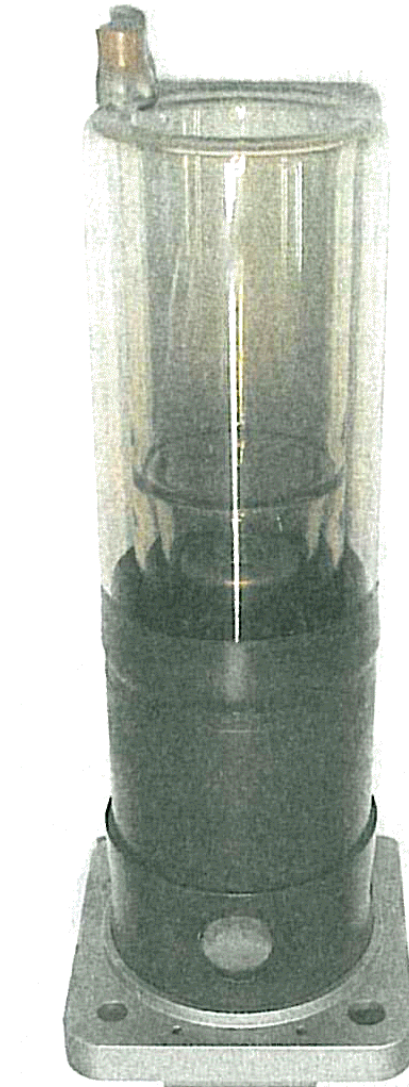
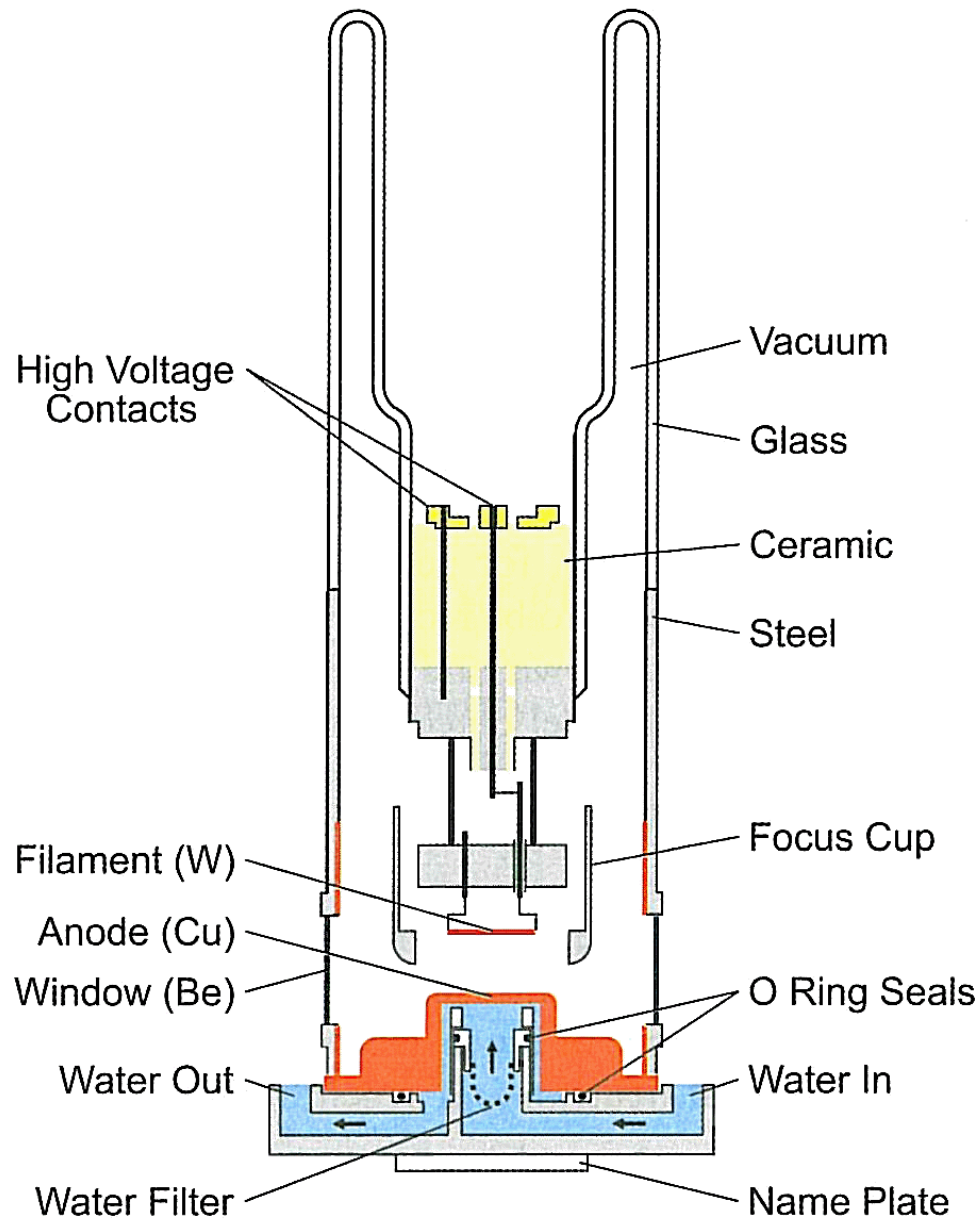
Bragg-Brentano and Guinier diffractometer



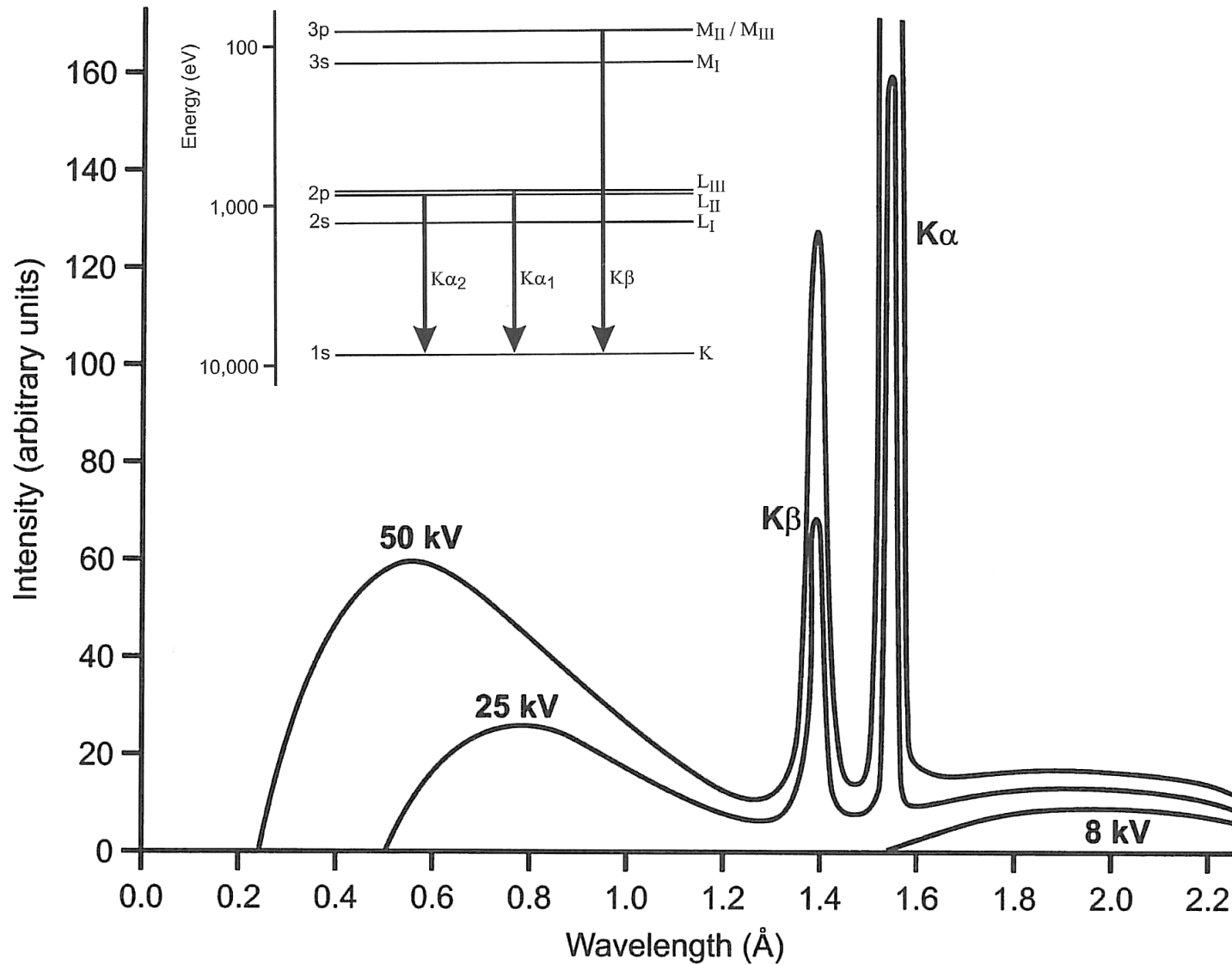
Bragg-Brentano diffractometer with monochromator



Generation of x-ray

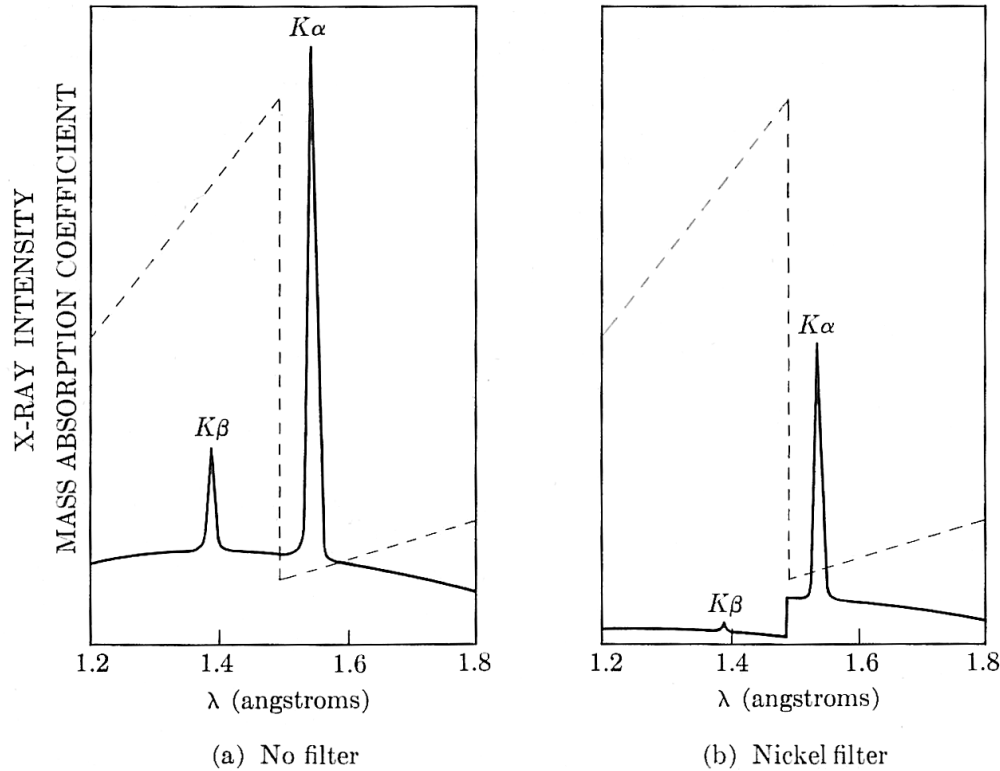


Generation of x-ray



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

Generation of x-ray

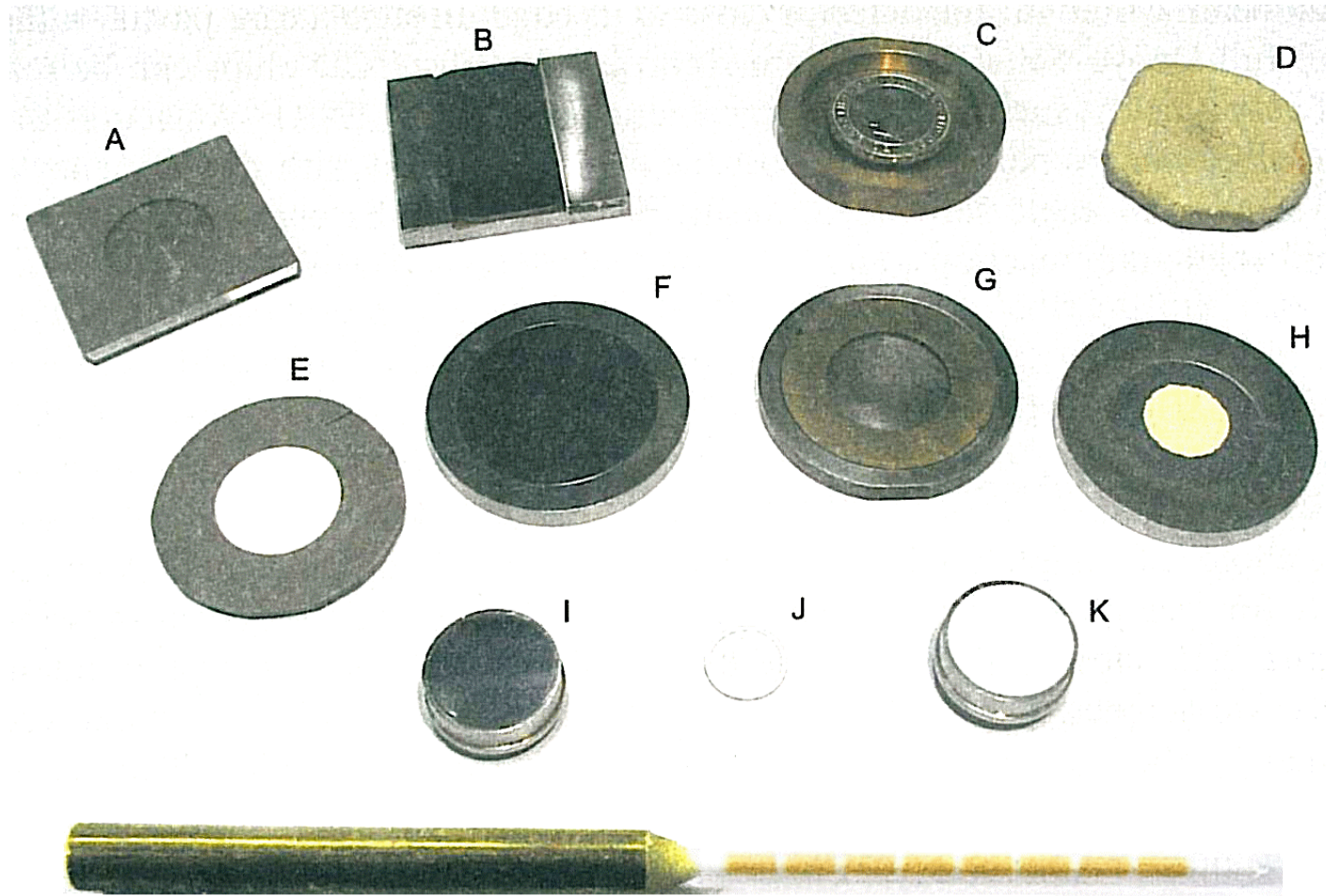


Target	Filter	Incident beam* $\frac{I(K\alpha)}{I(K\beta)}$	Filter thickness for $\frac{I(K\alpha)}{I(K\beta)} = \frac{500}{1}$ in trans. beam		$\frac{I(K\alpha) \text{ trans.}}{I(K\alpha) \text{ incident}}$
			mg/cm ²	in.	
Mo	Zr	5.4	77	0.0046	0.29
Cu	Ni	7.5	18	0.0008	0.42
Co	Fe	9.4	14	0.0007	0.46
Fe	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



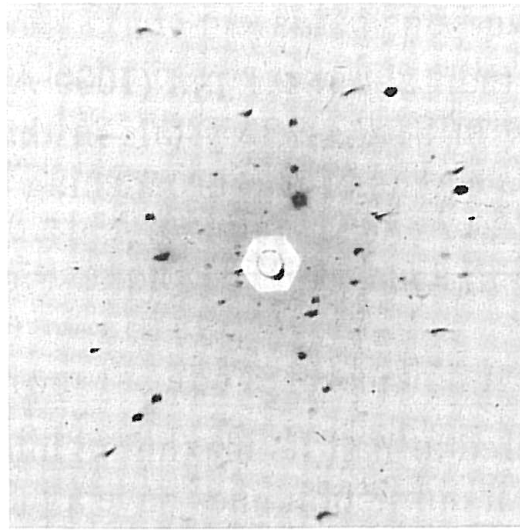
Well prepared samples at the right sample holder is the key for success!!!

