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X-Ray Diffraction

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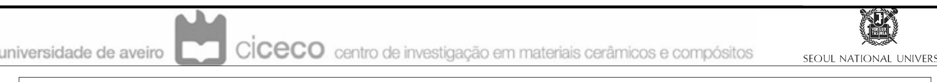
The atoms in a crystal are a periodic array of coherent scatterers and thus can diffract light.

- Diffraction occurs when each object in a periodic array scatters radiation coherently, producing concerted constructive interference at specific angles.
- The **electrons** in an atom coherently scatter light.
  - The electrons interact with the oscillating electric field of the light wave.
- Atoms in a crystal form a periodic array of coherent scatterers.
  - The wavelength of X-rays are similar to the distance between atoms.
  - Diffraction from different planes of atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal
- X-Rays are also reflected, scattered incoherently, absorbed, refracted, and transmitted when they interact with matter.



XRD can be used to determine:

- Phase Composition of a Sample
  - Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities
- Unit cell lattice parameters and Bravais lattice symmetry
  - Index peak positions
  - Lattice parameters can vary as a function of, and therefore give you information about, alloying, doping, solid solutions, strains, etc.
- Residual Strain (macrostrain)
- Crystal Structure
  - By Rietveld refinement of the entire diffraction pattern
- Epitaxy/Texture/Orientation
- Crystallite Size and Microstrain
  - Indicated by peak broadening
  - Other defects (stacking faults, etc.) can be measured by analysis of peak shapes and peak width

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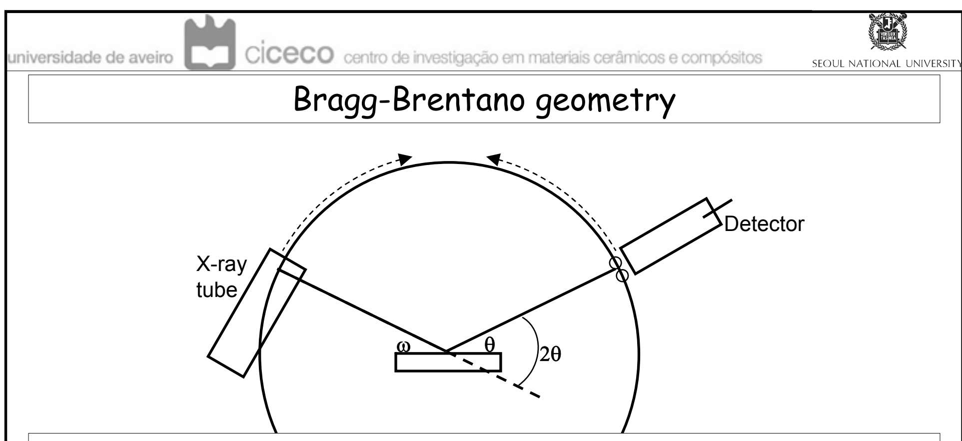
Bragg-Brentano geometry



- The incident angle, ω, is defined between the X-ray source and the sample.
- The diffracted angle, 2θ, is defined between the incident beam and the detector angle.
- The incident angle ω is always ½ of the detector angle 2θ .
- In a θ:2θ instrument (e.g. Rigaku RU300), the tube is fixed, the sample rotates at θ °/min and the detector rotates at 2θ °/min.
- In a θ:θ instrument (e.g. PANalytical X'Pert Pro), the sample is fixed and the tube rotates at a rate -θ °/min and the detector rotates at a rate of θ °/min.

