

Supplementary material for manuscript "An estimation of correctness of XRD results
obtained at analysis of materials with bimodal crystallite size distribution".

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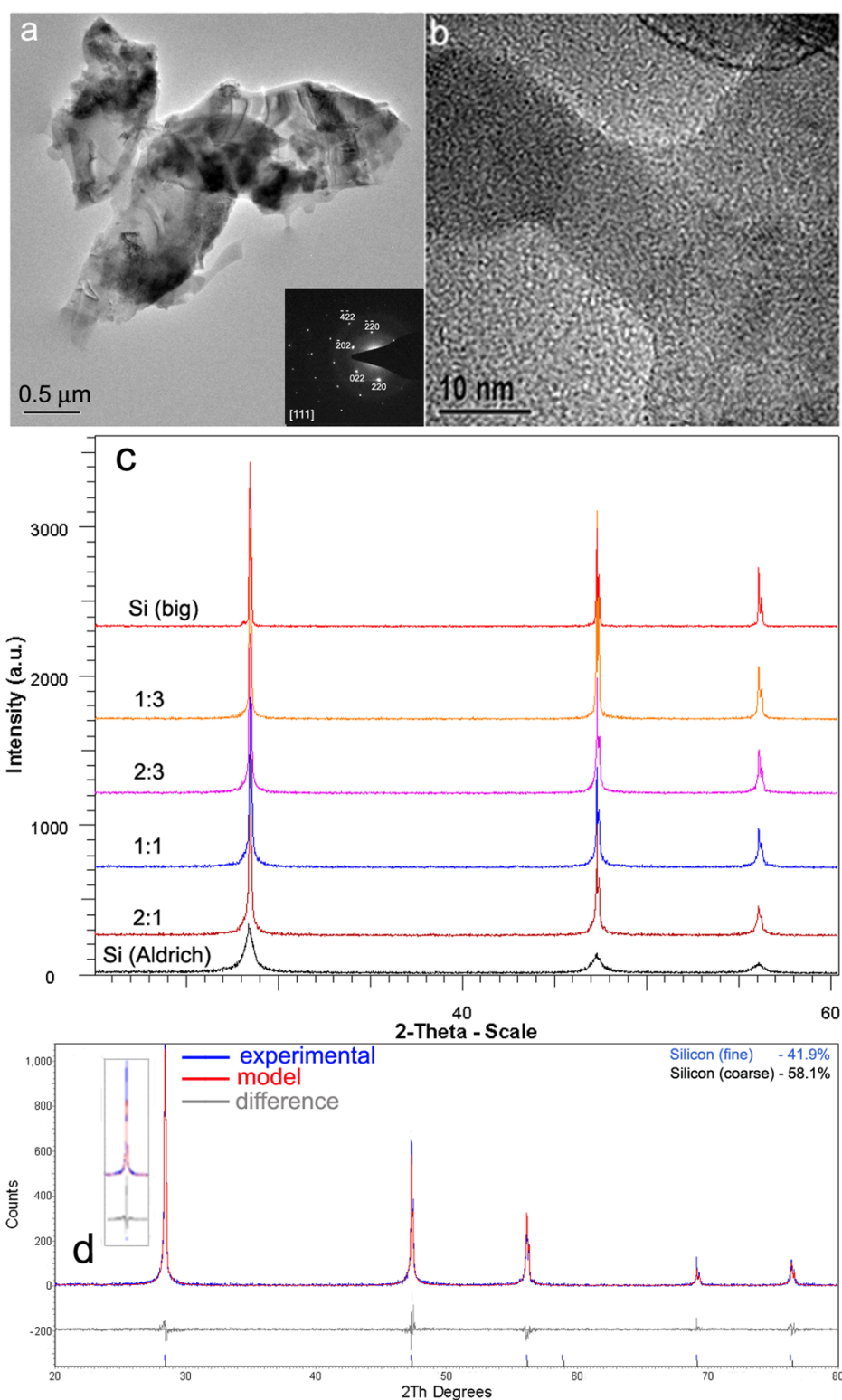


Fig.S1. TEM images of "coarse" (a) and "fine" (b) Si crystallites, in inset the electron diffraction pattern obtained from [111] zone axis of Si crystal; XRD patterns acquired from the same and their mixtures (c) and graphical representation of Rietveld refinement results for 2:3 mixture (d). In inset the results obtained at the assumption that samples contain only one phase.