Samples for x-ray powder diffraction

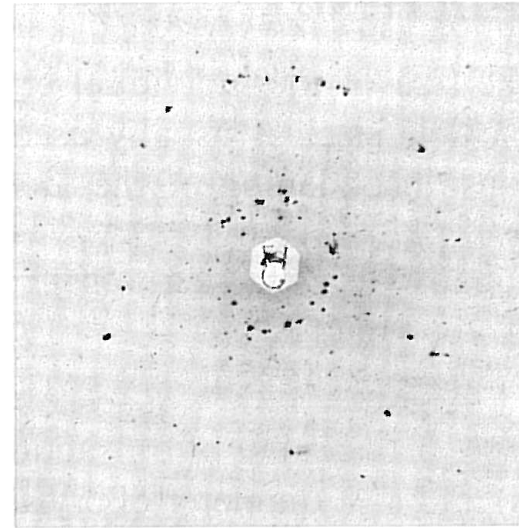


Hygiene in preparing the powder is the second key for success!!!

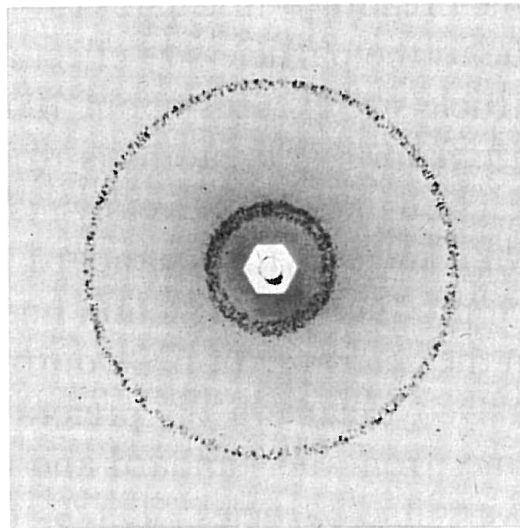
Samples for x-ray powder diffraction



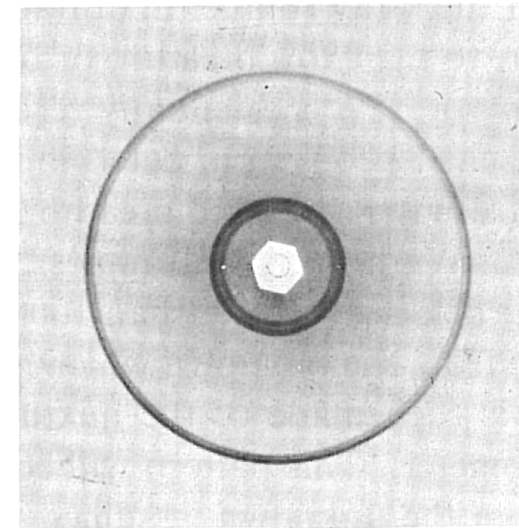
(a)



(b)



(c)



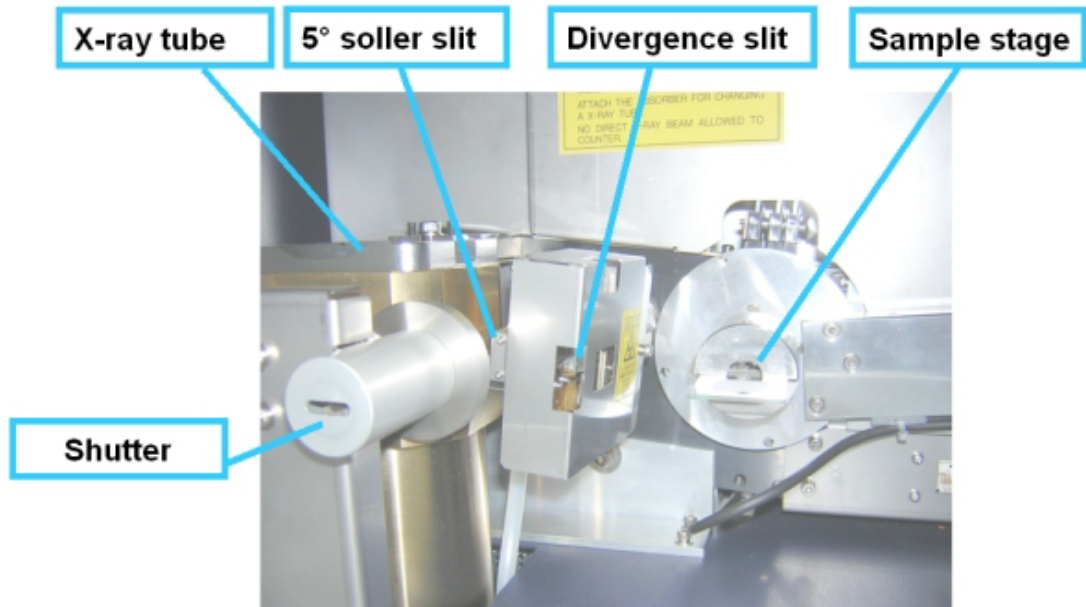
(d)

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

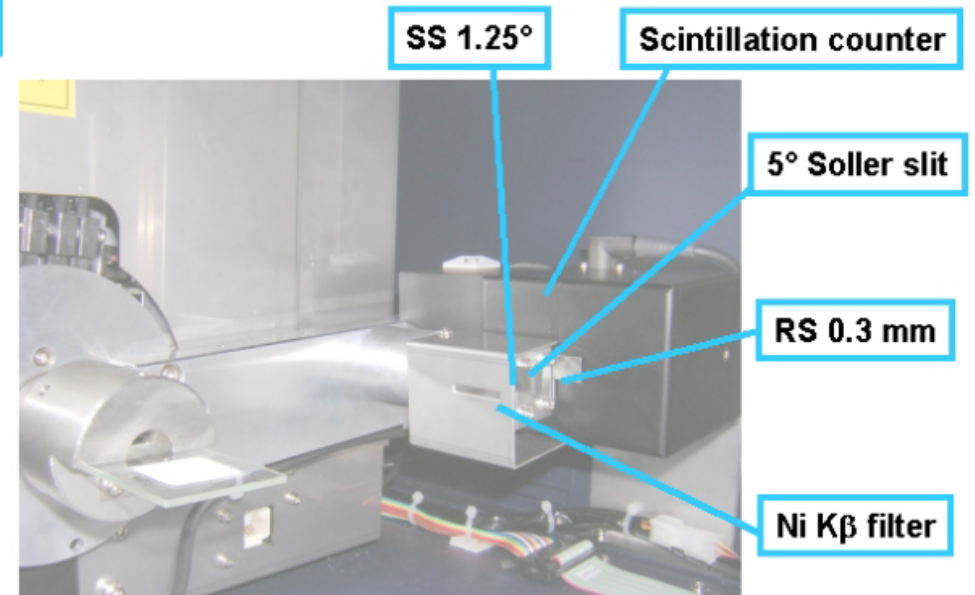
Bragg-Brentano diffractometer for the desk



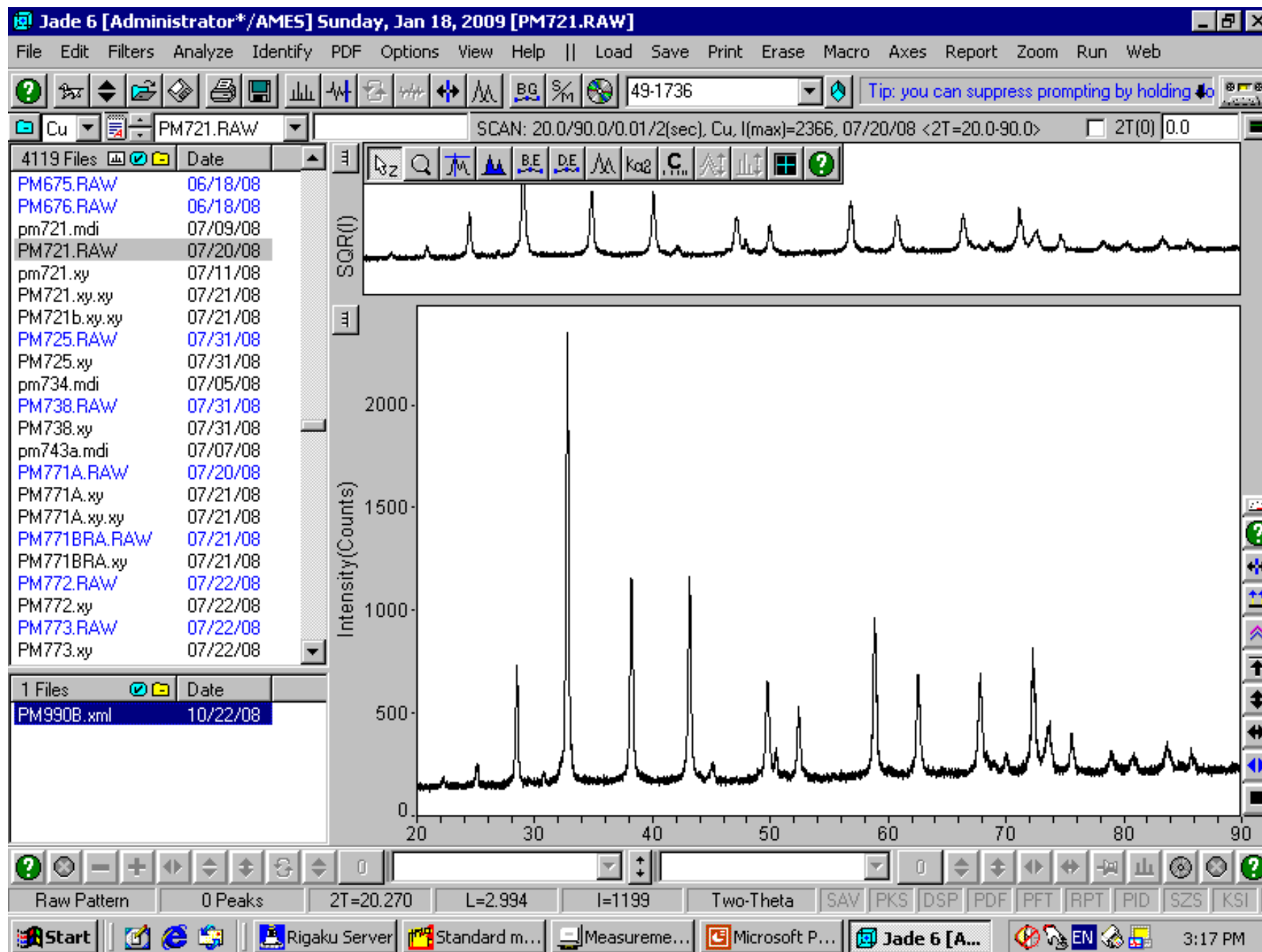
Goniometer & optics (incident)



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 ₂ O				
I/I ₁ 1-0024	100	83	67	100	ZIRCONIUM OXYCHLORIDE OCTA HYDRATE				
Rad. MoKα	λ 0.709	Filter ZrO ₂		d Å	I/I ₁	hkl	d Å	I/I ₁	hkl
Dia. 16 INCHES	Cut off	Coll.		12.8	100	100	2.07	13	
I/I ₁ CALIBRATED STRIPS		d corr. abs.? No		10.6	27	001	2.00	7	
Ref. H				7.9	20	101	1.91	13	
				6.9	67	111	1.81	13	
				4.80	13	102	1.71	13	
Sys. TETRAGONAL		S.G.		4.12	27	221	1.62	13	
a ₀ 12.9	b ₀	c ₀ 10.6	A	3.82	20	212,311	1.57	7	
α	β	γ	Z	3.60	83	320	1.51	7	
Ref. B.P.	(COMPUTED FROM POWDER DATA)			3.24	40	400	1.46	7	
ε α	n ω β	1.552	γ 1.563	2.96	7	213	1.42	7	
2V	D	mp	Color	2.74	7	402			
Ref. WA				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. CuKα ₁	λ 1.540598	Filter Mono.	Dia.	d Å	I/I ₁	hkl
Cut off	I/I ₁ Diffraction	I/I cor.		4.257	22	100
Ref. Nat. Bur. Stand. (U.S.)	Monogr. 25, Sec. 18 (1981)			3.342	100	101
				2.457	8	110
				2.282	8	102
				2.237	4	111
Sys. Hexagonal		S.G. P3 ₁ 21 (152)		2.127	6	200
a ₀ 4.9133(2)	b ₀	c ₀ 5.4053(4)	A	1.9792	4	201
α	β	γ	Z 3	1.8179	14	112
Ref. Ibid.		Dx 2.649		1.8021	<1	003
				1.6719	4	202
ε α	n ω β	1.544	ε γ 1.553	1.6591	2	103
2V	D	2.656	mp	1.6082	<1	210
Ref. Ibid.				1.5418	9	211
				1.4536	1	113
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.				1.4189	<1	300
				1.3820	6	212
				1.3752	7	203
				1.3718	8	301
				1.2880	2	104
				1.2558	2	302
						6 reflections to 0.9089

1-0378 MAJOR CORRECTION

0631 d 1-0363	4.30	3.81	4.08	4.30	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		d Å	I/I ₁	hkl	d Å	I/I ₁	hkl
Dia. 16 INCHES	Cut off	Coll.		4.30	100		1.44	3	
I/I ₁ CALIBRATED STRIPS		d corr. abs.? No		4.08	33		1.40	7	
Ref. H ₁				3.81	67		1.36	3	
				3.43	1		1.31	4	
				3.21	1		1.25	3	
Sys. ORTHORHOMBIC		S.G.		2.96	17		1.19	5	
a ₀ 9.88	b ₀ 17.1	c ₀ 16.3	A 0.578	2.80	3		1.15	3	
α	β	γ	Z 64 ?	2.49	27		1.10	1	
Ref. Wy (FOR ONLY ONE TYPE OF TRIDYMITE)				2.31	11				
				2.08	5				
ε α 1.478	n ω β 1.479	γ 1.481	Sign +	1.84	3				
2V 35°	D 2.26	mp	Color COLORLESS	1.69	8				
Ref. Wn, C.C. (FOR ONLY ONE TYPE OF TRIDYMITE)				1.64	4				
				1.60	4				
				1.53	5				
T.P. TO β ₁ (LOWER HIGH-TRIDYMITE) AT 117°C									
T.P. TO β ₂ (UPPER HIGH-TRIDYMITE) AT 163°C									
SPECIMEN WAS HAWK REFRACTORY BRICK									
LOW TRIDYMITE OCCURS IN MANY POLYTYPE 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.									

