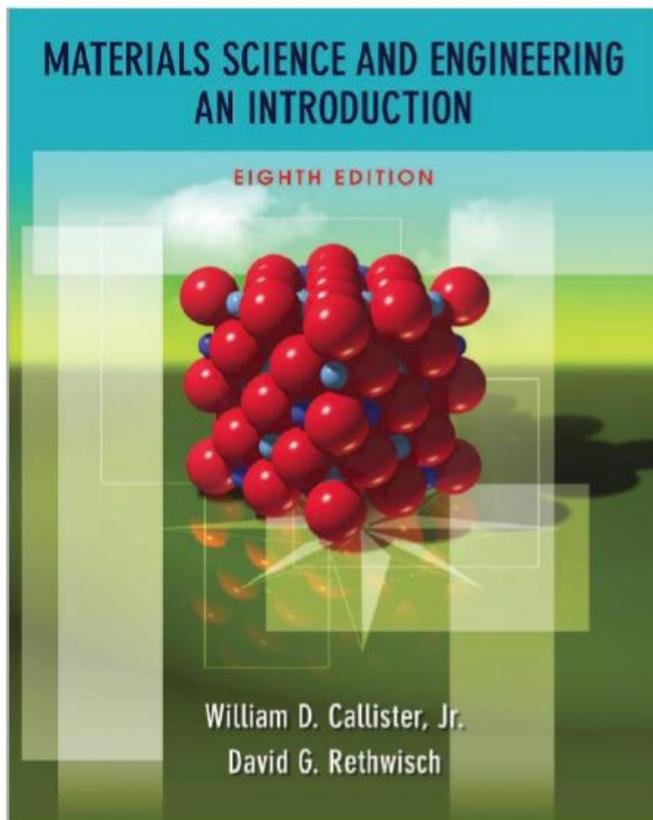
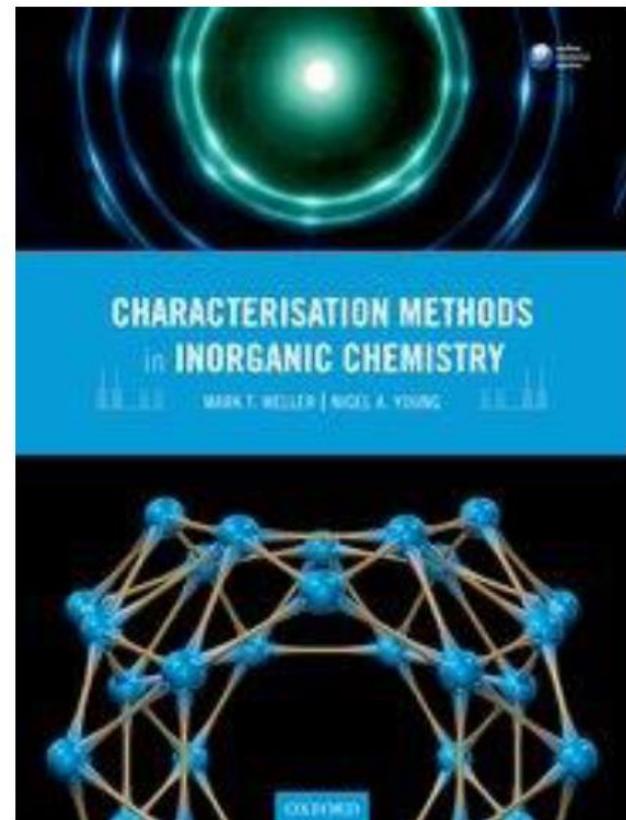


QFL 1655 – Estrutura Cristalina e DRX

William D. Callister Jr., David G. Rethwisch Materials Science and Engineering An Introduction, 8th Edition 2010