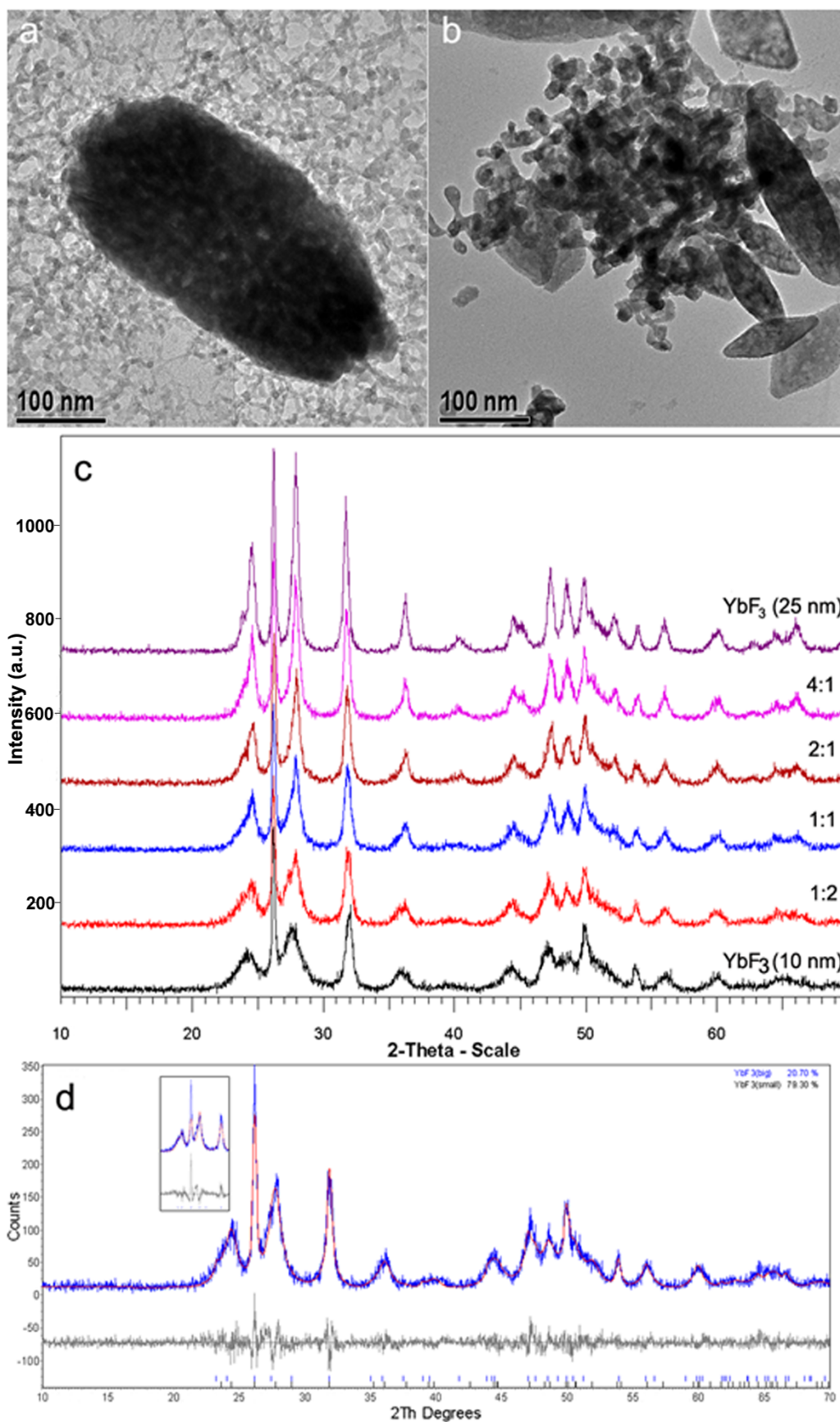


Fig.S2. TEM images of "small" (a) and "big" (b) YbF₃ crystallites, XRD patterns acquired from the same and their mixtures (c) and graphical representation of Rietveld refinement results for 83:17 mixture (d). In insets the results obtained at the assumption that samples contain only one phase.