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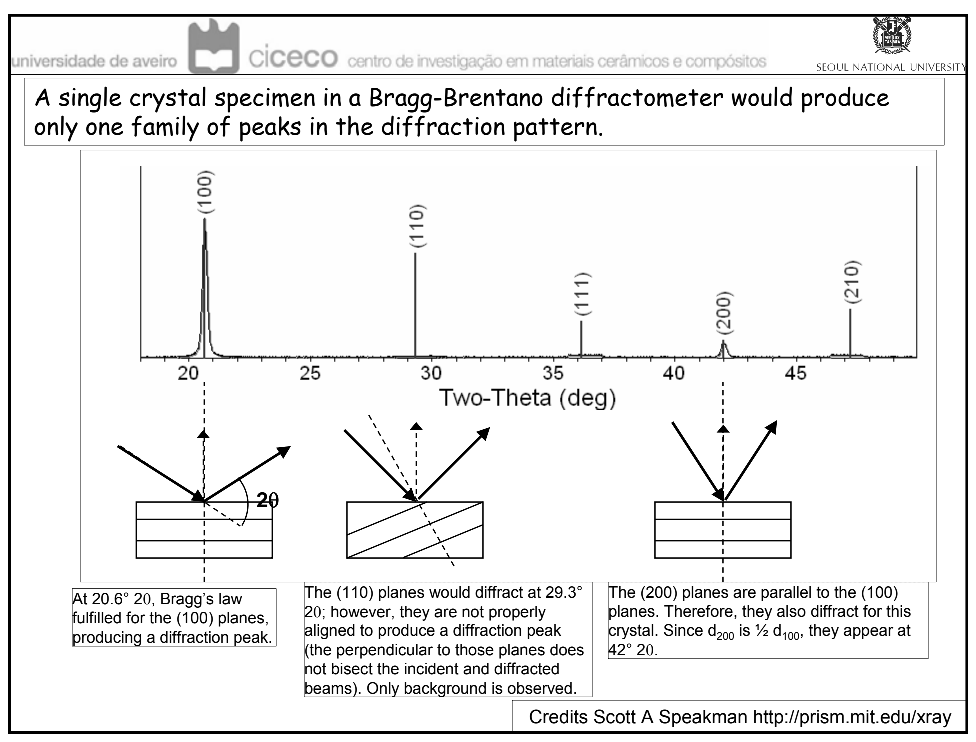
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A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.
(100)
(110)
(111)
(200)
(210)
20
25
30
35
40
45
Two-Theta (deg)
2θ
At 20.6° 2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.
The (110) planes would diffract at 29.3° 2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.
The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d200 is ½ d100, they appear at 42° 2θ.
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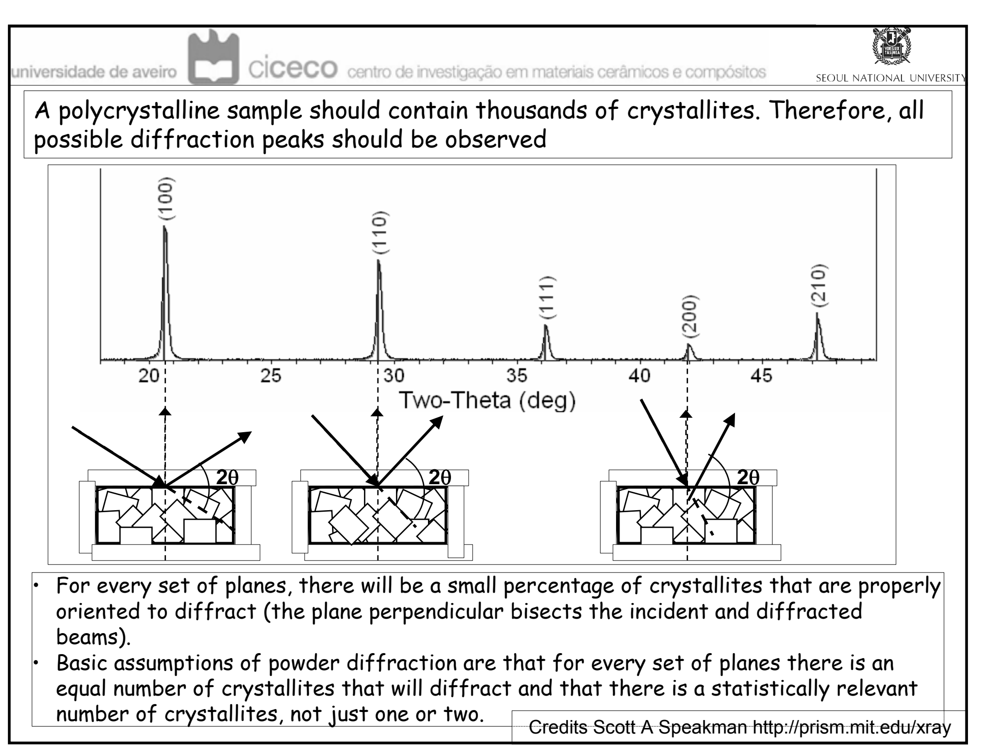
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A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed
(100)
(110)
(111)
(200)
(210)
20
25
30
35
40
45
Two-Theta (deg)
2θ
2θ
2θ
• For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
• Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.
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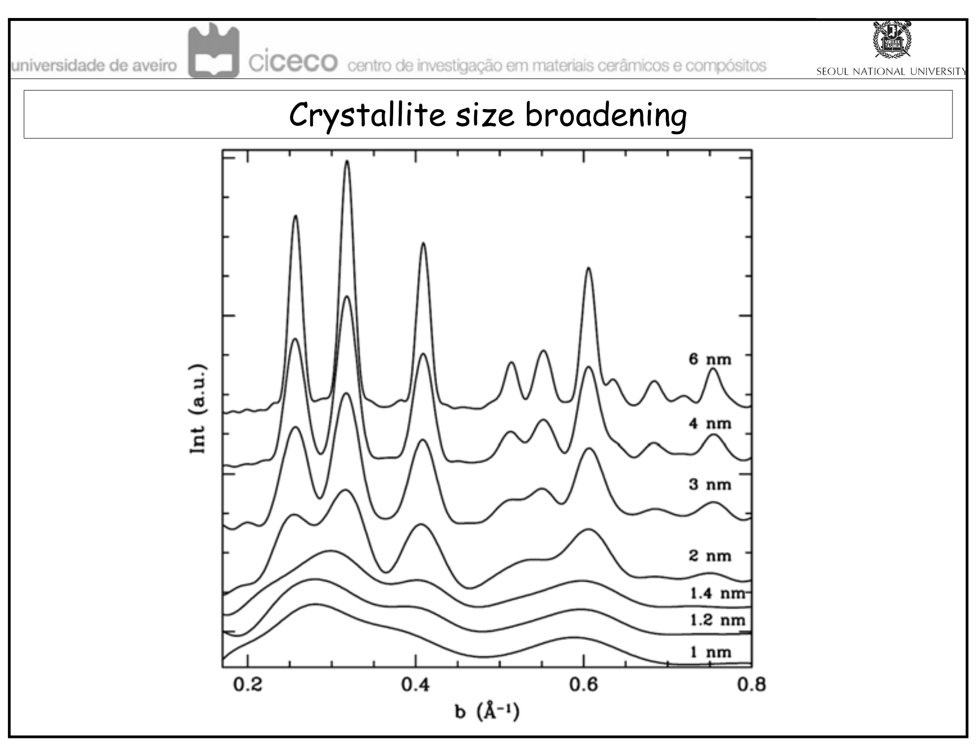
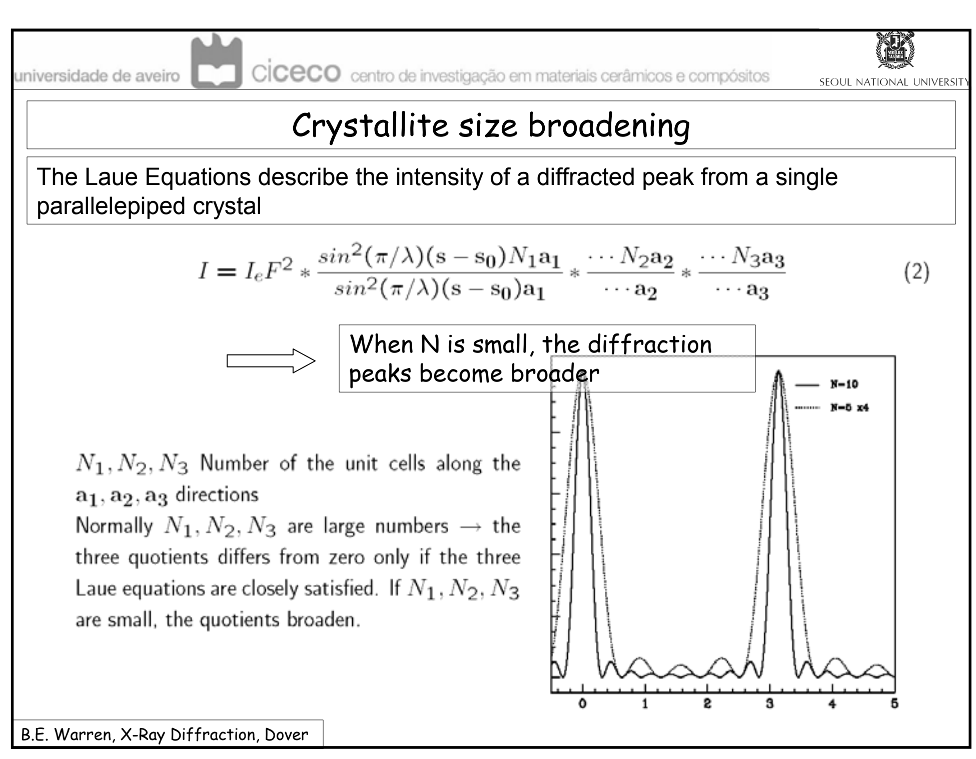
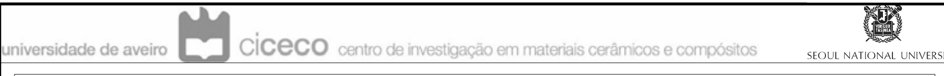