Example: growth of PrAuSi out of Sn flux

The screenshot shows the Jade 6 software interface. The main window displays an XRD pattern with a scan range from 20 to 90 degrees 2θ. The pattern shows several sharp peaks, with the most prominent ones between 30 and 60 degrees. A 'Current Chemistry [Retrieval]' dialog box is open, showing a search for 'Pr' and 'Au'. The dialog box includes a search criteria dropdown set to 'Metallics (52/15393 @11/04/03)', a search button, and a 'Read Fluorescent Data...' button. The periodic table in the dialog box has 'Pr' and 'Au' highlighted. The software interface also shows a file list on the left, a menu bar at the top, and a status bar at the bottom.

File Edit Filters Analyze Identify PDF Options View Help || Load Save Print Erase Macro Axes Report Zoom Run Web

Cu PM721.RAW SCAN: 20.0/90.0/0.01/2(sec), Cu, I(max)=2366, 07/20/08 <2T=20.0-90.0> 2T(0) 0.0

4119 Files Date

- PM675.RAW 06/18/08
- PM676.RAW 06/18/08
- pm721.mdi 07/09/08
- PM721.RAW 07/20/08
- pm721.xy 07/11/08
- PM721.xy.xy 07/21/08
- PM721b.xy.xy 07/21/08
- PM725.RAW 07/31/08
- PM725.xy 07/31/08
- pm734.mdi 07/05/08
- PM738.RAW 07/31/08
- PM738.xy 07/31/08
- pm743a.mdi 07/07/08
- PM771A.RAW 07/20/08
- PM771A.xy 07/21/08
- PM771A.xy.xy 07/21/08
- PM771BRA.RAW 07/21/08
- PM771BRA.xy 07/21/08
- PM772.RAW 07/22/08
- PM772.xy 07/22/08
- PM773.RAW 07/22/08
- PM773.xy 07/22/08

1 Files Date

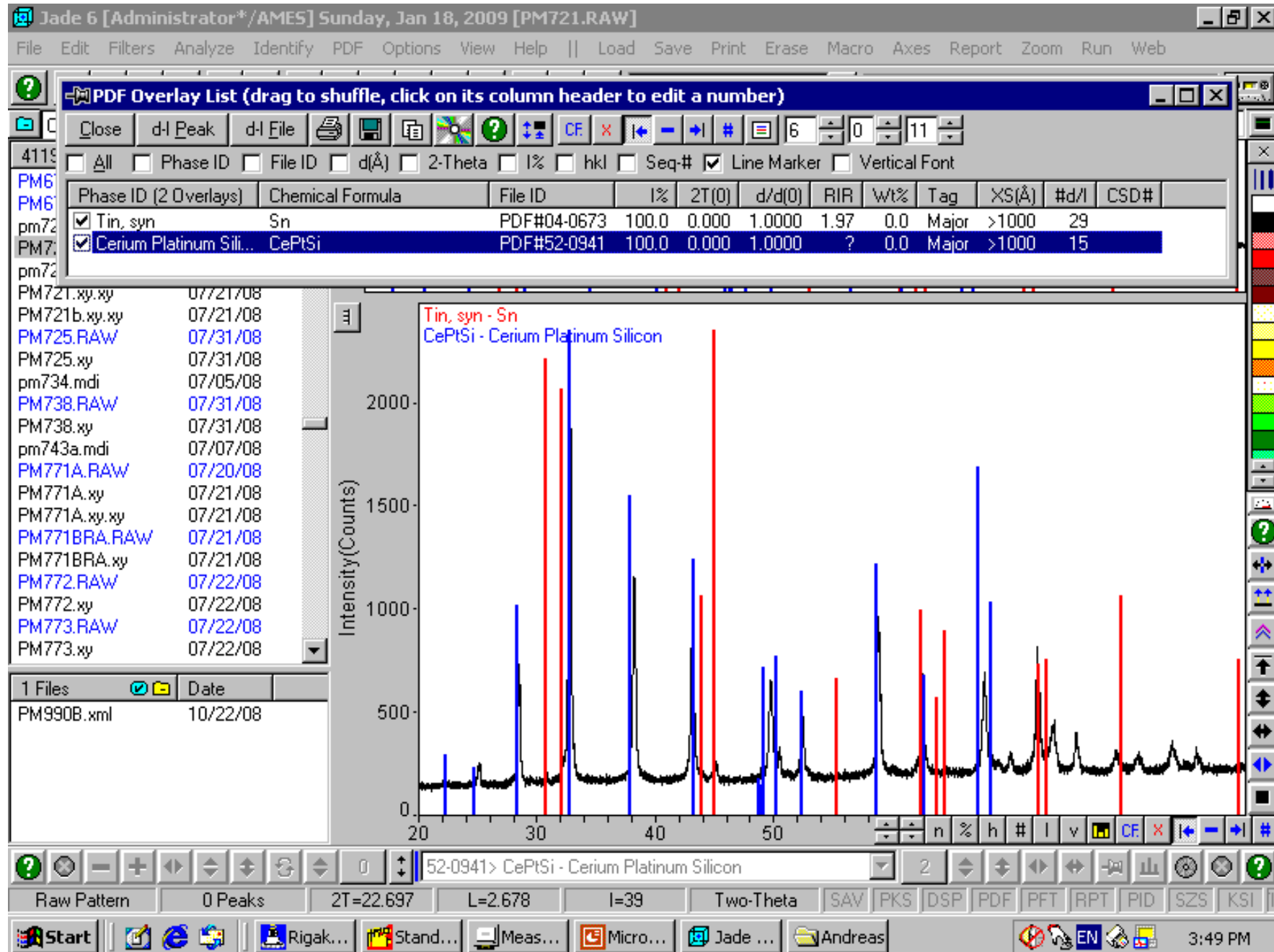
- PM990B.xml 10/22/08

Raw Pattern 0 Peaks 2T=21.646 L=2.806 I=1289 Two-Theta SAV PKS DSP PDF PFT RPT PID SZS KSI

Start Rigaku ... Standar... Measur... Microso... Jade 6 [... 3:26 PM

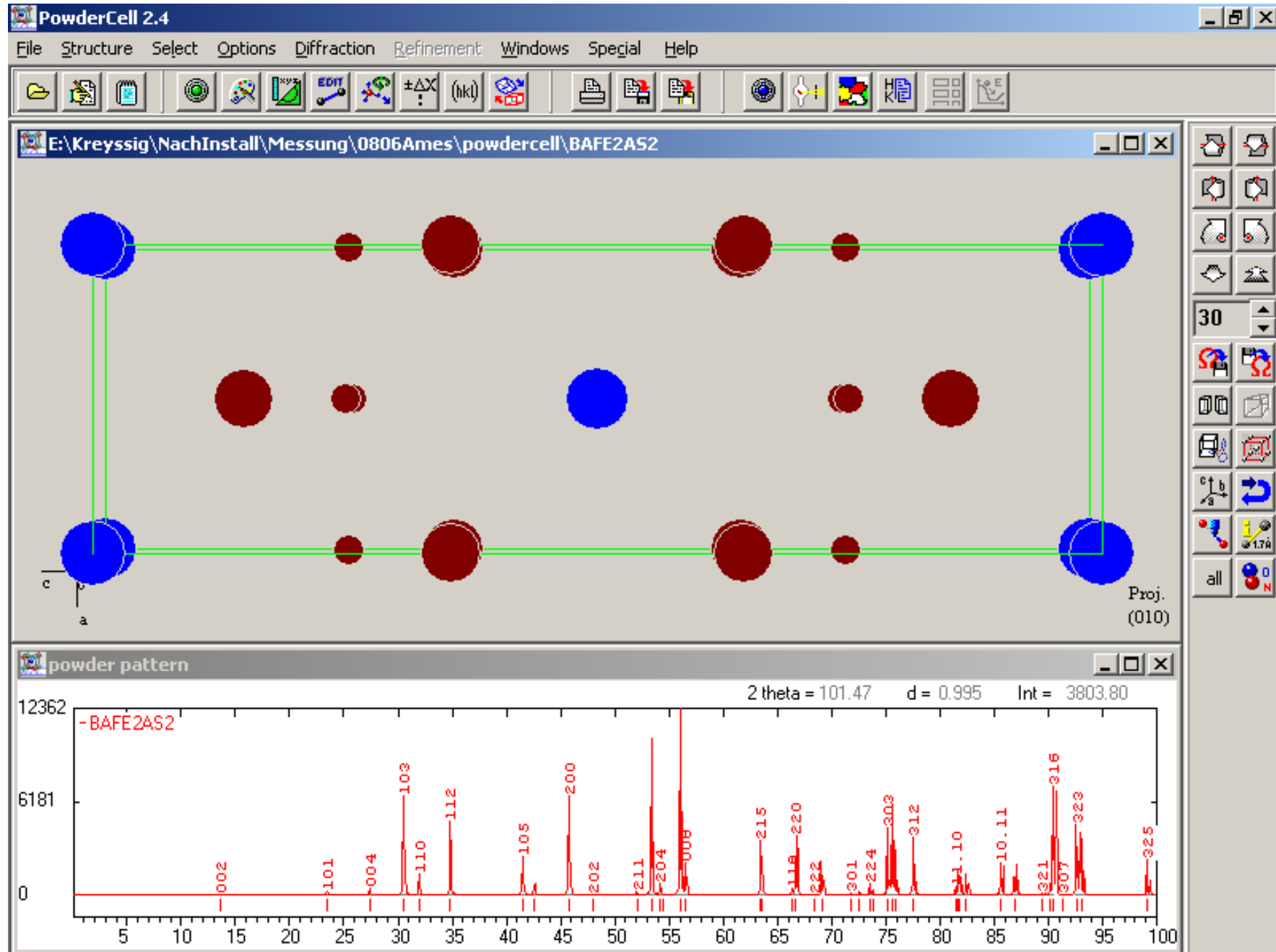
Which elements can/must be present?

Example: growth of PrAuSi out of Sn flux



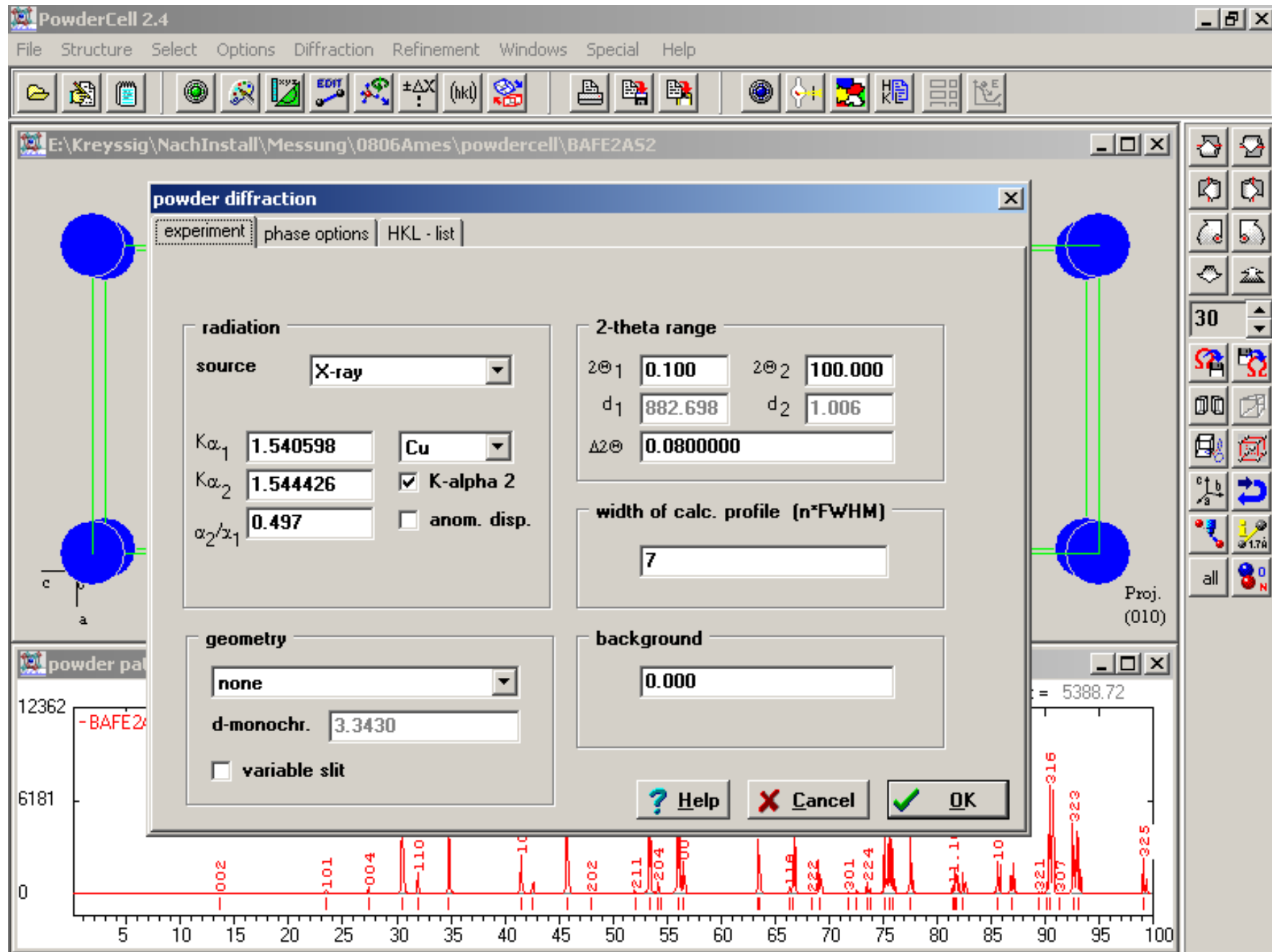
If your phase is not in the database – search for isostructural compounds...