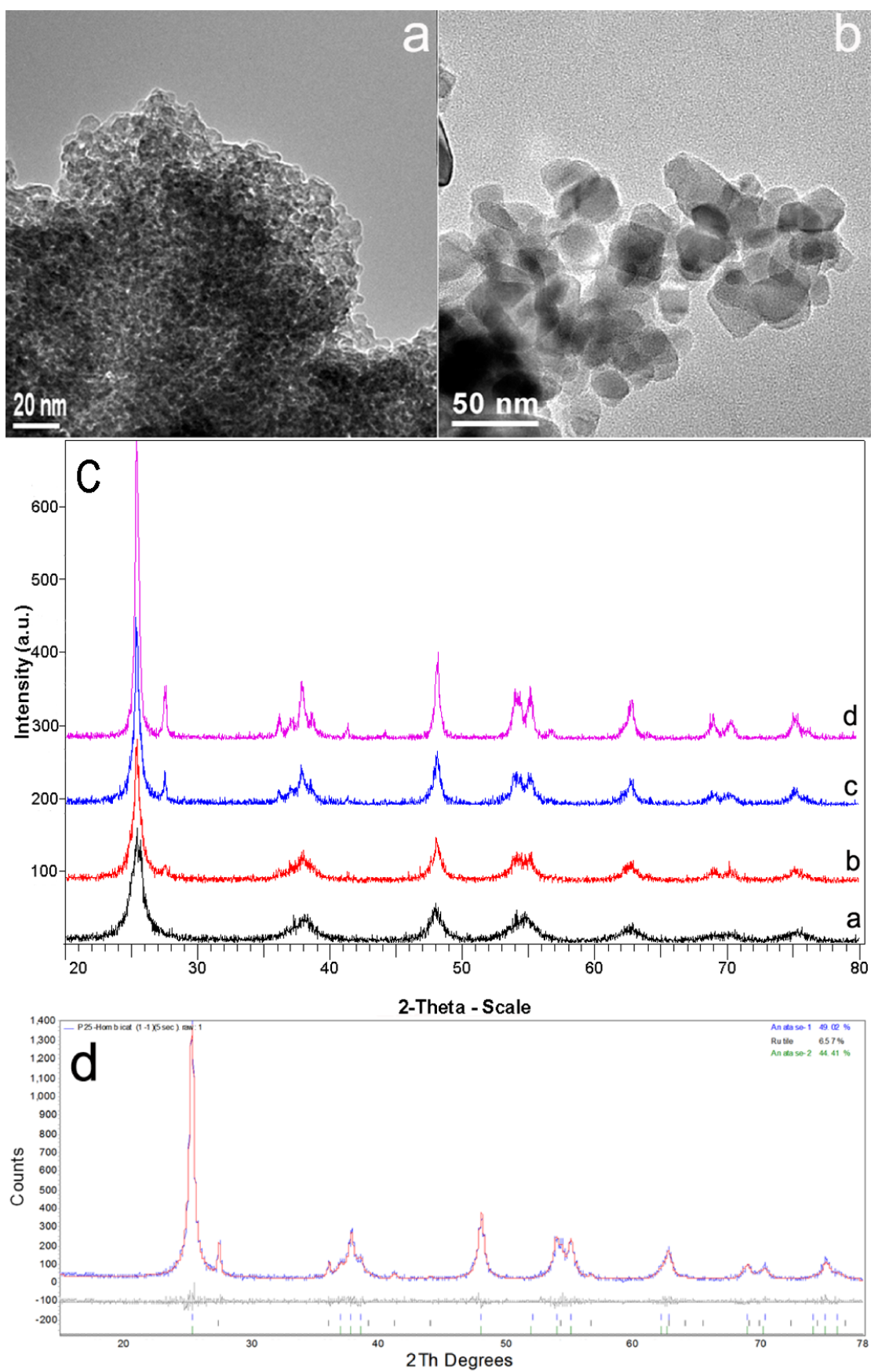


Fig.S3. TEM images of "small" (a) and "big" (b) anatase crystallites, XRD patterns acquired from the same and their mixtures (c) and graphical representation of Rietveld refinement results for 50:50 mixture (d).

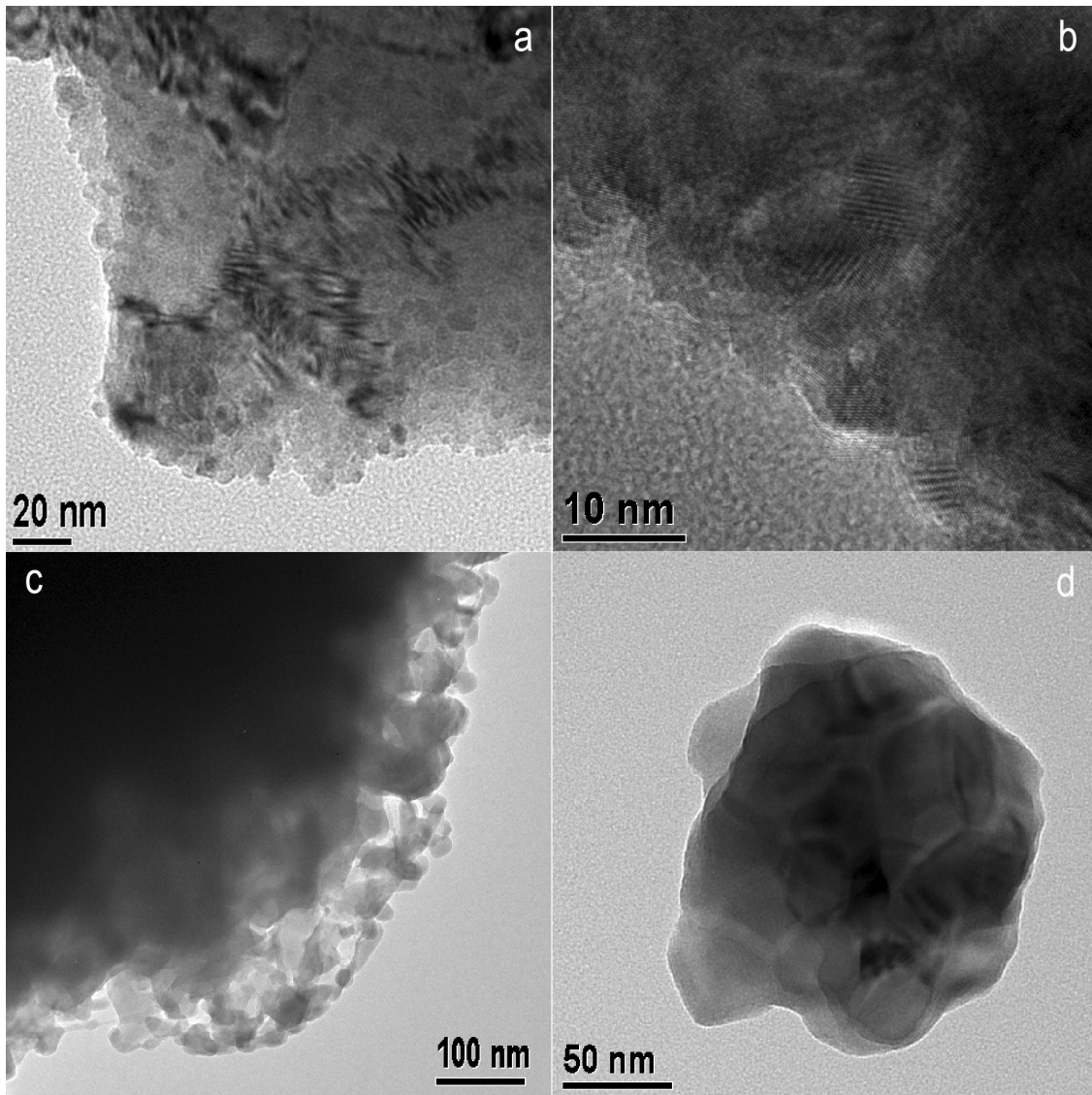


Fig.S4. TEM images obtained from Cu₂O (*a* and *b*) and Se (*c* and *d*) specimens.