$$I = I_e F^2 * \frac{sin^2(\pi/\lambda)(\mathrm{s}-\mathrm{s}_0)N_1\mathrm{a}_1}{sin^2(\pi/\lambda)(\mathrm{s}-\mathrm{s}_0)\mathrm{a}_1} * \frac{\cdots N_2\mathrm{a}_2}{\cdots \mathrm{a}_2} * \frac{\cdots N_3\mathrm{a}_3}{\cdots \mathrm{a}_3} \quad (2)$$

N_1, N_2, N_3 Number of the unit cells along the $\mathrm{a}_1, \mathrm{a}_2, \mathrm{a}_3$ directions
Normally N_1, N_2, N_3 are large numbers $\rightarrow$ the three quotients differs from zero only if the three Laue equations are closely satisfied. If N_1, N_2, N_3 are small, the quotients broaden.



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Many factors may contribute to the observed peak profile

- Instrumental Peak Profile
- Crystallite Size
- Microstrain
  - Non-uniform Lattice Distortions
  - Faulting
  - Dislocations
  - Antiphase Domain Boundaries
  - Grain Surface Relaxation
- Solid Solution Inhomogeneity
- Temperature Factors

- ***The peak profile is a convolution of the profiles from all of these contributions***

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Scherrer Equation

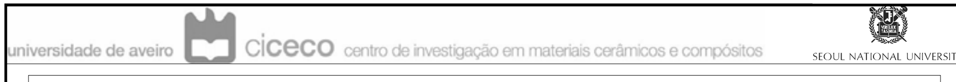
Approximations:
1) The shape of the crystal is well defined (cubic, spherical, etc.)
2) Crystal free from strains and defects! peak broadening is only due to the small crystallite size
3) The system is monodisperse.

$$B(2\theta) = \frac{K\ \lambda}{L\ cos\theta}$$

$B(2\theta)$: full width in radians at half maximum intensity of the powder pattern peak.
L: cube edge dimension
K: constant which depends on the particle morphology and how the peak width is determined

$$K = 2\ [(ln\ 2)/\pi]^{1/2} = 0.94$$

Even though the Scherrer equation should be applied for isotropic crystals only, it can be used for anisotropic materials, with acceptable results, if for each *hkl*-reflection the *L* value is interpreted as an average crystal dimension perpendicular to the reflecting plane



The Scherrer Constant, K

- The constant of proportionality, K (the Scherrer constant) depends on the how the width is determined, the shape of the crystal, and the size distribution
  - the most common values for K are:
    - 0.94 for FWHM of spherical crystals with cubic symmetry
    - 0.89 for integral breadth of spherical crystals w/ cubic symmetry
    - 1, because 0.94 and 0.89 both round up to 1
  - K actually varies from 0.62 to 2.08
- For an excellent discussion of K, refer to JI Langford and AJC Wilson, "Scherrer after sixty years: A survey and some new results in the determination of crystallite size," *J. Appl. Cryst.* **11** (1978) p102-113.

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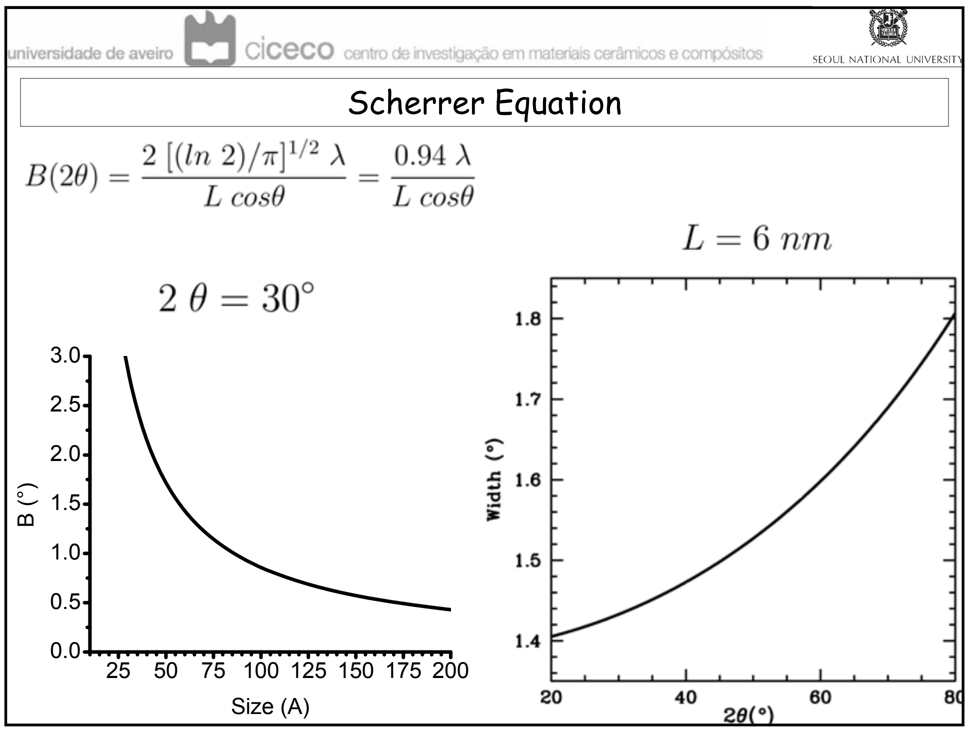