Caps. 3 e 12



Cap. 2

Definições

- Histórico
- Material cristalino
- Estrutura cristalina
- Cella unitária
- Rede

Histórico

- Johannes Kepler (1611): *Strena seu de nive sexangula*: a geometria hexagonal de flocos de neve seria consequência do empacotamento de partículas de água.
- Nicolas Streno (1669): os ângulos entre as faces de cristais do mesmo tipo são sempre iguais.
- René Just Haüy (1784): qualquer face de um cristal pode ser descrita por padrões simples de empacotamento de esferas de mesma forma e tamanho.
- William Hallowes Miller (1839): Atribuiu a cada face um nome único composto por três números inteiros (os índices de Miller)

Histórico

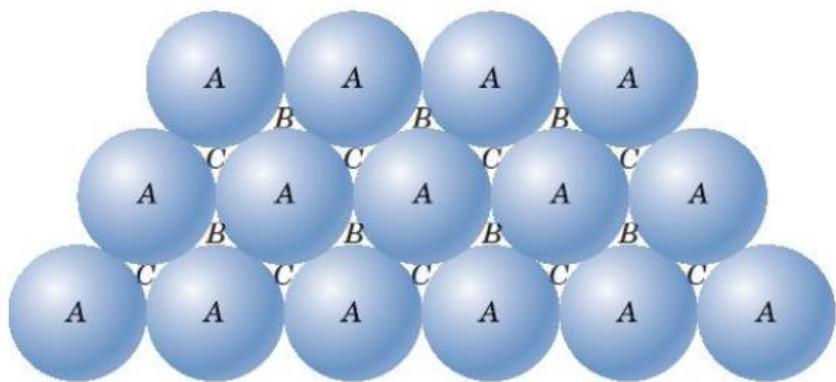
- Haüy: cristais são arranjos regulares tridimensionais (retículo de Bravais) de átomos e moléculas; uma cela unitária se repete infinitamente em três direções não necessariamente perpendiculares.
- Johan Hassel, Auguste Bravais, Evgrafov Fedorov, Arthur Schönflies e William Barlow (século 19): catalogaram as simetrias de todas as estruturas cristalinas possíveis.
- As estruturas de Barlow foram corretamente propostas e mais tarde confirmadas por cristalografia de raios X.
- Wilhelm Röntgen (1895): descoberta dos raios X. Seriam ondas ou partículas?

Histórico

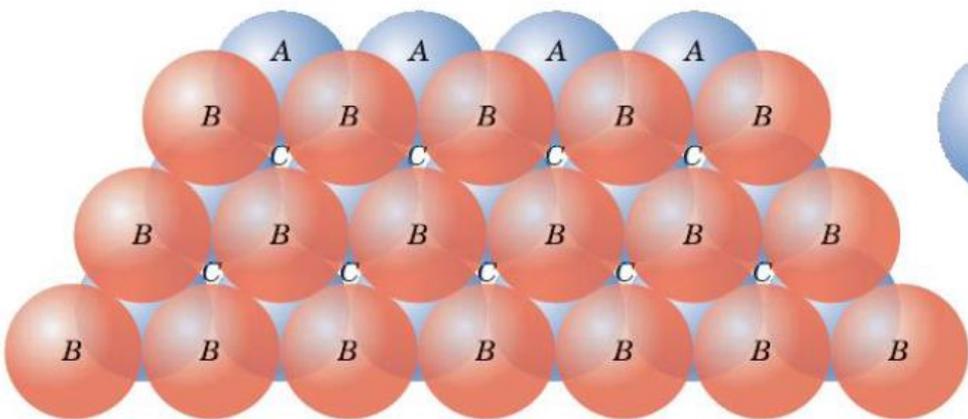
- Charles Glover Barkla: mostrou que os raios X exibiam propriedades de ondas eletromagnéticas – polarização transversa e linhas espectrais.
- Arnold Sommerfeld: raios X apresentam comprimento de onda de aproximadamente 1 \AA (0,1 nm).
- Albert Einstein (1905): efeito fotoelétrico
- Max Von Laue (1912): difração de raios X
- Arthur Compton (1922): espalhamento de raios X por elétrons
- William Henry Bragg (pai) e William Lawrence Bragg (filho) (1912-13): lei de Bragg, relacionando os espalhamentos a reflexões de planos espaçados regularmente. Prêmio Nobel de 1915.