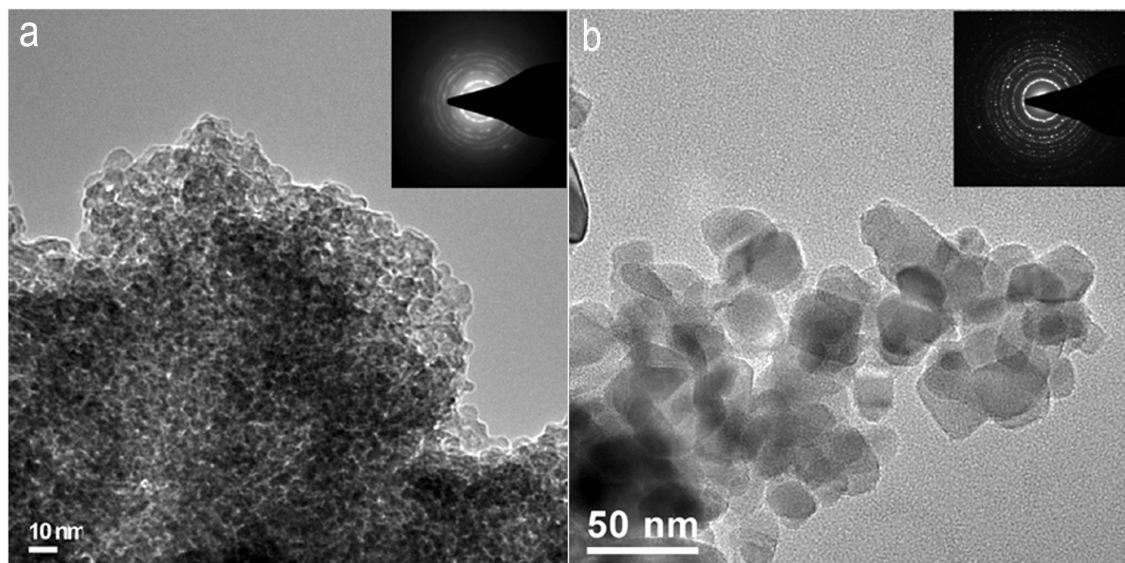
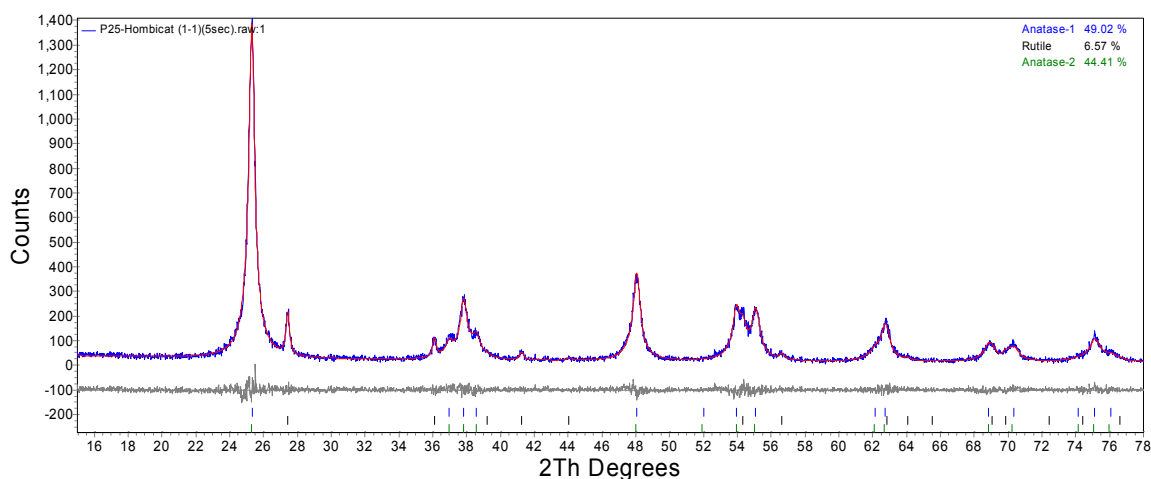


Fig.S5. TEM images obtained from Rutile with crystallite size of 13nm (*a*) and Rutile with crystallite size of 24.8 nm (*b*).

Example of full Rietveld refinement results (TOPAS software):



File 1 : "P25-Hombicat (1-1).raw"

R-Values

Re_p : 12.31 R_w : 13.23 R_p : 9.39 GOF : 1.07
Re_p : 16.33 R_w : 17.55 R_p : 13.42 DW : 1.82

Quantitative Analysis - Rietveld

Phase 1	: Anatase-1	49.0 (45) %
Phase 2	: Rutile	6.57 (75) %
Phase 3	: Anatase-2	44.4 (44) %

Background

Chebyshev polynomial, Coefficient	0	21.60 (22)
	1	-12.21 (32)
	2	4.74 (23)
	3	-0.67 (20)

Instrument

Primary radius (mm)	217.5
Secondary radius (mm)	217.5
Receiving slit width (mm)	0.2
Divergence angle (°)	1
Full Axial Convolution	
Filament Length (mm)	12
Sample Length (mm)	15
Receiving Slit Length (mm)	12
Primary Soller (°)	2.3
Secondary Soller (°)	2.3

Corrections

Zero Error	0.02 (33)
Specimen displacement	-0.00 (60)
LP Factor	26.4
Surface Roughness Pitschke et al	0.0789 (73)
Absorption (1/cm)	14 (12)
Sample Thickness (mm)	0.25

Structure 1

Phase name	Anatase-1
R-Bragg	1.235
Space group	I41/amdZ
Scale	0.00085 (12)
Cell Mass	319.516

Cell Volume (Å³) 135.97(26)
 Wt% - Rietveld 49.0(45)
 Crystallite Size
 Cry Size Lorentzian (nm) 29.9(31)
 k: 1 LVol-IB (nm) 19.1(19)
 k: 0.89 LVol-FWHM (nm) 26.6(27)
 Crystal Linear Absorption Coeff. (1/cm) 486.02(91)
 Crystal Density (g/cm³) 3.9021(73)
 Lattice parameters
 a (Å) 3.7827(32)
 c (Å) 9.5026(79)