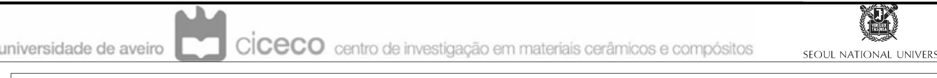

Crystallite size broadening

- Peak Width due to crystallite size varies inversely with crystallite size
  - as the crystallite size gets smaller, the peak gets broader
- The peak width varies with 2θ as 1/cos θ
  - The crystallite size broadening is most pronounced at large angles 2theta
    - However, the instrumental profile width and microstrain broadening are also largest at large angles 2theta
    - Peak intensity is usually weakest at larger angles 2theta
  - If using a single peak, often get better results from using diffraction peaks between 30 and 50 deg 2theta
    - below 30deg 2theta, peak asymmetry compromises profile analysis

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Crystallite Shape

- Although the shape of crystallites is usually irregular, we can often approximate them as:
  - sphere, cube, tetrahedra, or octahedra
  - parallelepipeds such as needles or plates
  - prisms or cylinders
- Most applications of Scherrer analysis assume spherical crystallite shapes
- If we know the average crystallite shape from another analysis, we can select the proper value for the Scherrer constant K
- Anisotropic peak shapes can be identified by anisotropic peak broadening
  - if the dimensions of a crystallite are 2x * 2y * 200z, then (h00) and (0k0) peaks will be more broadened than (00l) peaks.

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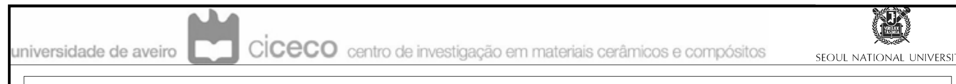


Debye Scattering Equation

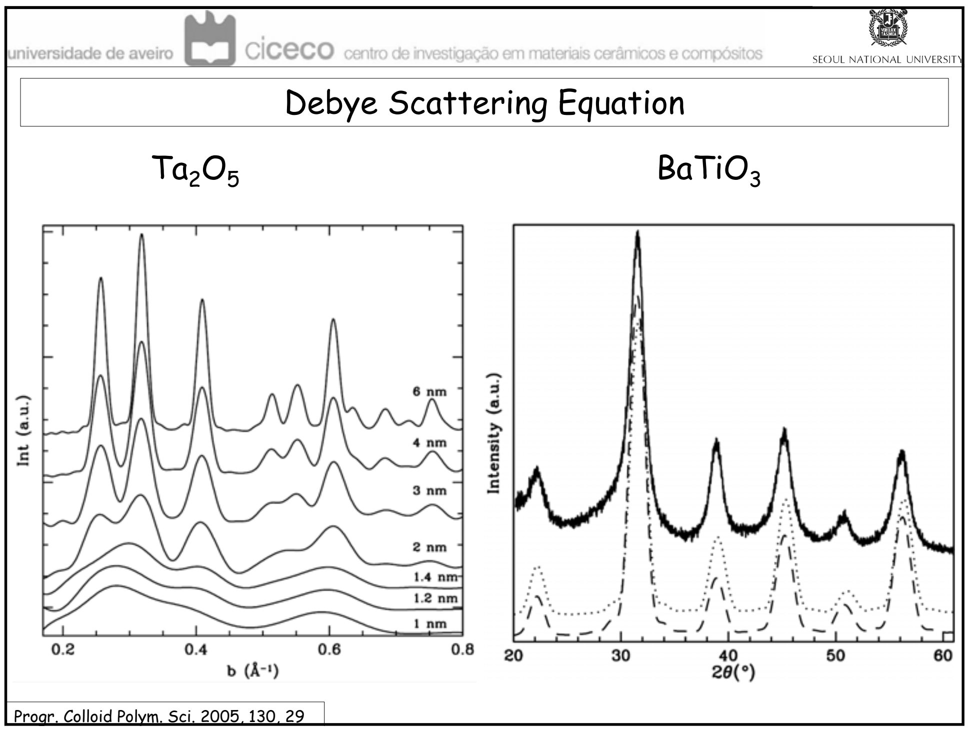
The intensity distribution spherical averaged over the reciprocal space is descibed by the Debye formula:

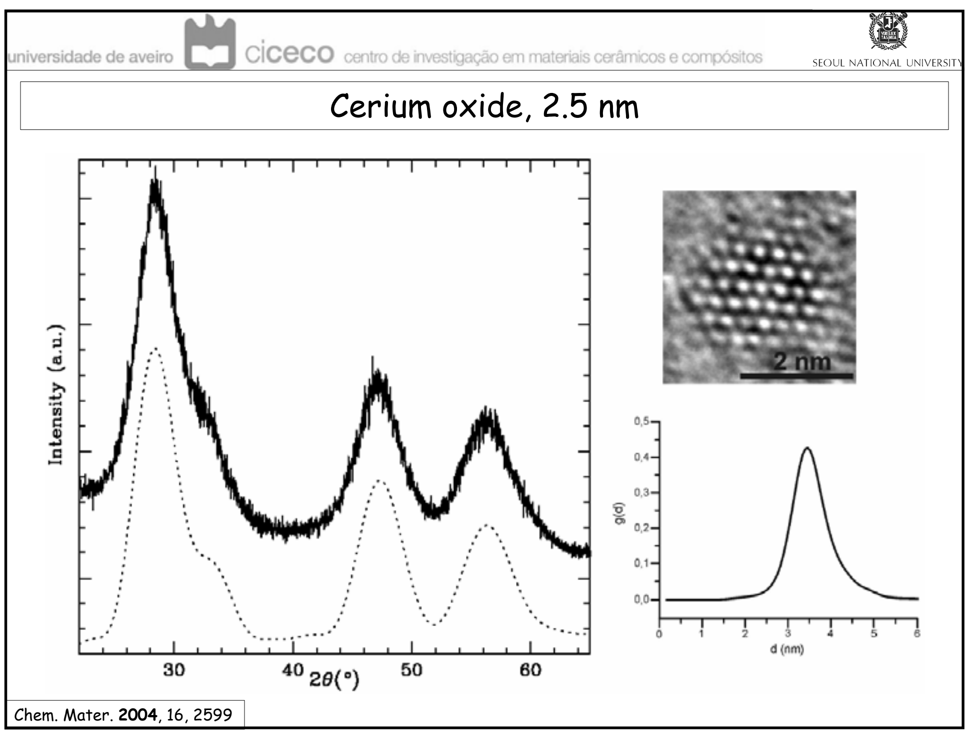
$$I_N(b) = \sum_{n,m\neq n}^{N} f_n f_m \frac{sin(2\pi b r_{nm})}{2\pi b r_{nm}} \qquad (4)$$

$b = \frac{1}{d} = \frac{2sin\theta}{\lambda}$
r_{nm} distance between atom n, m
f_n, f_m atomic scattering factors

- General equation valid for any form of matter in which there is a random orientation: gases, liquids, amorphous solids, and crystalline powders.
- No limitation on the number of different kinds of atoms in the sample.
- The number of terms increases proportional to the sixth order!