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 screenshot displays the PowderCell 2.4 software interface. The main window shows the 'structure data' dialog box, which is used for defining crystallographic parameters. The 'initial data' tab is active, showing the following information:

- File path: E:\Kreyssig\NachInstall\Messung\0806Ames\powdercell\BAFE2A52
- Space-group No: 139, setting 1, $I\ 4/m\ 2/m\ 2/m$, atoms in cell: 10.0 (10 pos)
- Lattice constants: a = 3.9625, b = 3.9625, c = 13.0168, $\alpha = 90.0000$, $\beta = 90.0000$, $\gamma = 90.0000$
- Cell volume: 204.382 Å³, density: 6.481 g/cm³, rel. mass: 797.754, mass abs coef: 231.147 cm²/g

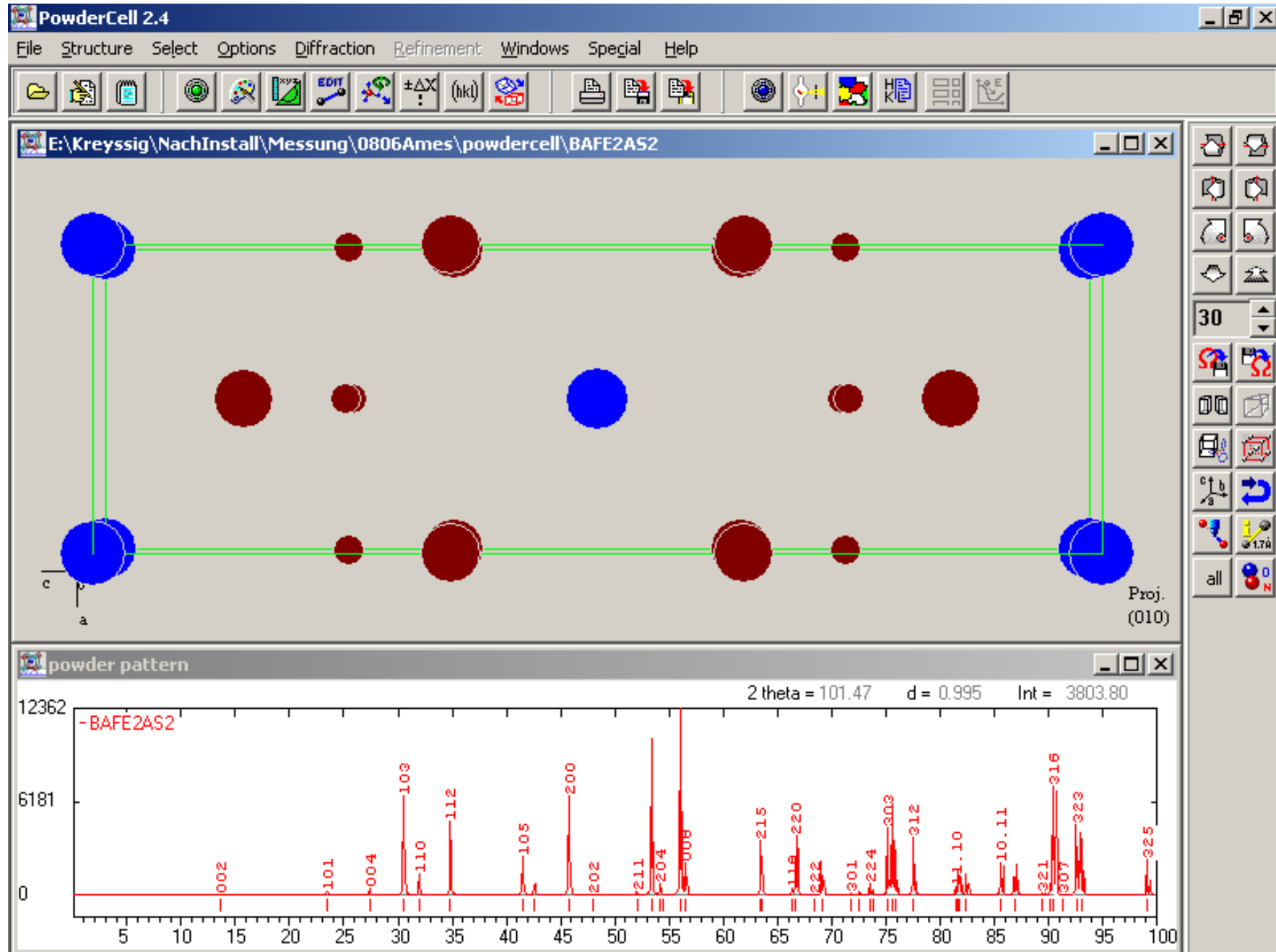
The structure data table is as follows:

name	Z	ion	Wyck	x	y	z	SOF	B (temp)
1 Ba1	56	Ba2+	2a	0.00000	0.00000	0.00000	1.0000	0.0000
2 Fe1	26	Fe3+	4d	0.00000	0.50000	0.25000	1.0000	0.0000
3 As	33	As	4e	0.00000	0.00000	0.35450	1.0000	0.0000

Below the structure data dialog, a 'powder pat' window shows a diffraction pattern. The x-axis represents the diffraction angle (2θ) in degrees, ranging from 5 to 100. The y-axis represents intensity. The pattern shows several sharp peaks, with the most prominent ones labeled with their Miller indices: 002, 101, 004, 110, 202, 211, 204, 118, 222, 301, 224, 110, 321, 307, 316, 323, and 325. The peak at 316 is the most intense. The pattern is labeled '-BAFE2A' and the projection is 'Proj. (010)'. The software version 'PowderCell 2.4' is visible in the top-left corner of the window.

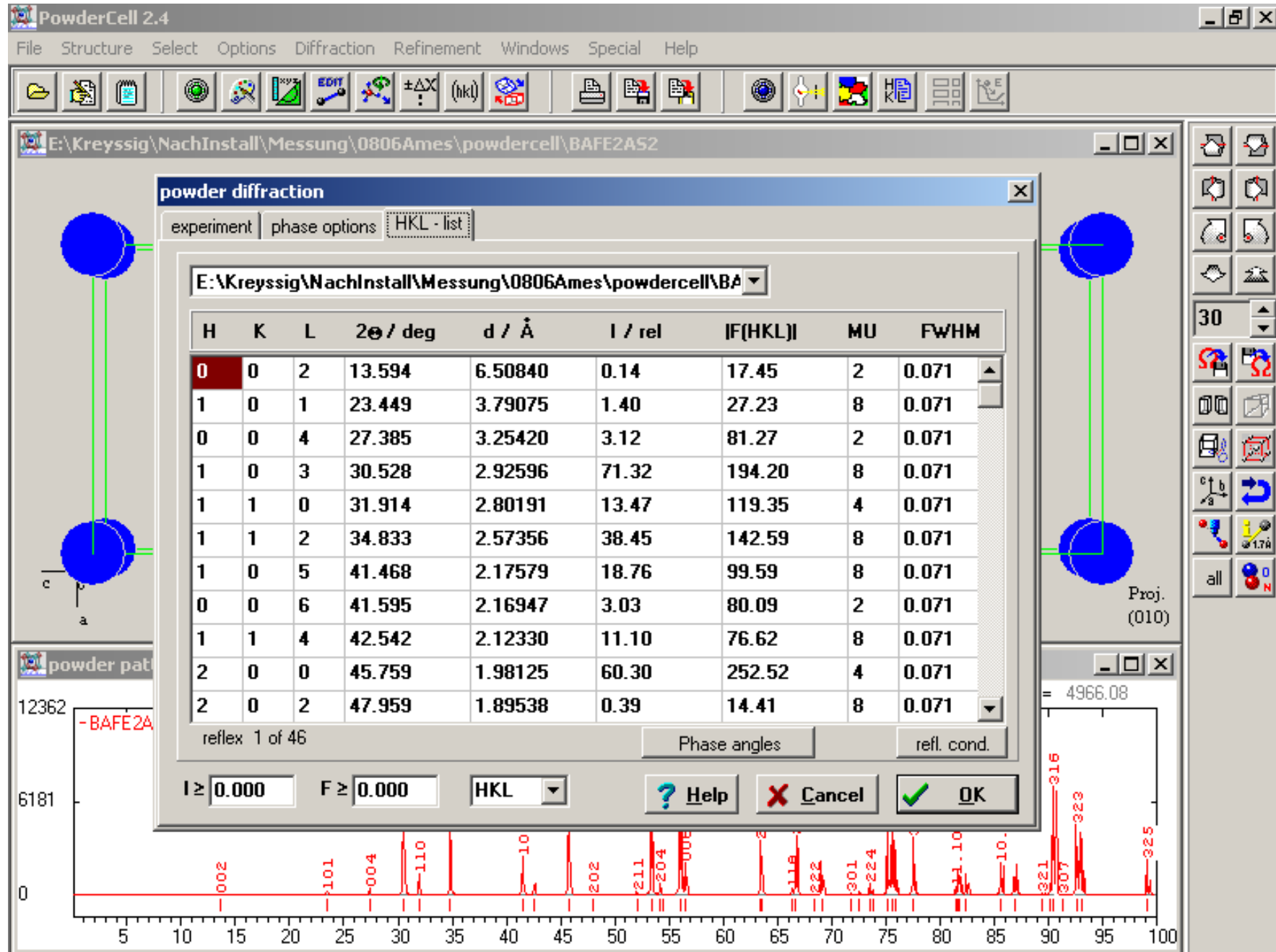
The best tool to calculate diffraction pattern, to verify structure data and more...

Powdercell



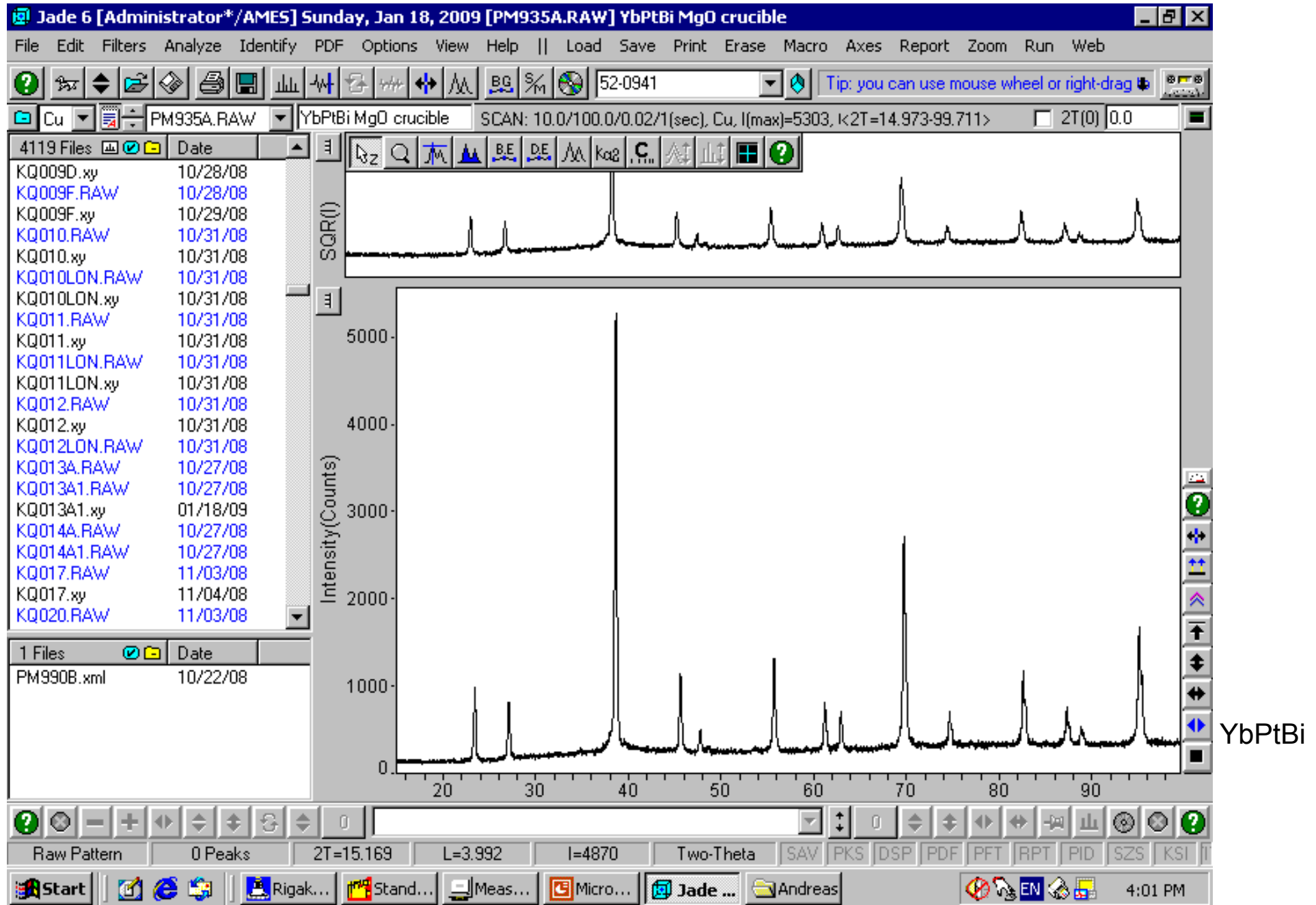
Verify the structure data visually and via plausible bonding length!!!