Site	Np	x	y	z	Atom Occ	Beg
Ti1	4	0.00000	0.25000	0.37500	Ti+4 1	2.31(52)
O1	8	0.00000	0.25000	0.17060	O-2 1	2.59(44)

Structure 2

Phase name Rutile
 R-Bragg 1.815
 Space group P42/mnm
 Scale 0.000496(38)
 Cell Mass 159.758
 Cell Volume (Å³) 62.35(12)
 Wt% - Rietveld 6.57(75)
 Crystallite Size
 Cry Size Lorentzian (nm) 51.1(42)
 k: 1 LVol-IB (nm) 32.5(27)
 k: 0.89 LVol-FWHM (nm) 45.5(37)
 Crystal Linear Absorption Coeff. (1/cm) 530.0(10)
 Crystal Density (g/cm³) 4.2549(81)
 Preferred Orientation Spherical Harmonics
 Order 4
 y00 1
 y20 0.593(90)
 y40 0.14(12)
 y44p -0.295(80)
 Lattice parameters
 a (Å) 4.5924(39)
 c (Å) 2.9562(25)

Site	Np	x	y	z	Atom Occ	Beg
Ti1	2	0.00000	0.00000	0.00000	Ti+4 1	1.58(51)
O1	4	0.31860	0.31860	0.00000	O-2 1	2.38(64)

Structure 3

Phase name Anatase-2
 R-Bragg 1.504
 Space group I41/amdZ
 Scale 0.000766(98)
 Cell Mass 319.516
 Cell Volume (Å³) 136.38(27)
 Wt% - Rietveld 44.4(44)
 Crystallite Size
 Cry Size Lorentzian (nm) 10.15(60)
 k: 1 LVol-IB (nm) 6.46(38)
 k: 0.89 LVol-FWHM (nm) 9.03(53)
 Crystal Linear Absorption Coeff. (1/cm) 484.55(97)
 Crystal Density (g/cm³) 3.8903(78)
 Lattice parameters
 a (Å) 3.7888(33)
 c (Å) 9.5008(92)

Site	Np	x	y	z	Atom Occ	Beg
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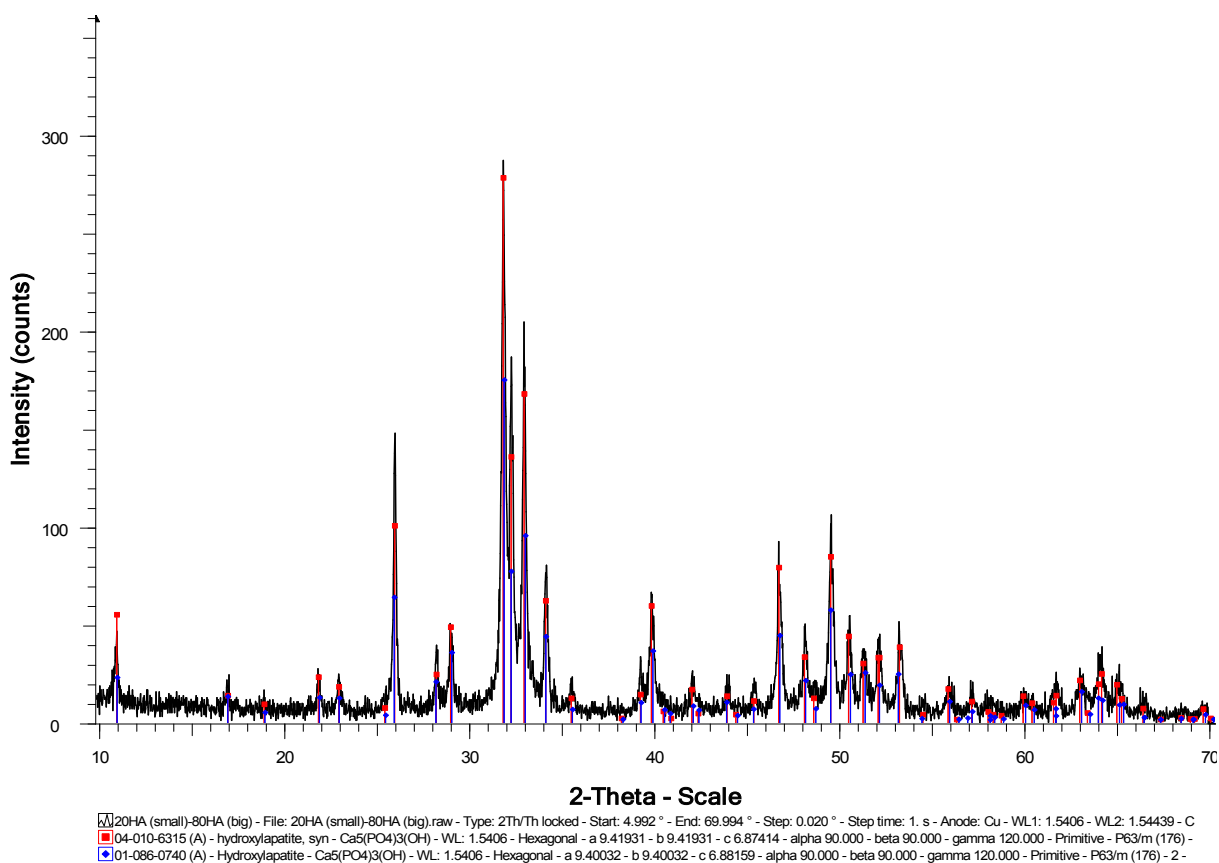
Ti1	4	0.00000	0.25000	0.37500	Ti+4	1	1.10 (33)
O1	8	0.00000	0.25000	0.17060	O-2	1	2.92 (50)

Table S1. Results of XRD analysis of hydroxylapatite mixtures with bimodal crystallite size distribution (EVA software).