B.E. Warren, X-Ray Diffraction, Dover - Cryst. Res. Technol. 1998, 33, 1141

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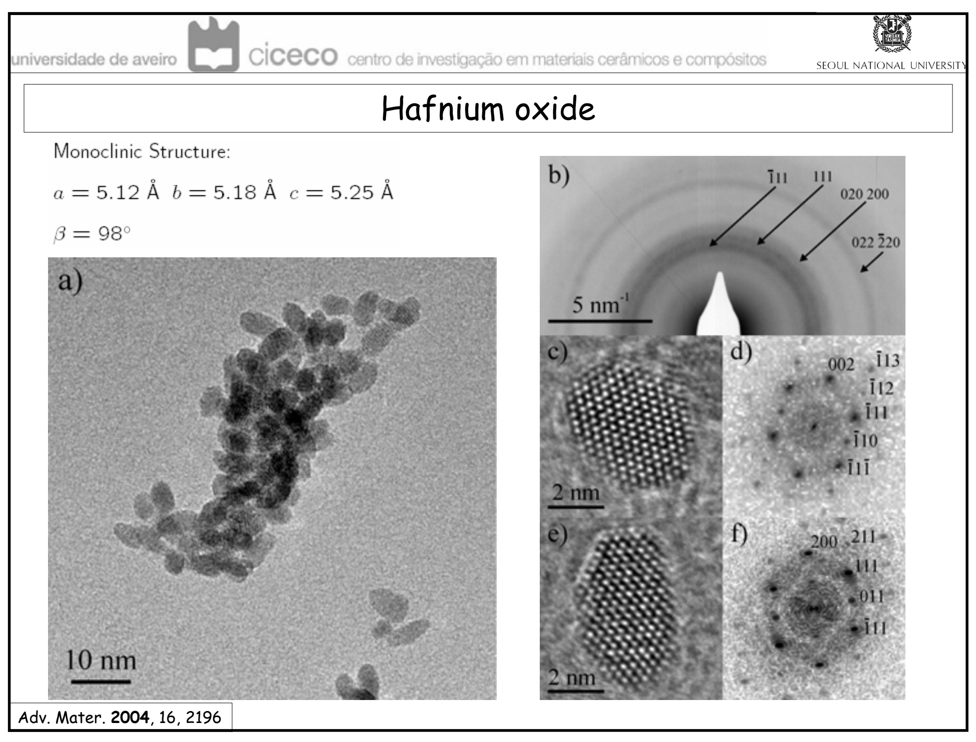
Cerium oxide, 2.5 nm
Intensity (a.u.)
30
40
2θ(°)
50
60
2 nm
g(d)
d (nm)
Chem. Mater. 2004, 16, 2599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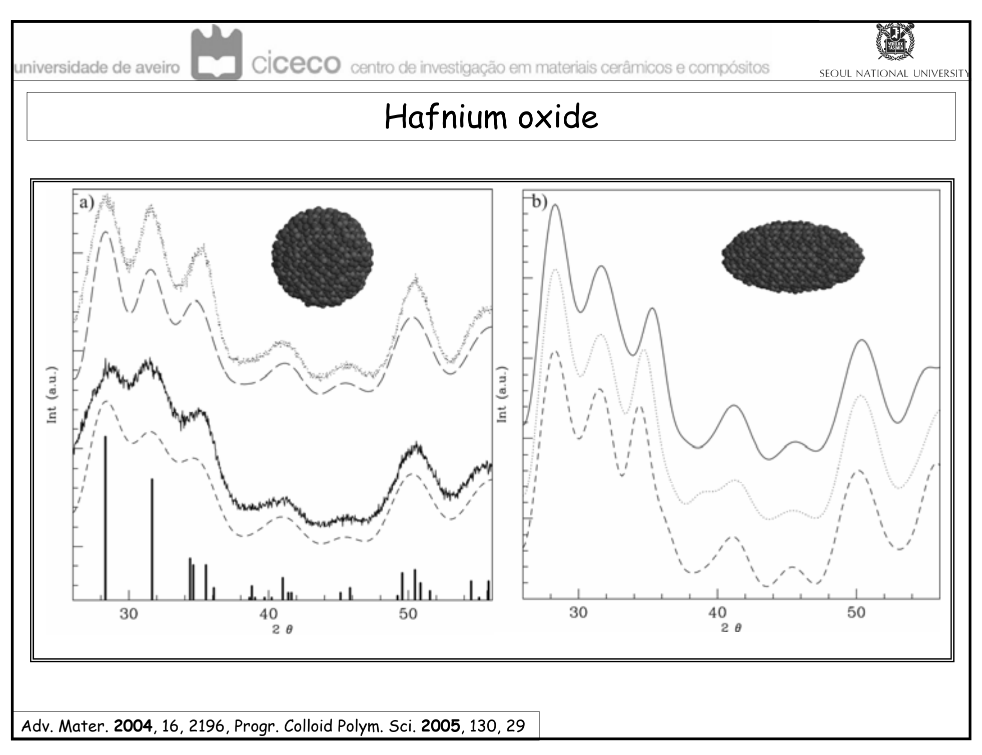
Hafnium oxide
Monoclinic Structure:
a = 5.12 Å b = 5.18 Å c = 5.25 Å
β = 98°
a)
10 nm
b)
5 nm-1
c)
2 nm
d)
e)
2 nm
f)
Adv. Mater. 2004, 16, 2196