Empacotamento de esferas

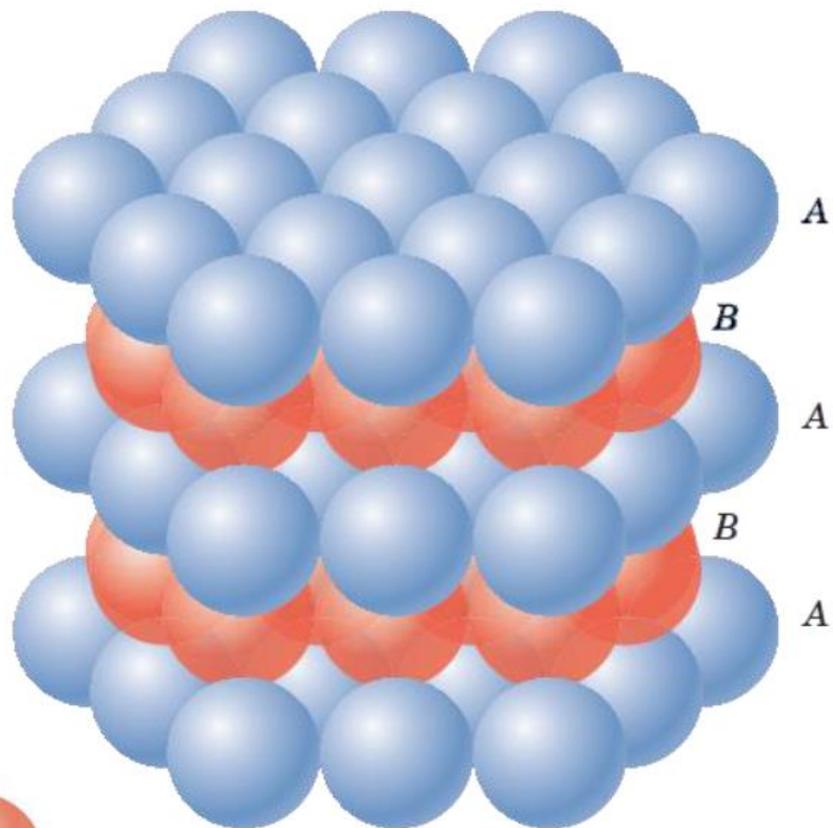
- Cúbico simples
- Hexagonal vs cúbico de face centrada