Components name	Mixtures description			Results of XRD analysis			
	Crystallite size ¹ , nm		Components ratio ("small"/"big"), %	"small" crystallites		"big" crystallites	
	"small"	"big"		size, nm	percentage, %	size, nm	percentage, %
Hydroxylapatite, Ca ₅ (PO ₄) ₃ (OH)	14	52	90:10	10.1	74.5	42.7	25.8
			75:25	11.5	60.2	40.2	39.8
			50:50	15.3	57.4	64.8	42.6
			20:80	12.7	23.2	53.2	76.8

¹Crystallite sizes of pure phases calculated using XRD method.

Examples of XRD analyses of hydroxylapatite artificial mixtures with bimodal crystallite size distribution using EVA software:



Sample name: 80HA (big)-20HA (small)

Concentrations:

04-010-6315 76.8% Ca₅(PO₄)₃(OH)

Hydroxylapatite, syn

01-086-0740 23.2% Ca₅(PO₄)₃(OH)

Hydroxylapatite

04-010-6315 Hydroxylapatite, syn----- Ca₅(PO₄)₃(OH)

Crystallite Size (Scherrer): 532.3 Å

System: Hexagonal

Space group: P63/m (176)

Cell param.: Initial Final

a: 9.42183 9.41931

c: 6.87844 6.87414

01-086-0740 Hydroxylapatite----- Ca₅(PO₄)₃(OH)

Crystallite Size (Scherrer): 127.2 Å

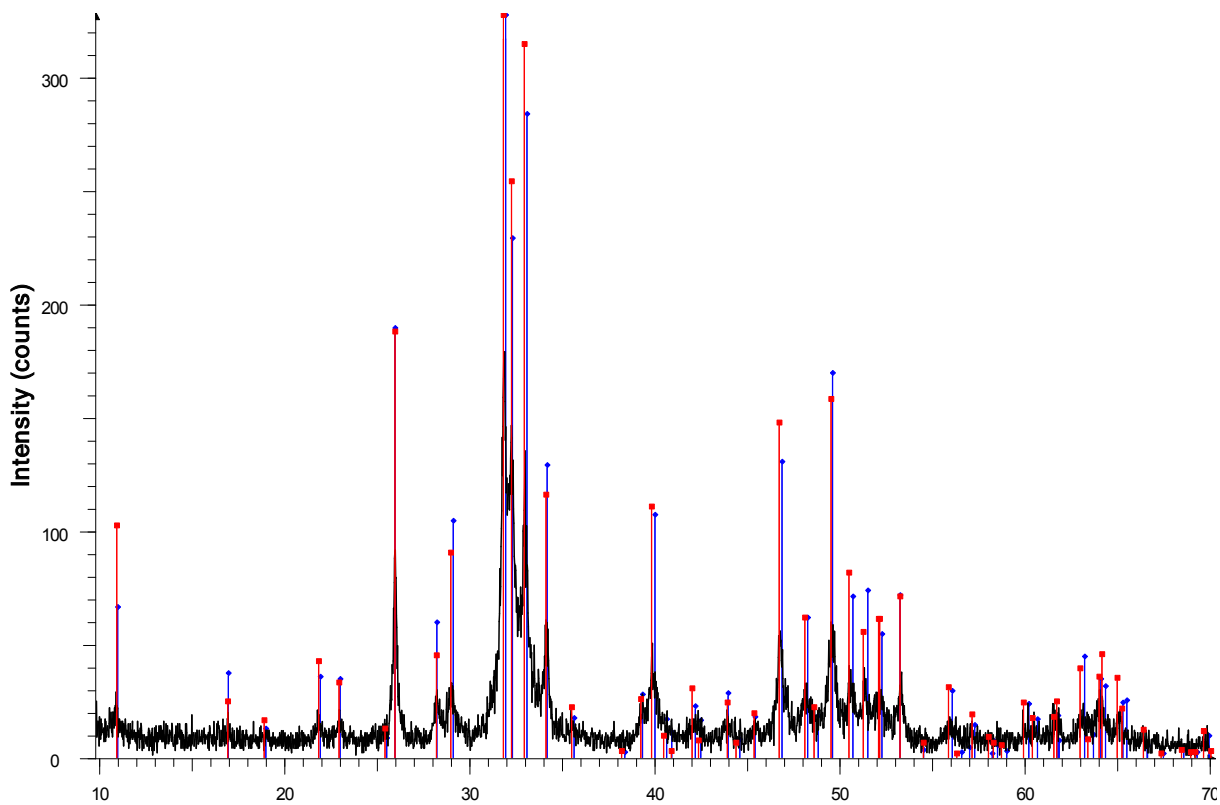
System: Hexagonal

Space group: P63/m (176)

Cell param.: Initial Final

a: 9.37276 9.40032

c: 6.87600 6.88159



2-Theta - Scale

75HA (small)-25HA (big) - File: 75HA (small)-25HA (big).raw - Type: 2Th/Th locked - Start: 4.984 ° - End: 69.987 ° - Step: 0.020 ° - Step time: 1. s - Anode: Cu - WL1: 1.5406 - WL2: 1.54439 - C
 04-010-6315 (A) - hydroxylapatite, syn - Ca5(PO4)3(OH) - WL: 1.5406 - Hexagonal - a 9.42264 - b 9.42264 - c 6.87535 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63/m (176) -
 01-086-0740 (A) - Hydroxylapatite - Ca5(PO4)3(OH) - WL: 1.5406 - Hexagonal - a 9.38193 - b 9.38193 - c 6.87481 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63/m (176) - 2 -