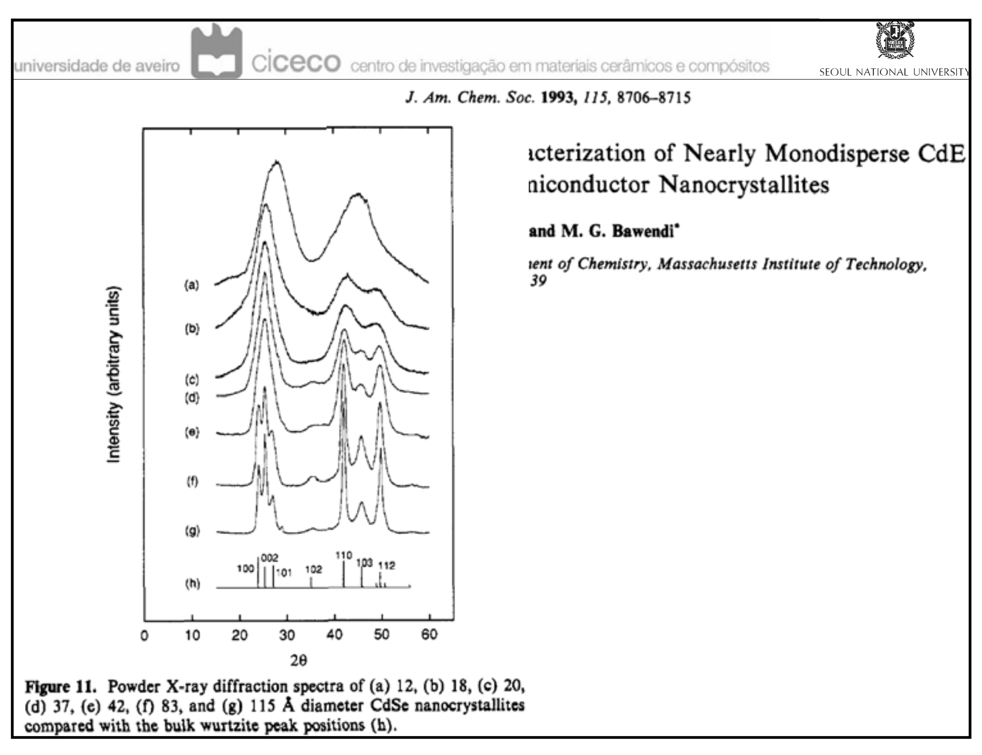


Figure 11. Powder X-ray diffraction spectra of (a) 12, (b) 18, (c) 20, (d) 37, (e) 42, (f) 83, and (g) 115 Å diameter CdSe nanocrystallites compared with the bulk wurtzite peak positions (h).

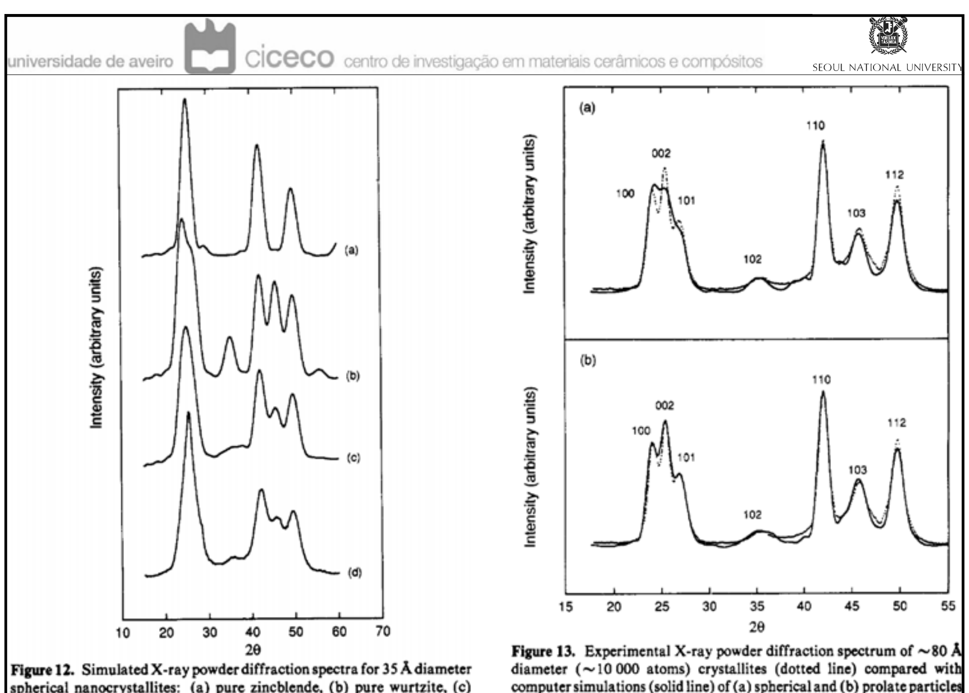
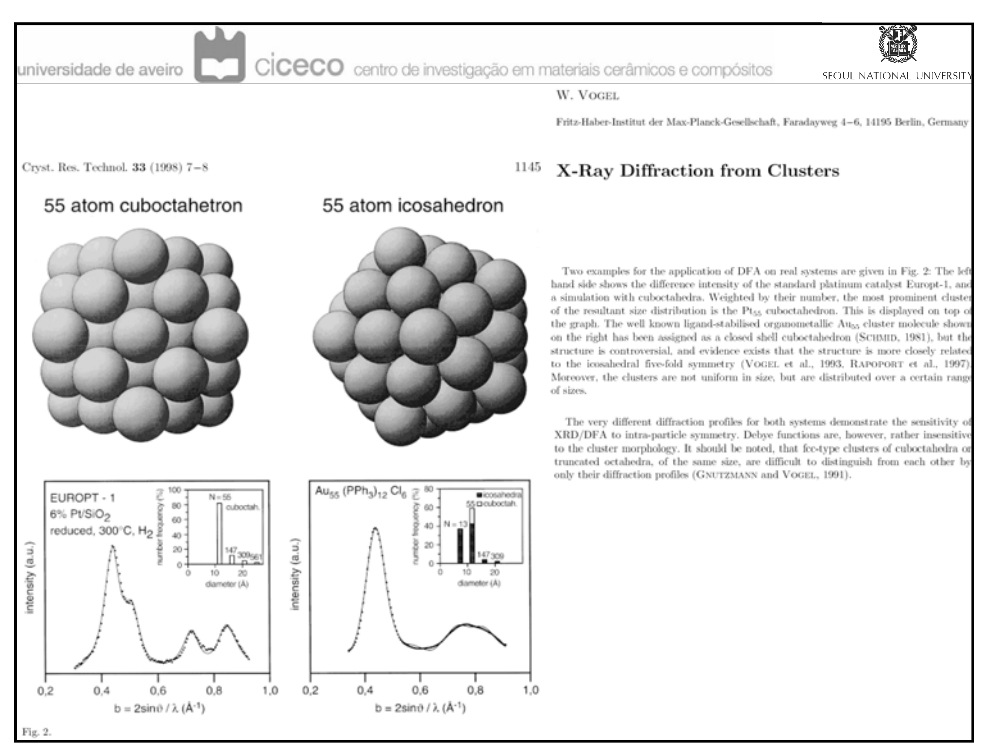


Figure 12. Simulated X-ray powder diffraction spectra for 35 Å diameter spherical nanocrystallites: (a) pure zincblende, (b) pure wurtzite, (c) wurtzite with one stacking fault. (d) Experimental powder spectrum of ~35 Å diameter crystallites.