Powdercell



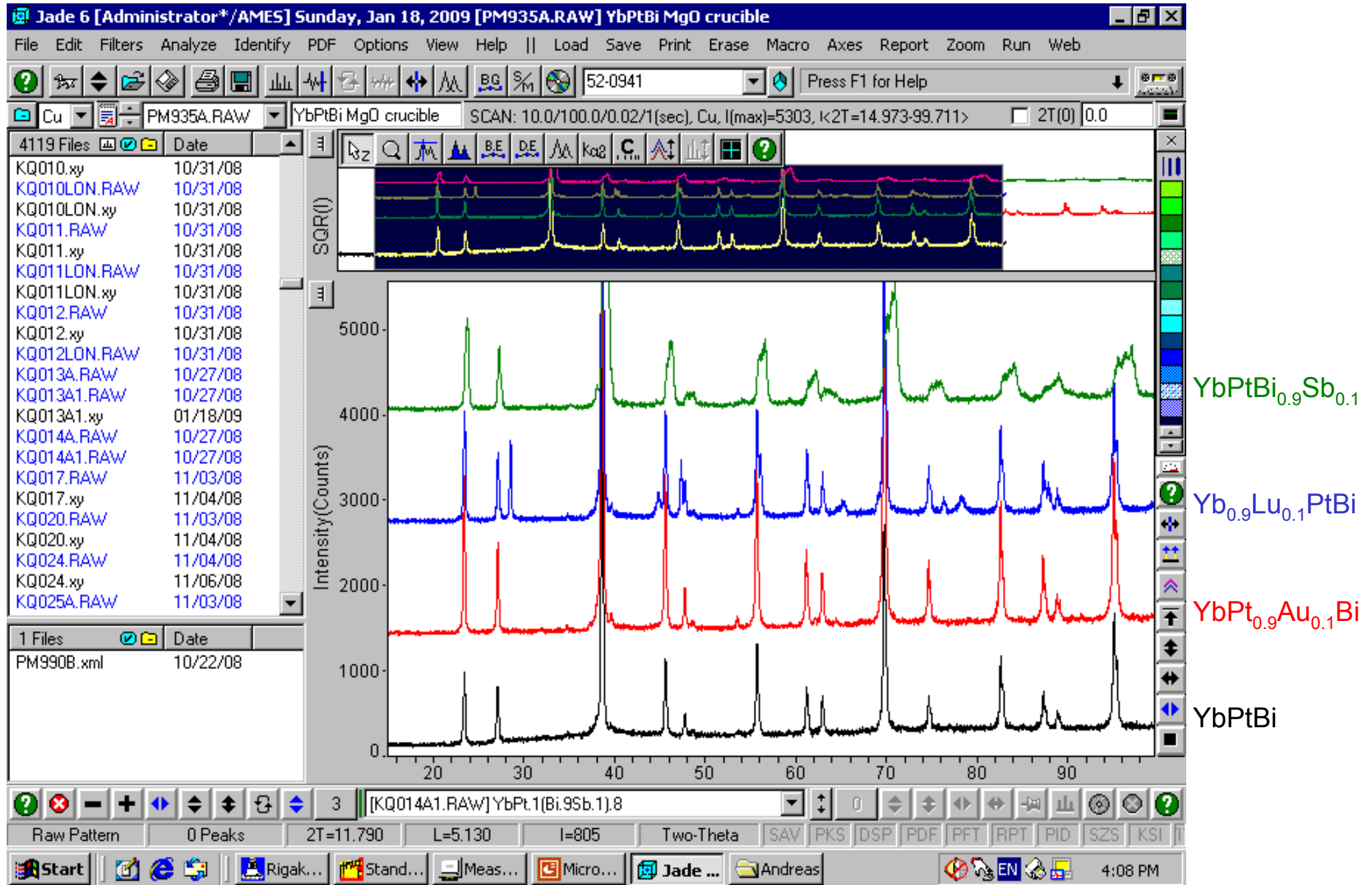
Extract the reflection list: (hkl) – position - intensity

Example: growth of YbPtBi with partial element substitution



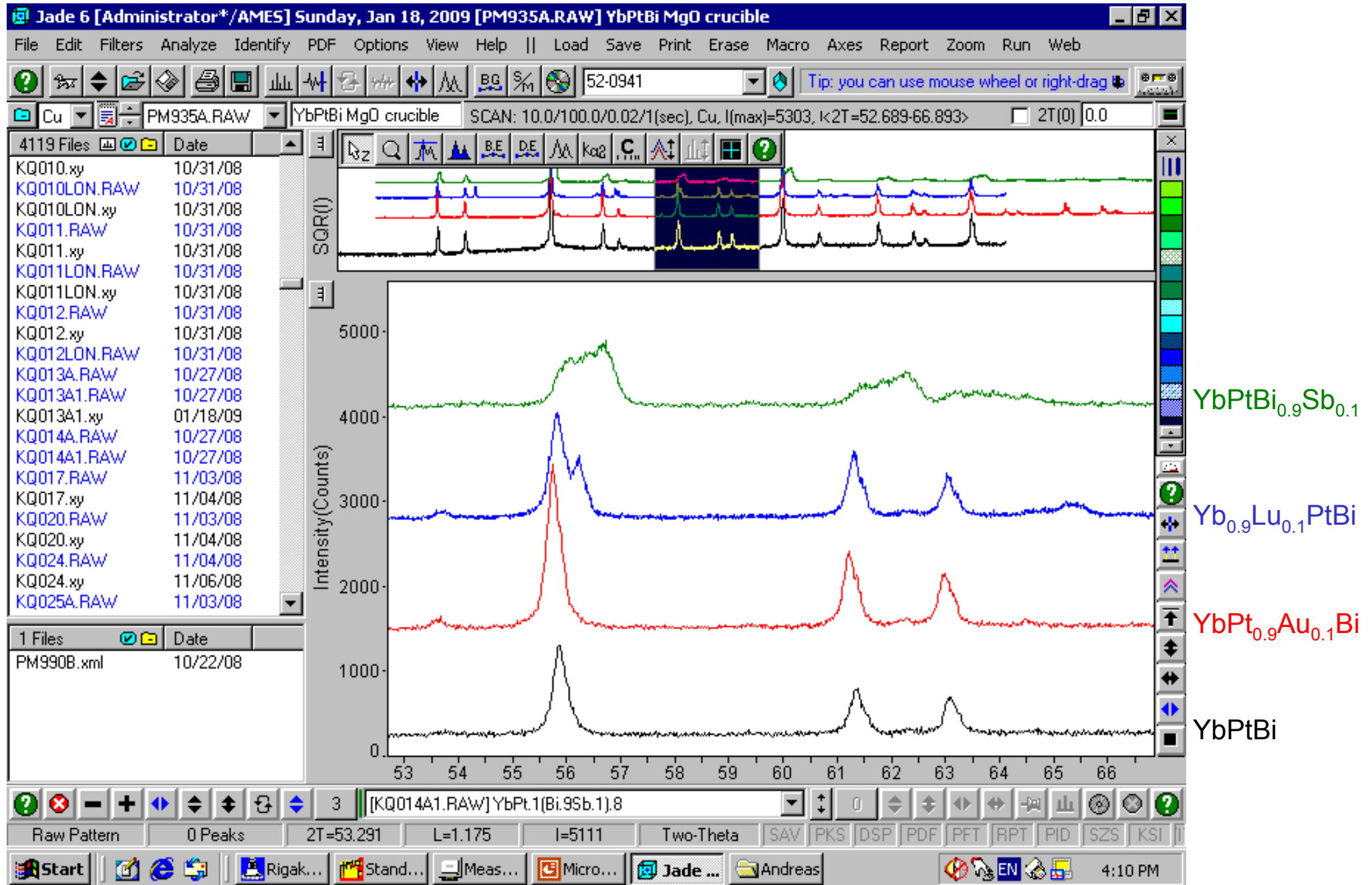
Nice crystals of parent compound

Example: growth of YbPtBi with partial element substitution



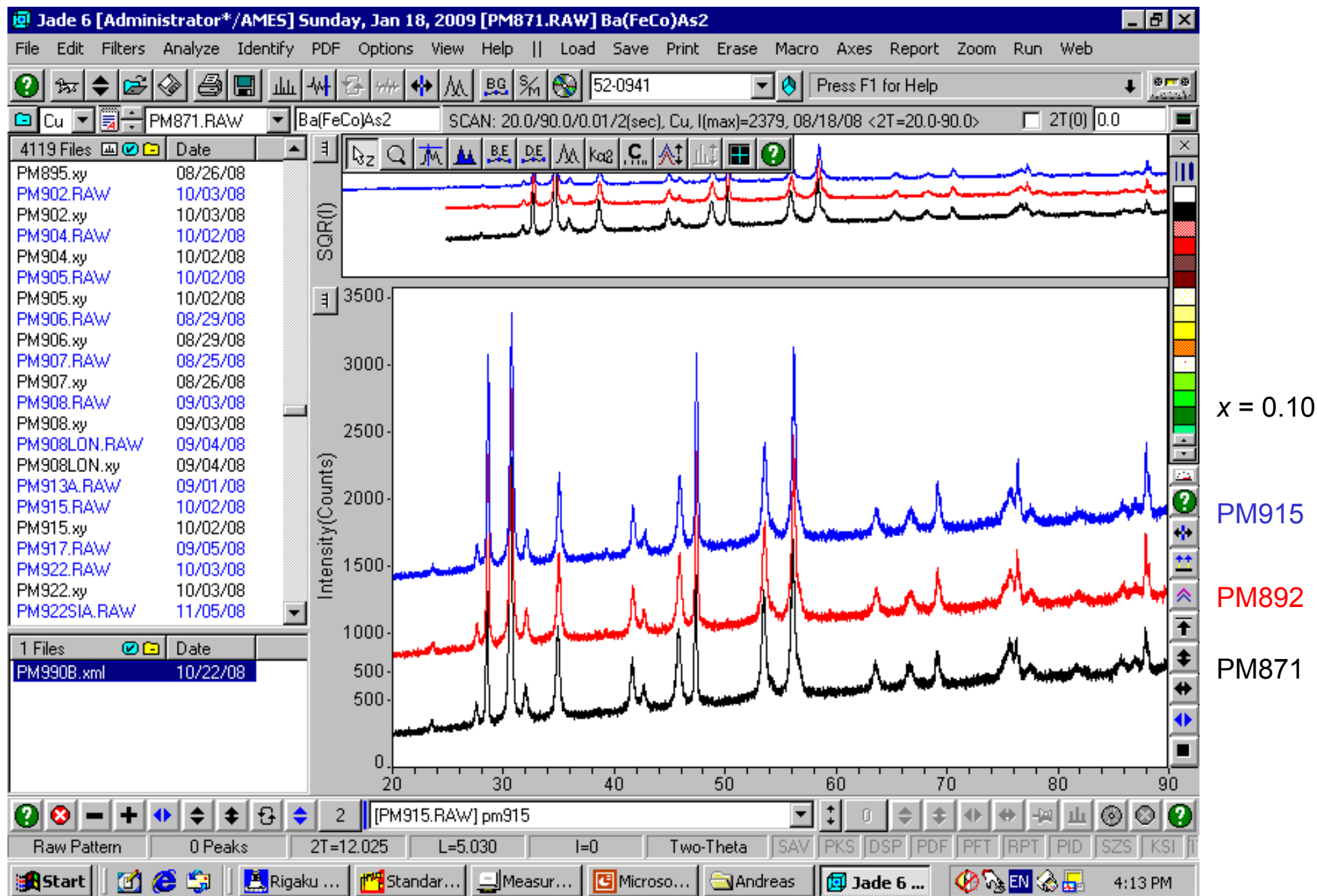
Which phases were grown successfully?

Example: growth of YbPtBi with partial element substitution



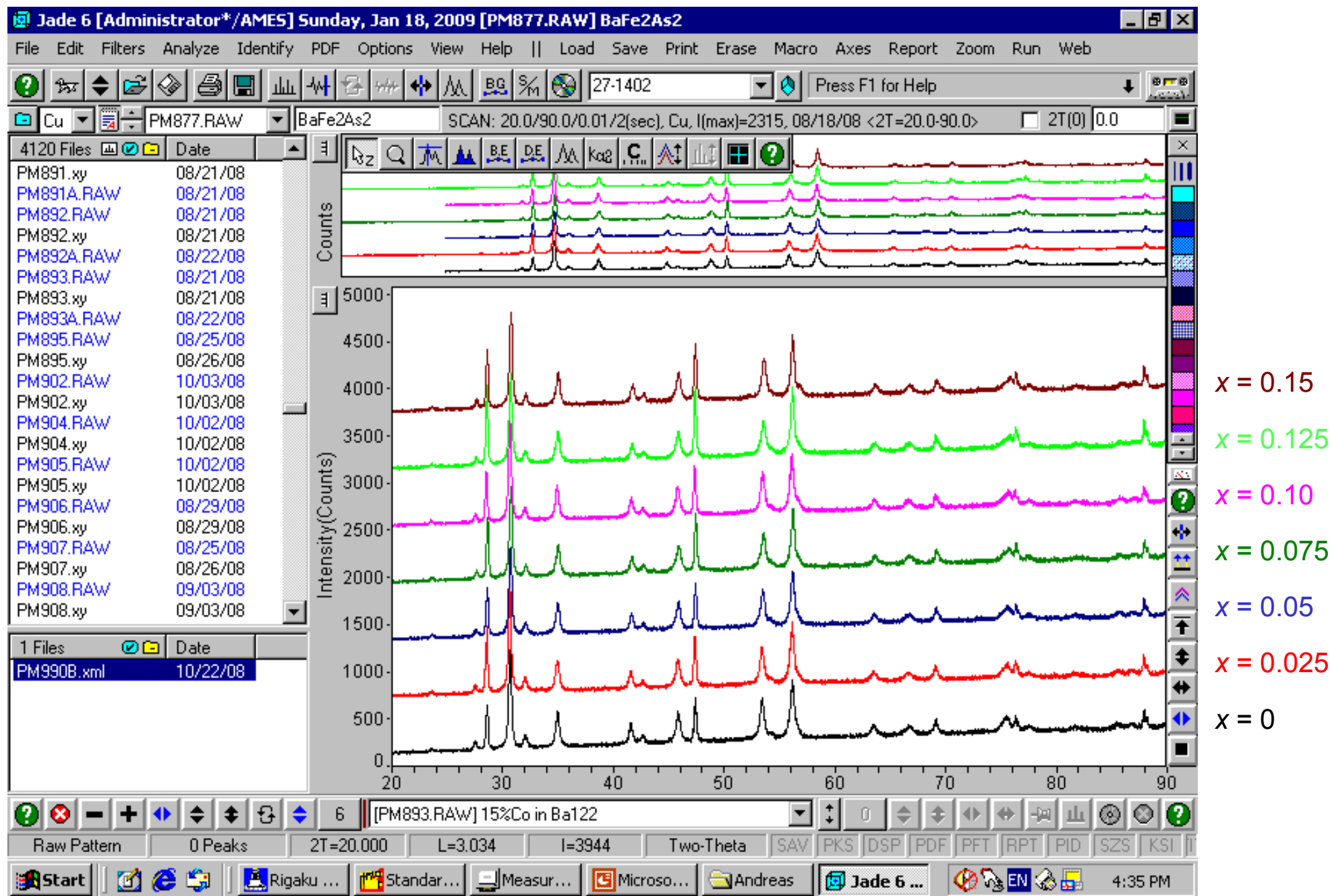
Only YbPt_{0.9}Au_{0.1}Bi was grown successfully.