75HA (small)-25HA (big)

Sample name: 25HA (big)-75HA (small)

Concentrations:

04-010-6315	39.8%	Ca5(PO4)3(OH)	Hydroxylapatite, syn
01-086-0740	60.2%	Ca5(PO4)3(OH)	Hydroxylapatite

04-010-6315 Hydroxylapatite, syn----- Ca5(PO4)3(OH)

Crystallite Size (Scherrer): 402.0 A

System: Hexagonal

Space group: P63/m (176)

Cell param.: Initial Final

a: 9.42319 9.42264

c: 6.87903 6.87535

01-086-0740 Hydroxylapatite----- Ca5(PO4)3(OH)

Crystallite Size (Scherrer): 115.0 A

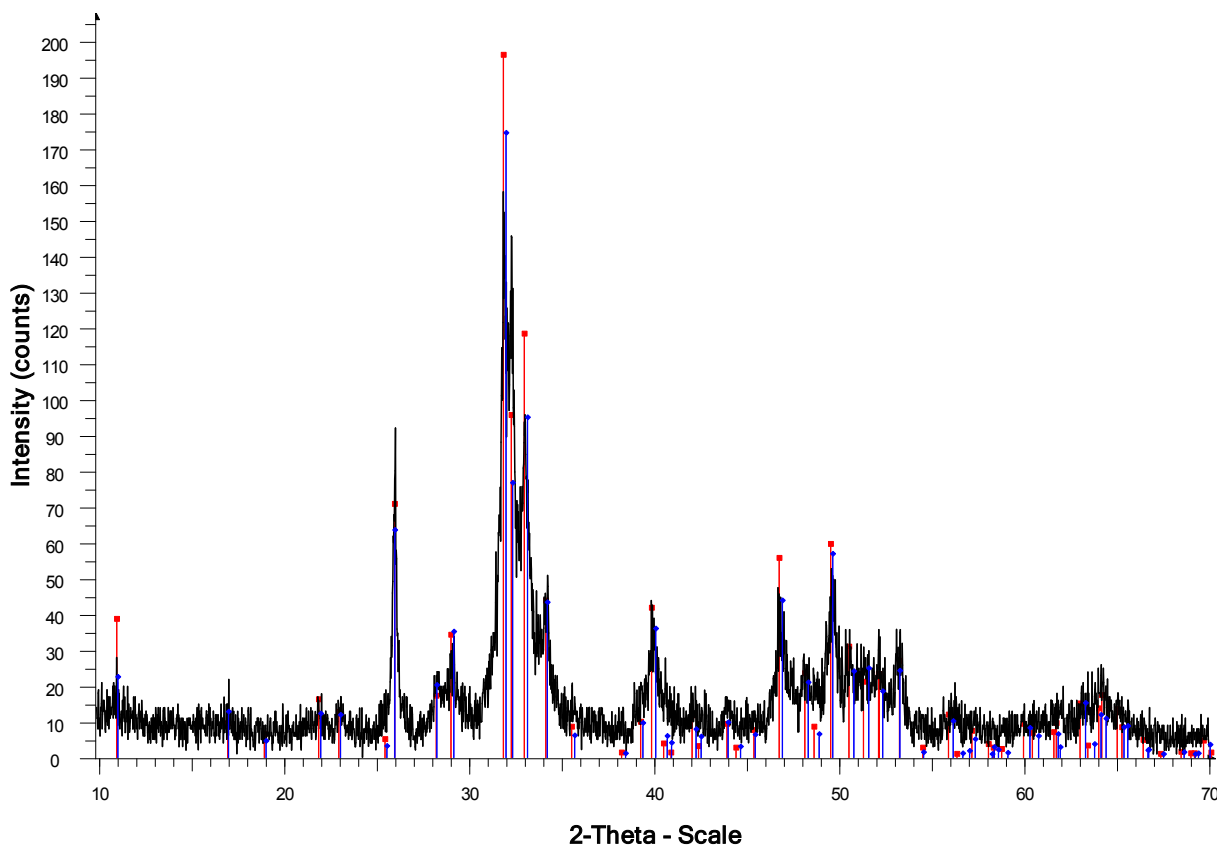
System: Hexagonal

Space group: P63/m (176)

Cell param.: Initial Final

a: 9.35200 9.38193

c: 6.88200 6.87481



90HA (small)-10HA (big) - File: 90HA (small)-10HA (big).raw - Type: 2Th/Th locked - Start: 4.989 ° - End: 69.991 ° - Step: 0.020 ° - Step time: 1. s - Anode: Cu - WL1: 1.5406 - WL2: 1.54439 - C
 04-010-6315 (A) - hydroxylapatite, syn - Ca₅(PO₄)₃(OH) - WL: 1.5406 - Hexagonal - a 9.42183 - b 9.42183 - c 6.87844 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63/m (176) -
 01-086-0740 (A) - Hydroxylapatite - Ca₅(PO₄)₃(OH) - WL: 1.5406 - Hexagonal - a 9.37276 - b 9.37276 - c 6.87600 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63/m (176) - 2 -

90HA (small)-10HA (big)