Figure 13. Experimental X-ray powder diffraction spectrum of ~80 Å diameter (~10 000 atoms) crystallites (dotted line) compared with computer simulations (solid line) of (a) spherical and (b) prolate particles [aspect ratio of 1.3 along the (002) direction]. Three stacking faults on average and bulk lattice constants are used.



Cryst. Res. Technol. 33 (1998) 7–8 1145

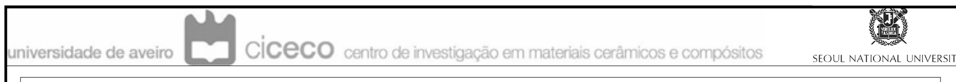
X-Ray Diffraction from Clusters

W. Vogel

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin, Germany

Two examples for the application of DFA on real systems are given in Fig. 2: The left hand side shows the difference intensity of the standard platinum catalyst Europt-1, and a simulation with cuboctahedra. Weighted by their number, the most prominent cluster of the resultant size distribution is the Pt_{55} cuboctahedron. This is displayed on top of the graph. The well known ligand-stabilised organometallic Au_{55} cluster molecule shown on the right has been assigned as a closed shell cuboctahedron (Schmid, 1981), but the structure is controversial, and evidence exists that the structure is more closely related to the icosahedral five-fold symmetry (Vogel et al., 1993, Rapoport et al., 1997). Moreover, the clusters are not uniform in size, but are distributed over a certain range of sizes.

The very different diffraction profiles for both systems demonstrate the sensitivity of XRD/DFA to intra-particle symmetry. Debye functions are, however, rather insensitive to the cluster morphology. It should be noted, that fcc-type clusters of cuboctahedra or truncated octahedra, of the same size, are difficult to distinguish from each other by only their diffraction profiles (Gnutzmann and Vogel, 1991).



The Rietveld Method

- The Rietveld method refines user-selected parameters to minimize the difference between an experimental pattern (observed data) and a model based on the hypothesized crystal structure and instrumental parameters (calculated pattern)

- Can refine information about a single crystal structure
  - confirm/disprove a hypothetical crystal structure
  - refine lattice parameters
  - refine atomic positions, fractional occupancy, and thermal parameter
- Refine information about a single sample
  - preferred orientation
- Refine information about a multiphase sample
  - determine the relative amounts of each phase

It Requires:
- High quality experimental diffraction pattern
- A structure model that makes physical and chemical sense
- Suitable peak and background functions

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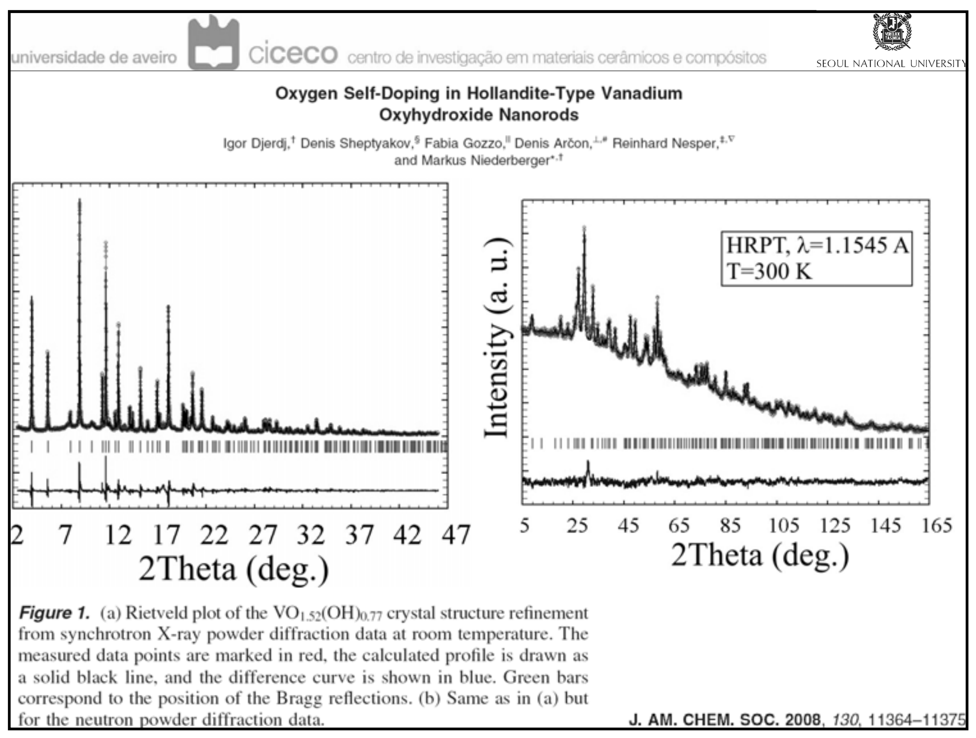

Figure 1. (a) Rietveld plot of the $VO_{1.52}(OH)_{0.77}$ crystal structure refinement from synchrotron X-ray powder diffraction data at room temperature. The measured data points are marked in red, the calculated profile is drawn as a solid black line, and the difference curve is shown in blue. Green bars correspond to the position of the Bragg reflections. (b) Same as in (a) but for the neutron powder diffraction data.