Example: growth of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$



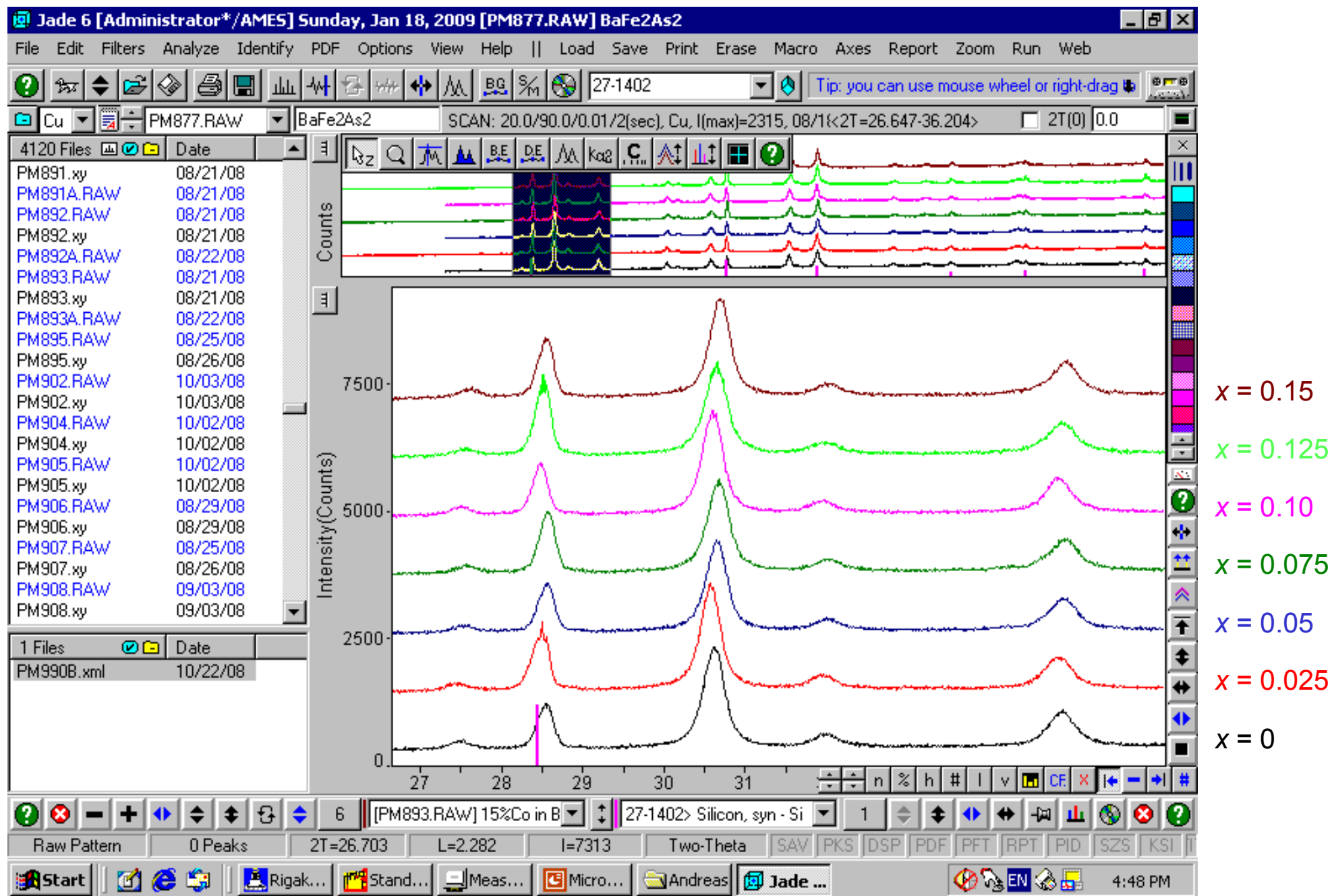
Preparation of samples with same stoichiometry is reproducible.

Example: growth of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$



Preparation of samples with varying stoichiometry seems also successful.

Example: growth of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$



Use of “inner” standard a MUST.

Position of Bragg reflections in powder pattern

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

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

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

$$S_{11} = b^2 c^2 \sin^2 \alpha$$

$$S_{22} = a^2 c^2 \sin^2 \beta$$

$$S_{33} = a^2 b^2 \sin^2 \gamma$$

$$S_{12} = abc^2 (\cos \alpha \cos \beta - \cos \gamma)$$

$$S_{13} = ab^2 c (\cos \gamma \cos \alpha - \cos \beta)$$

$$S_{23} = a^2 bc (\cos \beta \cos \gamma - \cos \alpha)$$

Factors affecting peak positions:

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

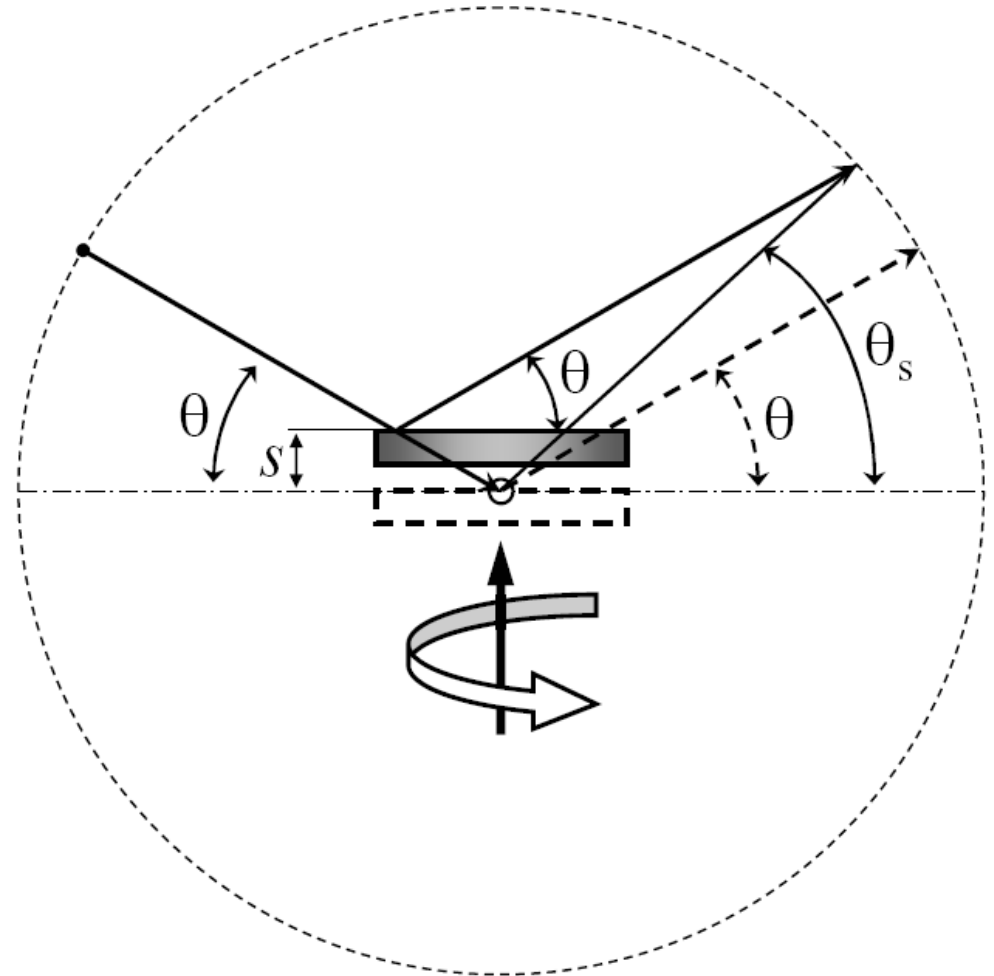
Asymmetry: $p_1 = -\frac{h^2 K_1}{3R^2}; \quad p_2 = -\frac{h^2 K_2}{3R^2}$

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

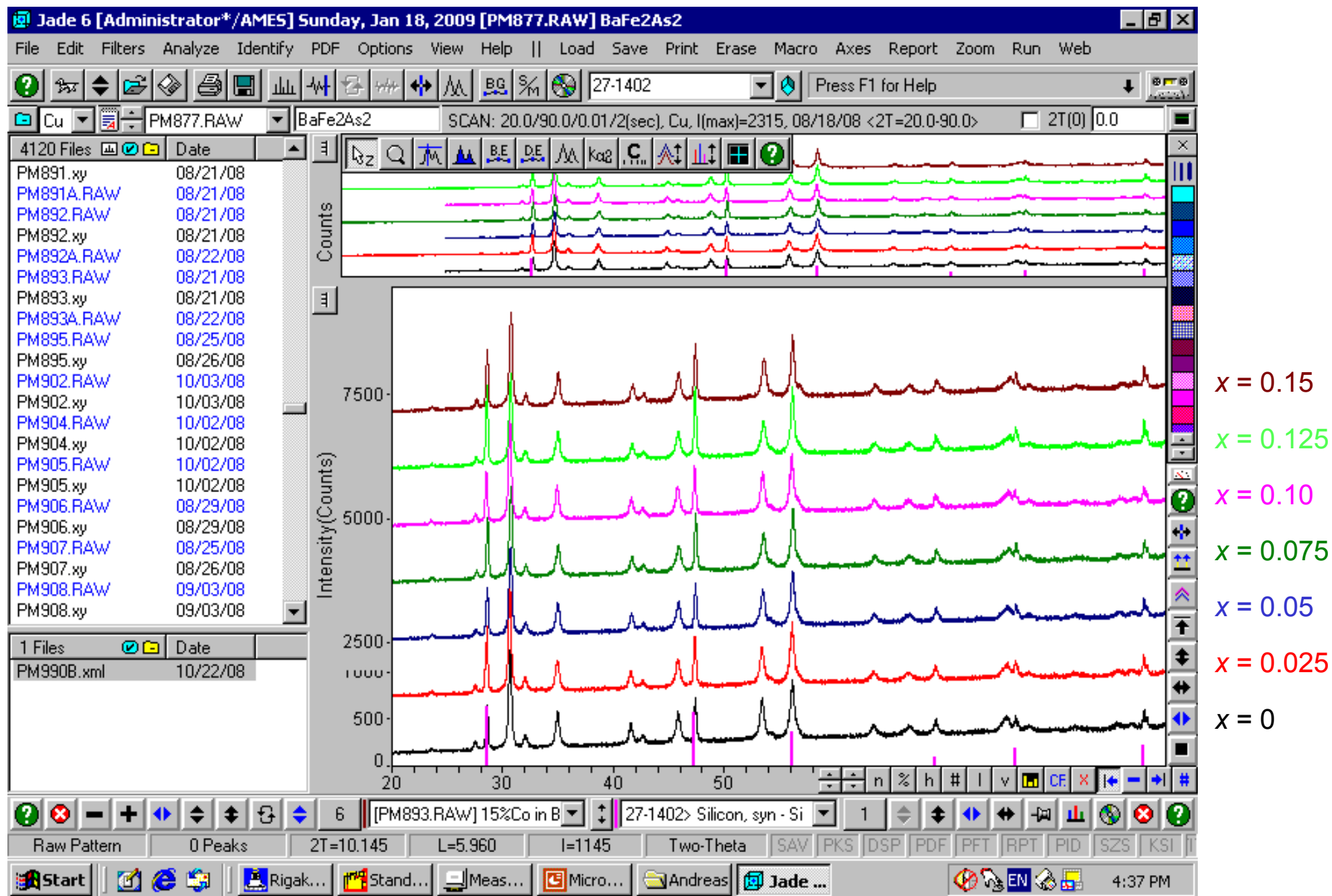
Transparency: $p_4 = \frac{1}{2\mu_{eff} R}$

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

Zero shift: p_6

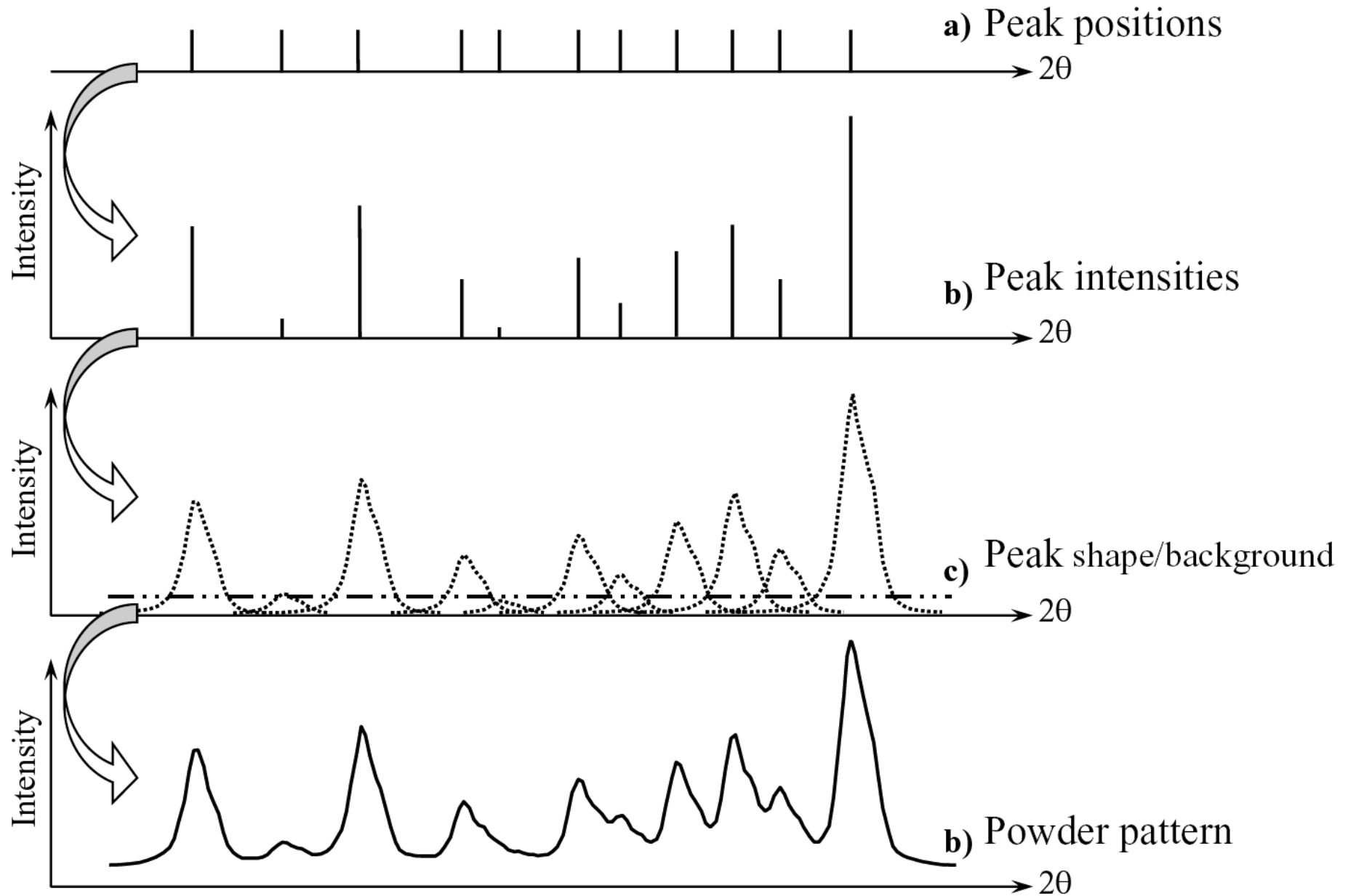


Example: growth of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$



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

Combined fitting of Bragg reflections



Example: growth of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$

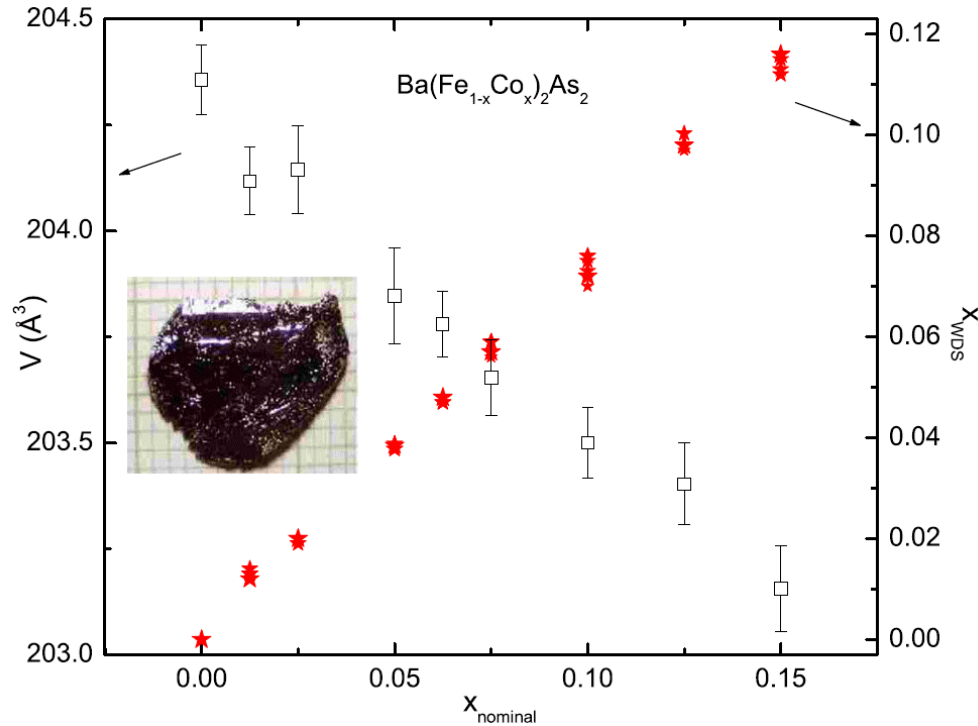


FIG. 2. (Color online) Unit-cell volume and Co concentration determined from WDS measurement as a function of nominal Co concentration. Multiple WDS data points were collected for each nominal x and are each plotted, giving a sense of measured variation in Co concentration. Inset: picture of a representative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