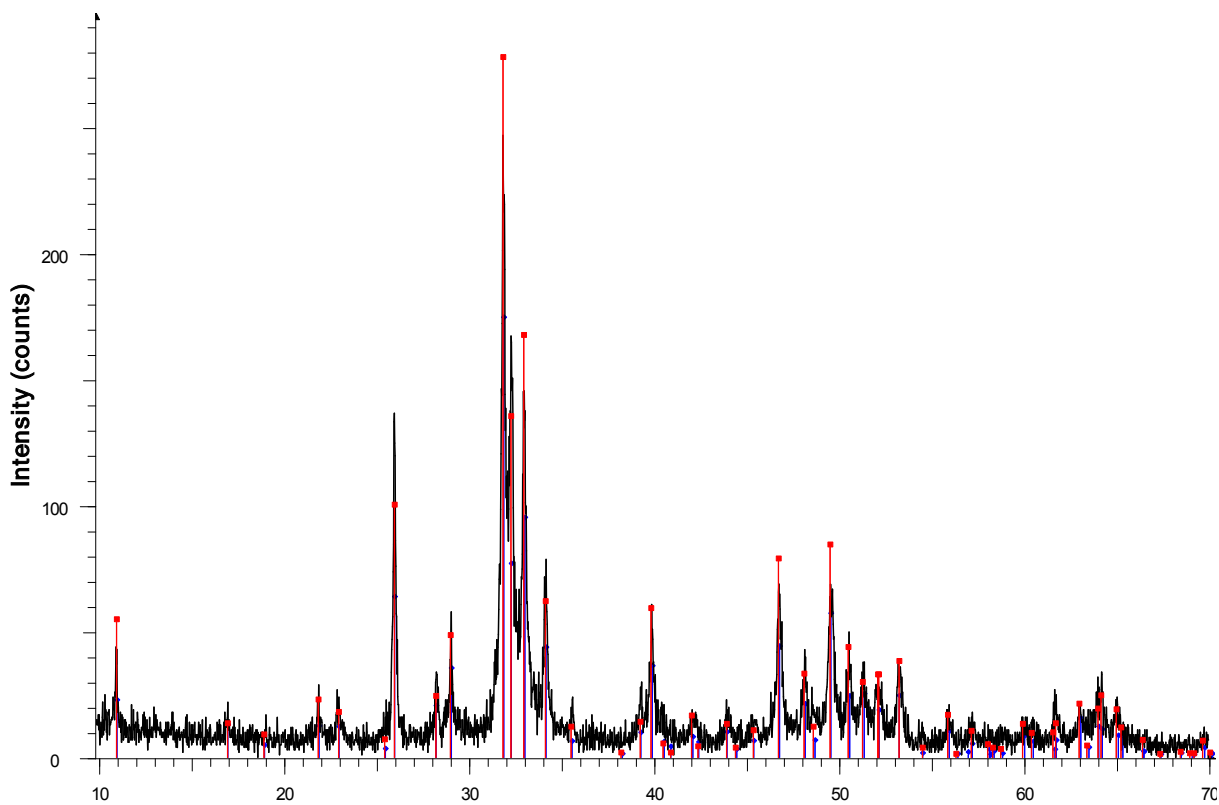
Sample name: 10HA (big)-90HA (small)

Concentrations:

04-010-6315	25.8%	Ca ₅ (PO ₄) ₃ (OH)	Hydroxylapatite, syn
01-086-0740	74.2%	Ca ₅ (PO ₄) ₃ (OH)	Hydroxylapatite

04-010-6315	Hydroxylapatite, syn-----	Ca ₅ (PO ₄) ₃ (OH)
Crystallite Size (Scherrer):	427.2	Å
System:	Hexagonal	
Space group:	P63/m (176)	
Cell param.:	Initial	Final
a:	9.42264	9.42183
c:	6.87535	6.87844

01-086-0740	Hydroxylapatite-----	Ca ₅ (PO ₄) ₃ (OH)
Crystallite Size (Scherrer):	101.4	Å
System:	Hexagonal	
Space group:	P63/m (176)	
Cell param.:	Initial	Final
a:	9.38193	9.37276
c:	6.87481	6.87600



50HA (small)-50HA (big) - File: 50HA (small)-50HA (big).raw - Type: 2Th/Th locked - Start: 5.005 ° - End: 70.004 ° - Step: 0.020 ° - Step time: 1. s - Anode: Cu - WL1: 1.5406 - WL2: 1.54439 - C
 04-010-6315 (A) - hydroxylapatite, syn - Ca₅(PO₄)₃(OH) - WL: 1.5406 - Hexagonal - a 9.42451 - b 9.42451 - c 6.87783 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63/m (176) -
 01-086-0740 (A) - Hydroxylapatite - Ca₅(PO₄)₃(OH) - WL: 1.5406 - Hexagonal - a 9.40909 - b 9.40909 - c 6.87724 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - P63/m (176) - 2 -

50HA (small)-50HA (big)

Sample name: 50HA (big)-50HA (small)

Concentrations:

04-010-6315	42.6%	Ca ₅ (PO ₄) ₃ (OH)	Hydroxylapatite, syn
01-086-0740	57.4%	Ca ₅ (PO ₄) ₃ (OH)	Hydroxylapatite

04-010-6315	Hydroxylapatite, syn-----	Ca ₅ (PO ₄) ₃ (OH)
Crystallite Size (Scherrer):	648.7	Å
System:	Hexagonal	
Space group:	P63/m (176)	
Cell param.:	Initial	Final
a:	9.41931	9.42451
c:	6.87414	6.87783

01-086-0740	Hydroxylapatite-----	Ca ₅ (PO ₄) ₃ (OH)
Crystallite Size (Scherrer):	153.5	Å
System:	Hexagonal	
Space group:	P63/m (176)	
Cell param.:	Initial	Final
a:	9.40032	9.40909
c:	6.88159	6.87724