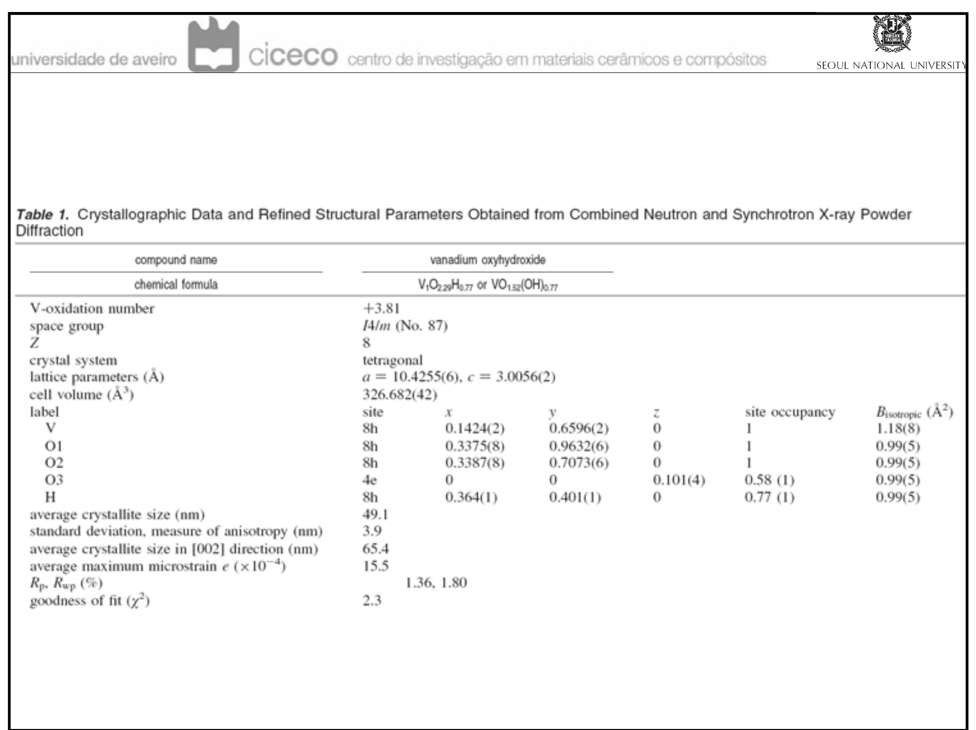

Table 1. Crystallographic Data and Refined Structural Parameters Obtained from Combined Neutron and Synchrotron X-ray Powder Diffraction

compound name	vanadium oxyhydroxide					
chemical formula	$V_1O_{2.29}H_{0.77}$ or $VO_{1.52}(OH)_{0.77}$					
V-oxidation number	+3.81					
space group	*I*4/*m* (No. 87)					
Z	8					
crystal system	tetragonal					
lattice parameters (Å)	a = 10.4255(6), c = 3.0056(2)					
cell volume (Å^3)	326.682(42)					
label	site	x	y	z	site occupancy	$B_{isotropic}$ (Å^2)
V	8h	0.1424(2)	0.6596(2)	0	1	1.18(8)
O1	8h	0.3375(8)	0.9632(6)	0	1	0.99(5)
O2	8h	0.3387(8)	0.7073(6)	0	1	0.99(5)
O3	4e	0	0	0.101(4)	0.58 (1)	0.99(5)
H	8h	0.364(1)	0.401(1)	0	0.77 (1)	0.99(5)
average crystallite size (nm)	49.1					
standard deviation, measure of anisotropy (nm)	3.9					
average crystallite size in [002] direction (nm)	65.4					
average maximum microstrain e ($\times10^{-4}$)	15.5					
R_p, R_{wp} (%)	1.36, 1.80					
goodness of fit (χ^2)	2.3					

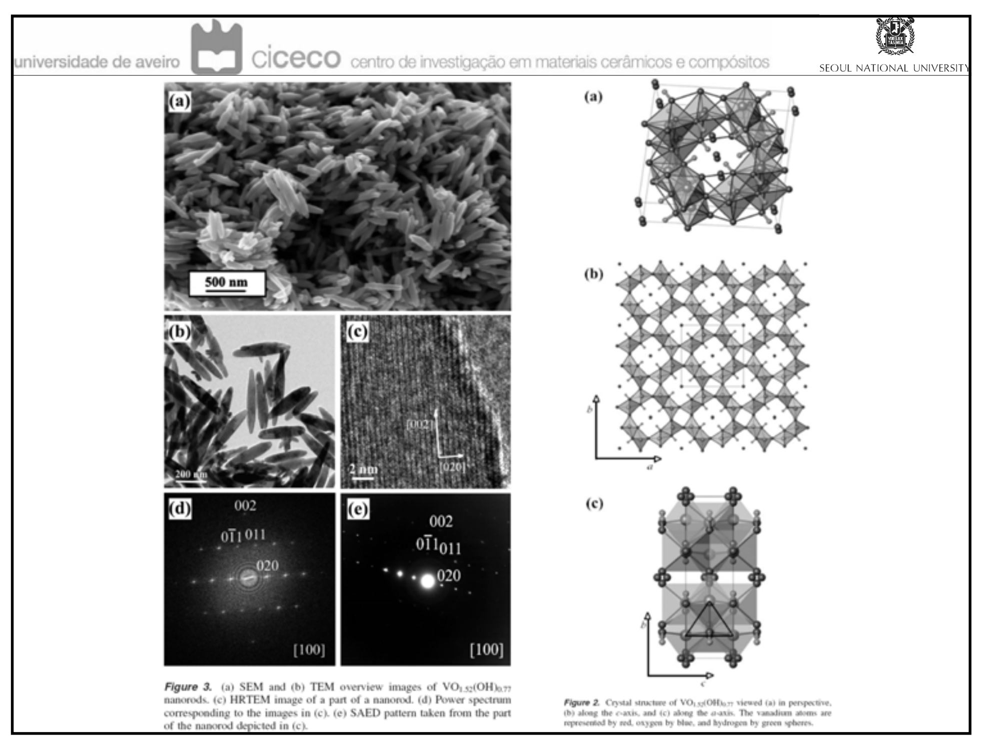

Figure 3. (a) SEM and (b) TEM overview images of $VO_{1.52}(OH)_{0.77}$ nanorods. (c) HRTEM image of a part of a nanorod. (d) Power spectrum corresponding to the images in (c). (e) SAED pattern taken from the part of the nanorod depicted in (c).

Figure 2. Crystal structure of $VO_{1.52}(OH)_{0.77}$ viewed (a) in perspective, (b) along the *c*-axis, and (c) along the *a*-axis. The vanadium atoms are represented by red, oxygen by blue, and hydrogen by green spheres.