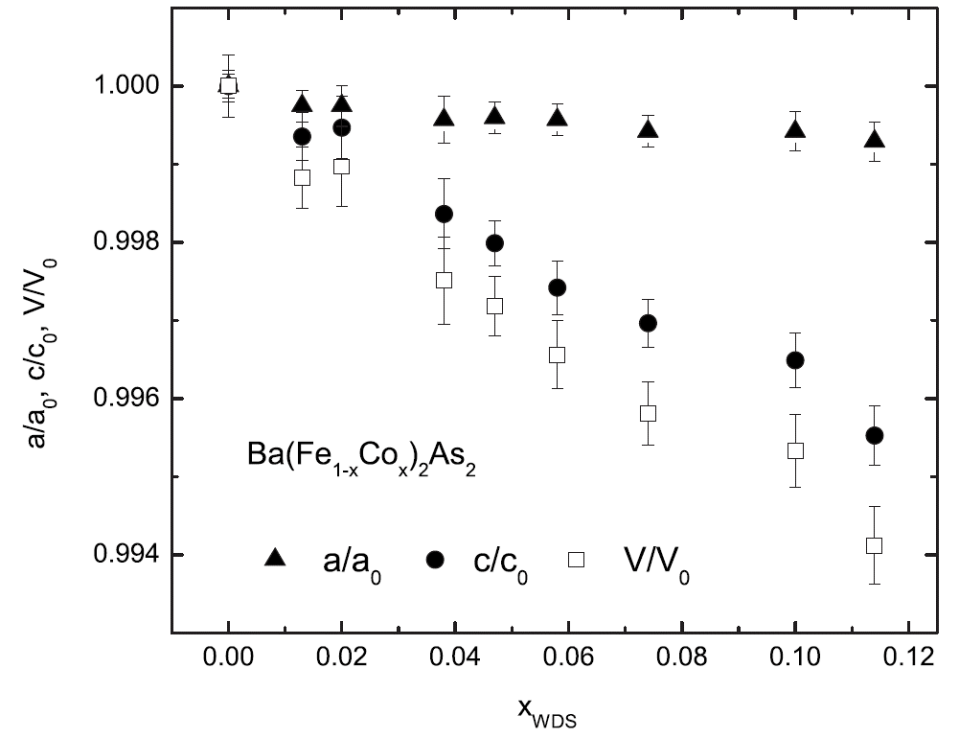
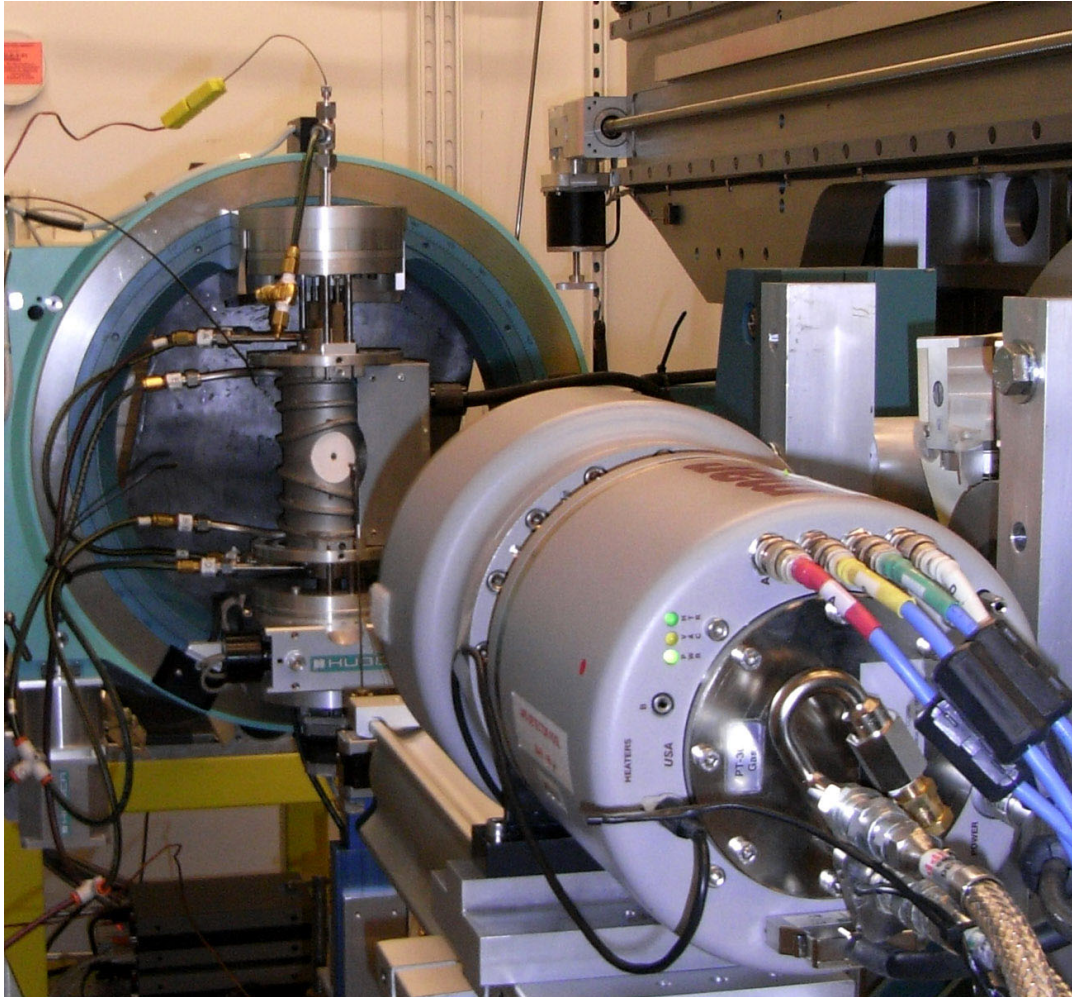


FIG. 3. Unit cell parameters, a and c , as well as unit-cell volume, V , normalized to $a_0=3.9621 \text{ \AA}$, $c_0=13.0178 \text{ \AA}$, and $V_0=204.3565 \text{ \AA}^3$ of undoped BaFe_2As_2 as a function of measured concentration of Co, x_{WDS} .

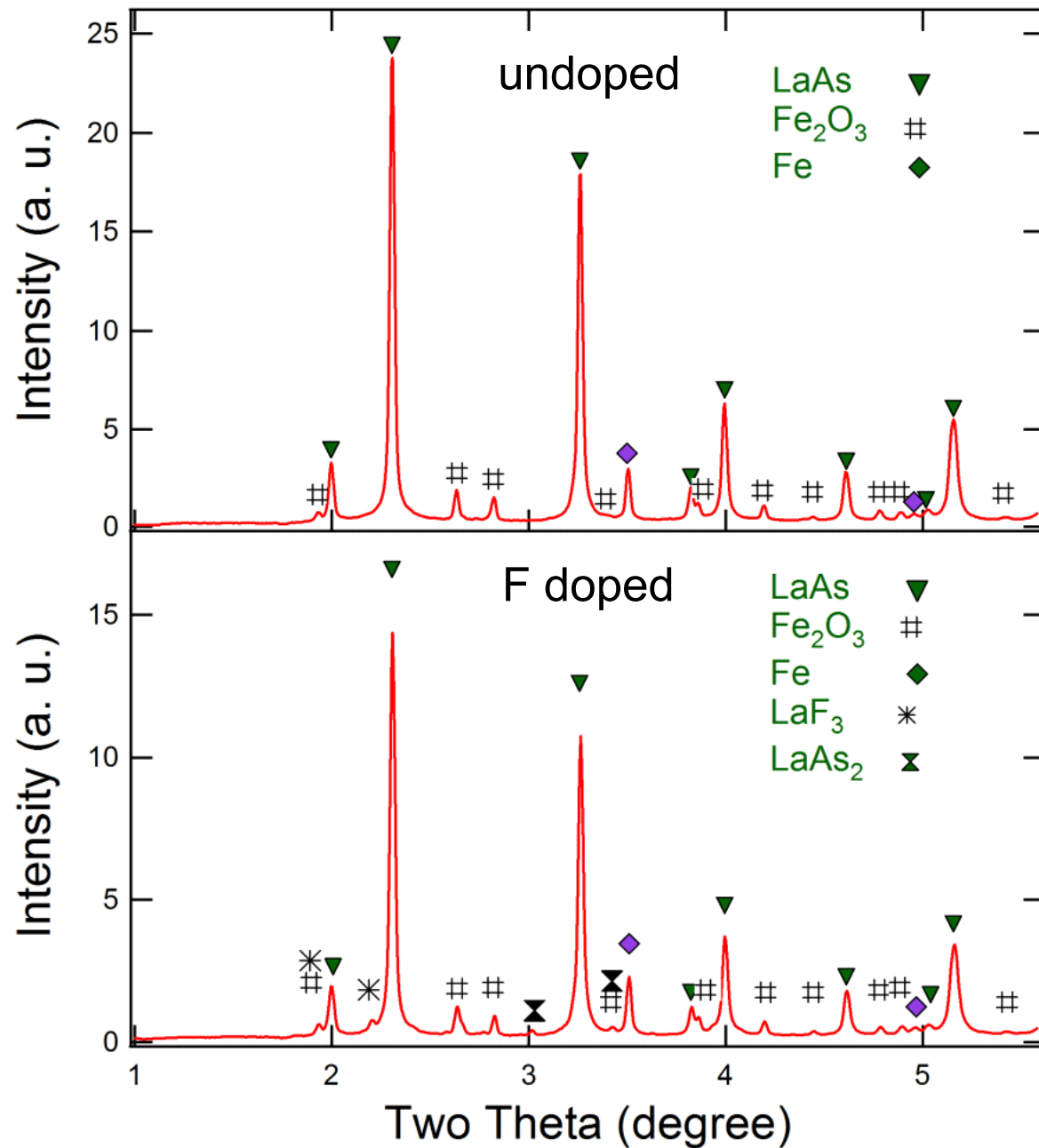
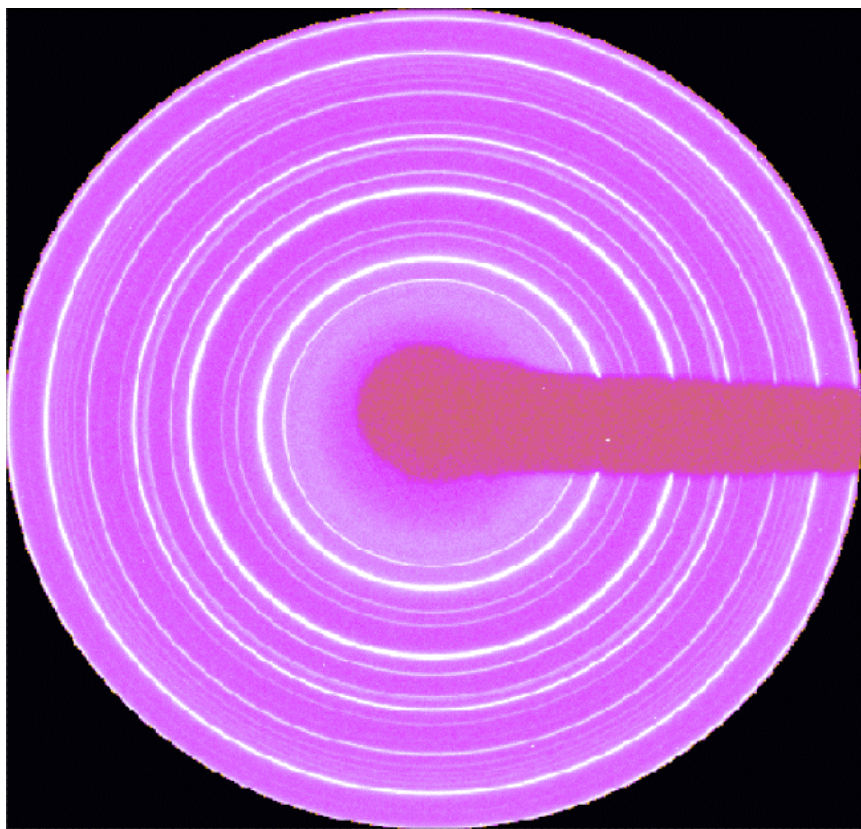
Realized stoichiometry by WDS study; Vegard's law for lattice parameter

Example: preparation of $RFeAs(O/F)$



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

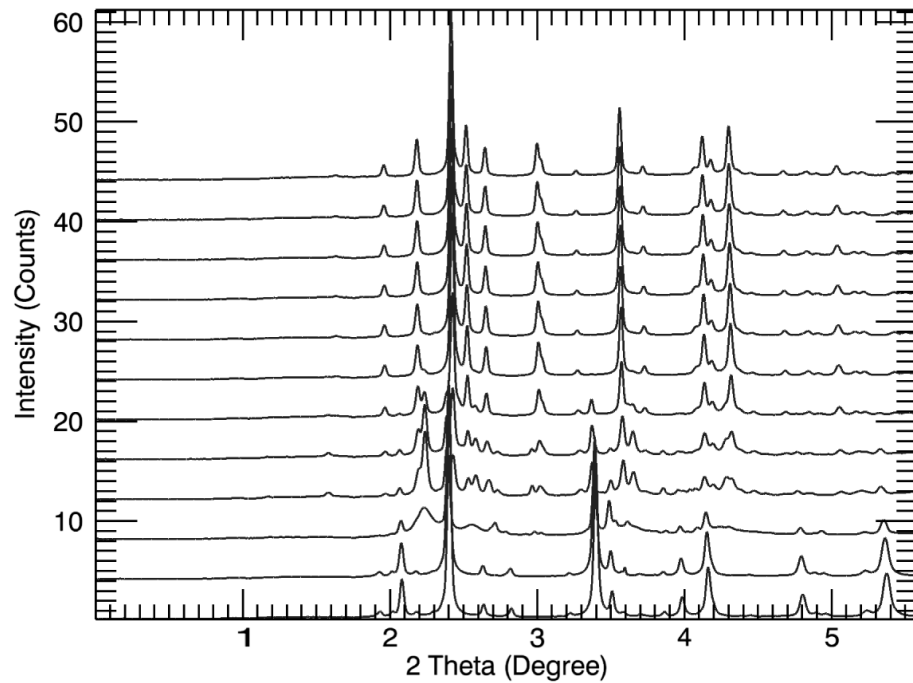
Example: preparation of $R\text{FeAs}(\text{O}/\text{F})$



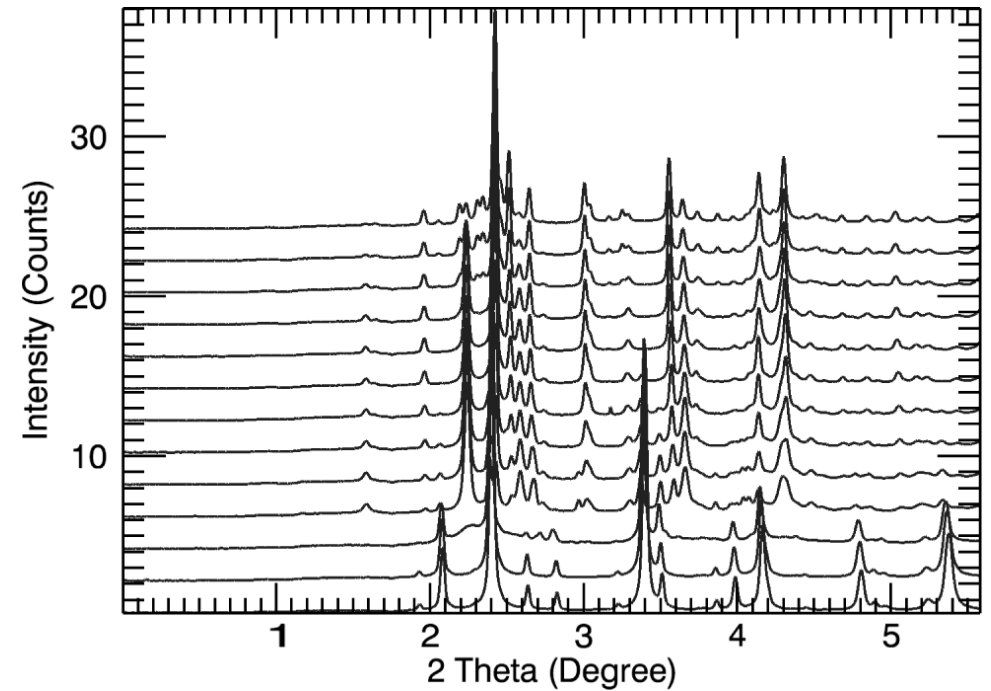
High-temperature x-ray diffraction with 2-dimensional detector

Example: preparation of $RFeAs(O/F)$

F doped



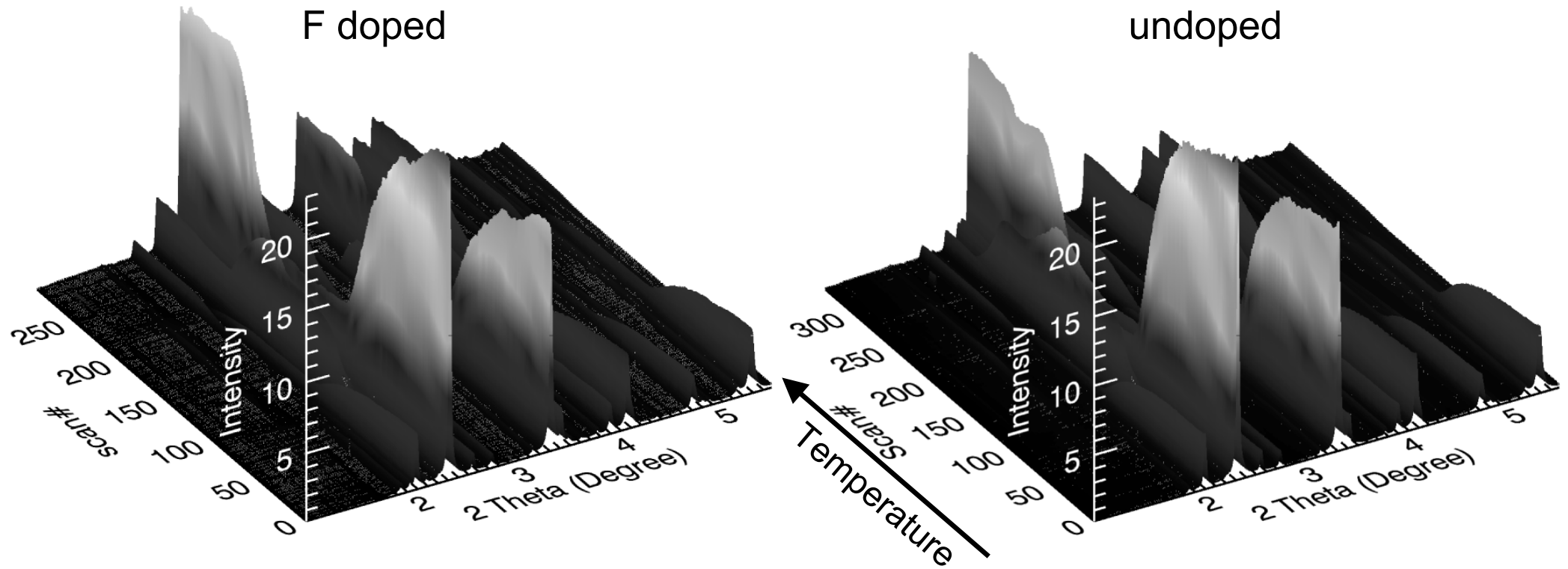
undoped



Temperature ↑

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

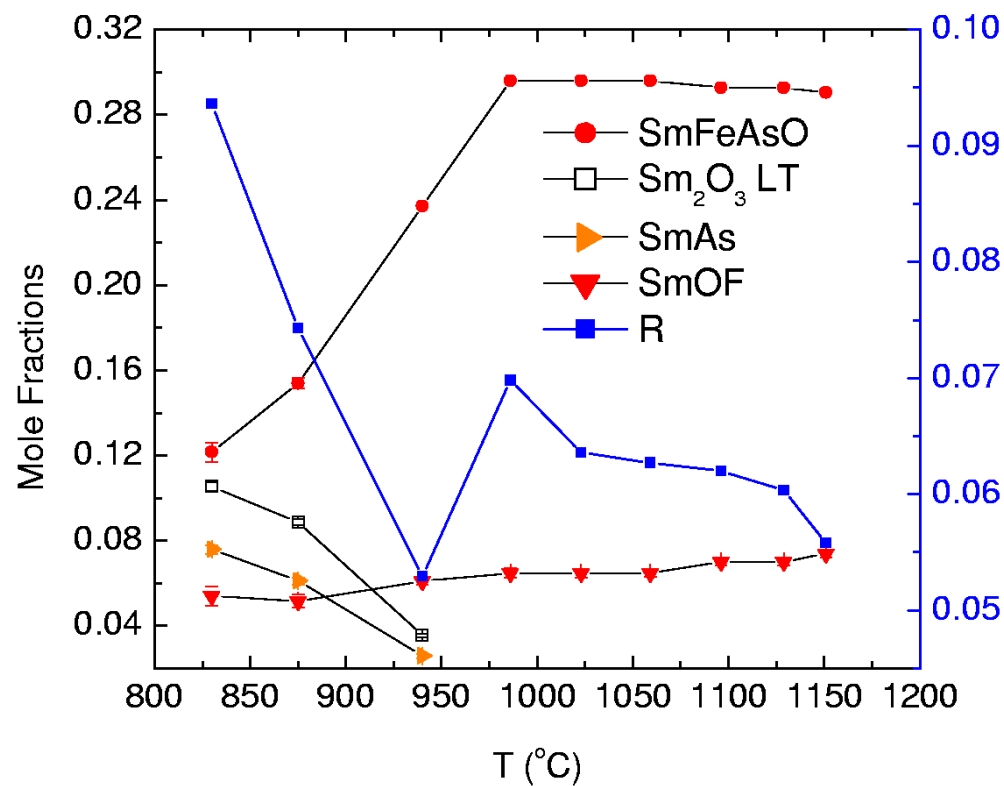
Example: preparation of $RFeAs(O/F)$



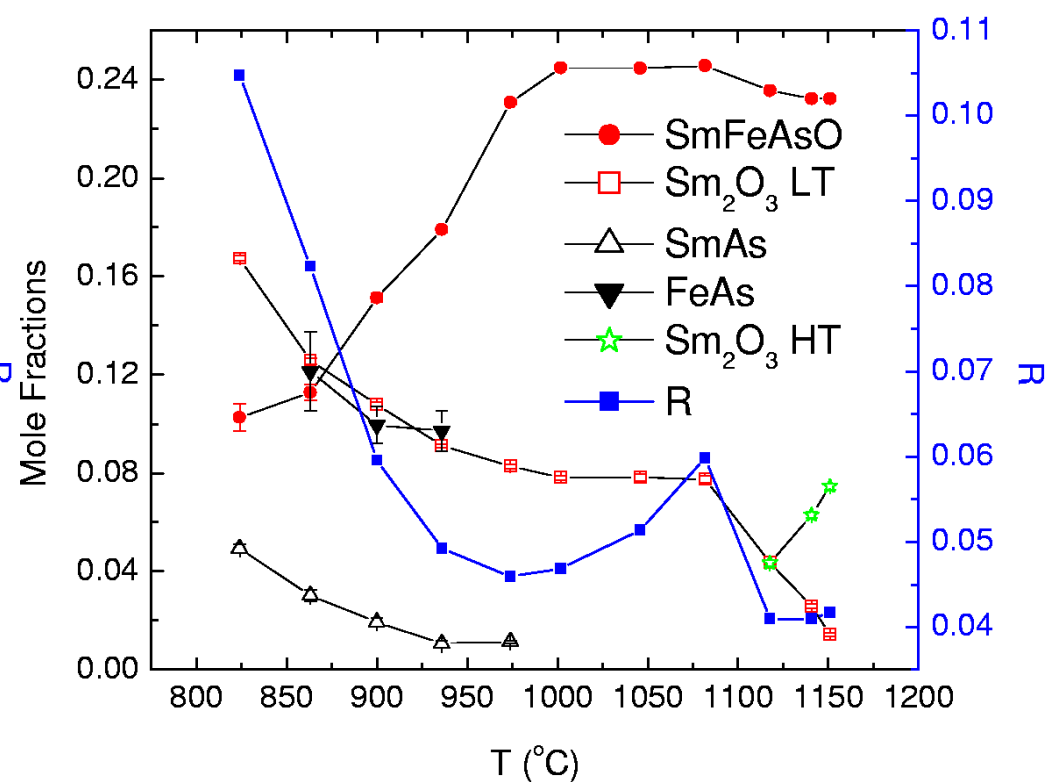
Temperature-dependent x-ray diffraction (20 sec. pattern)

Example: preparation of $RFeAs(O/F)$

F doped

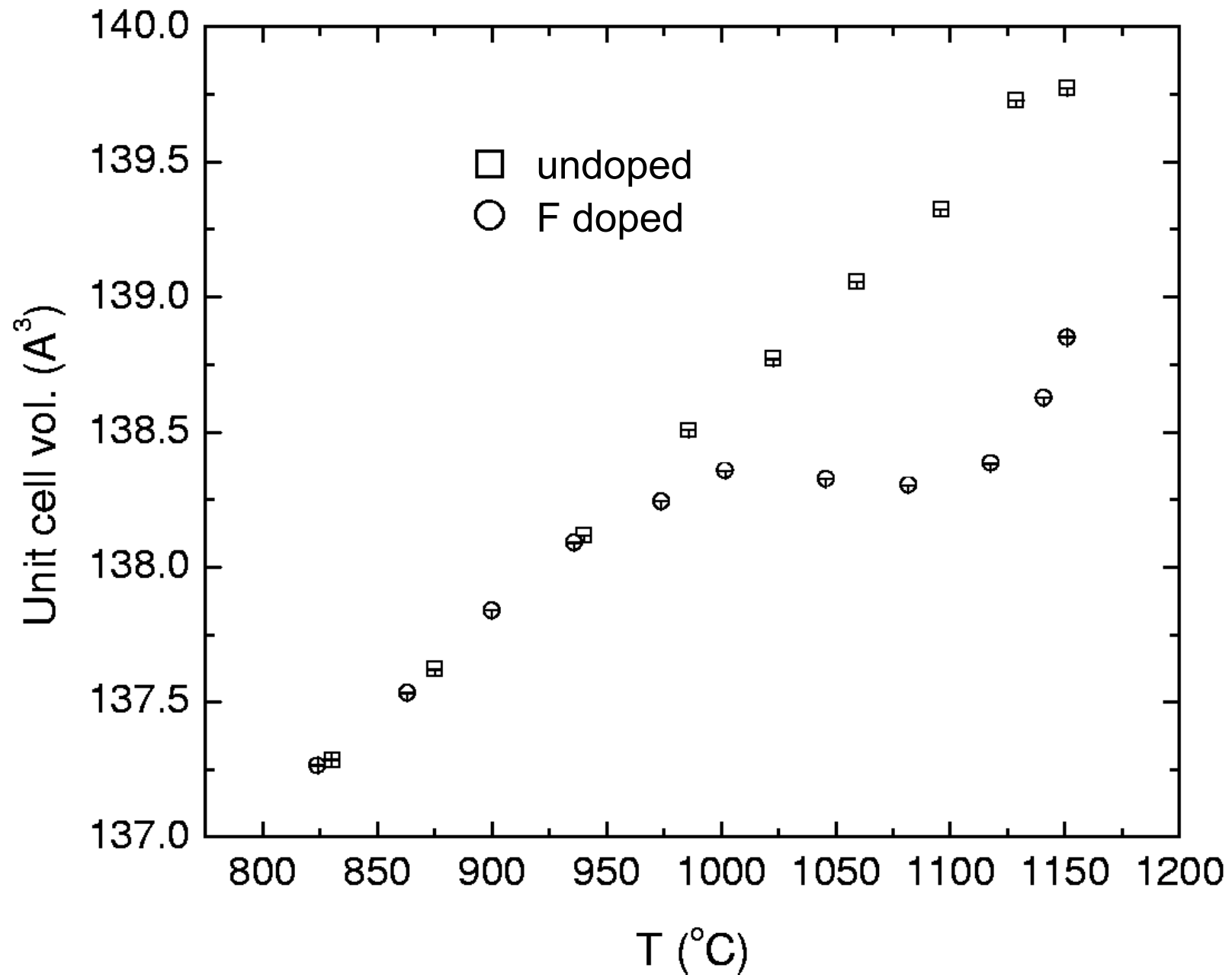


undoped



Crystalline phase fraction determined by Rietveld analysis

Example: preparation of $RFeAs(O/F)$



Unit-cell volume of $RFeAs(O/F)$ phase determined by Rietveld analysis