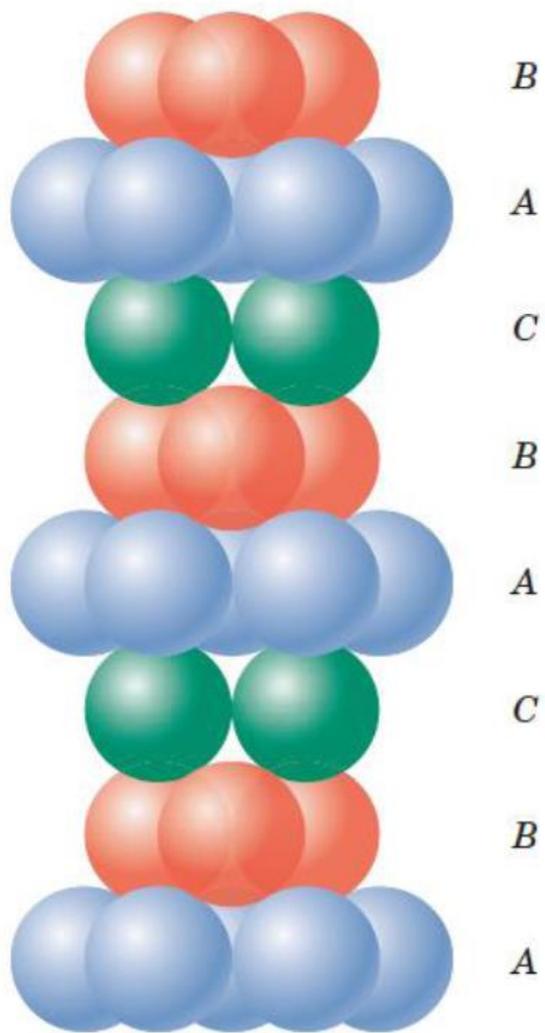


(a)

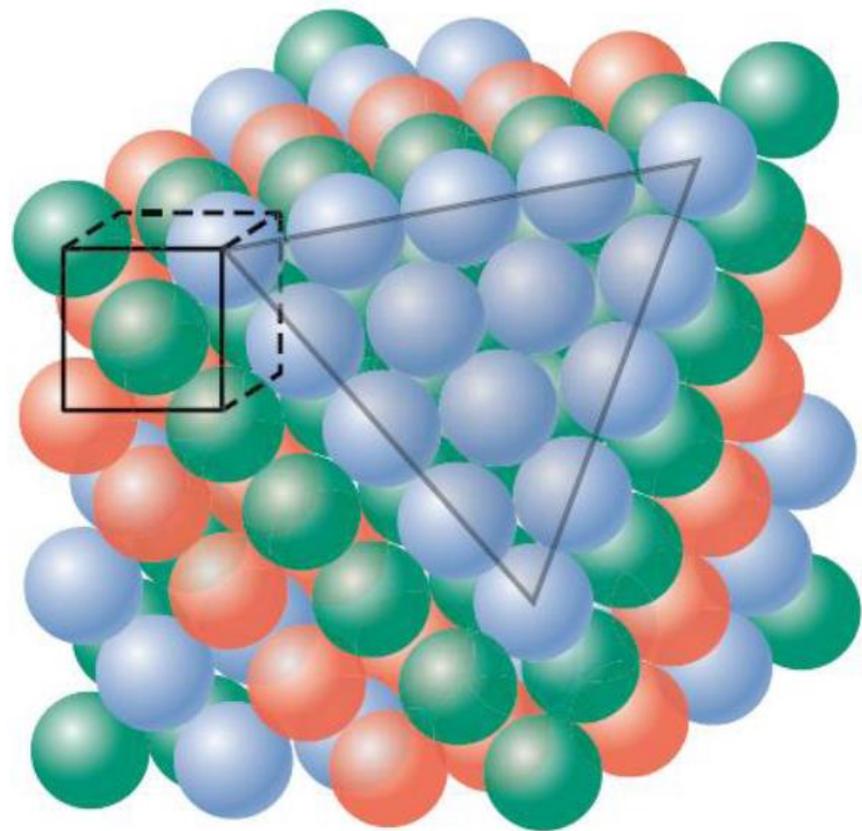


(b)

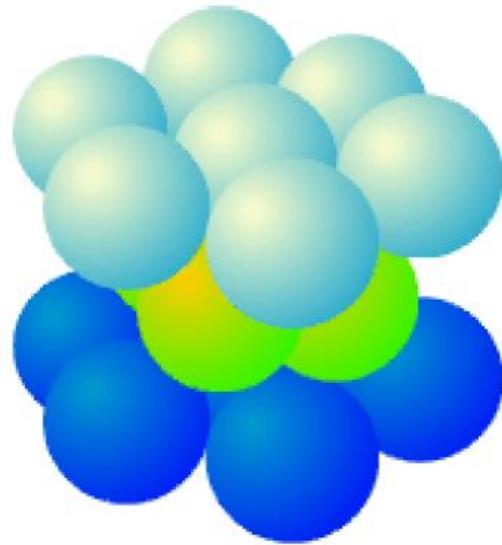




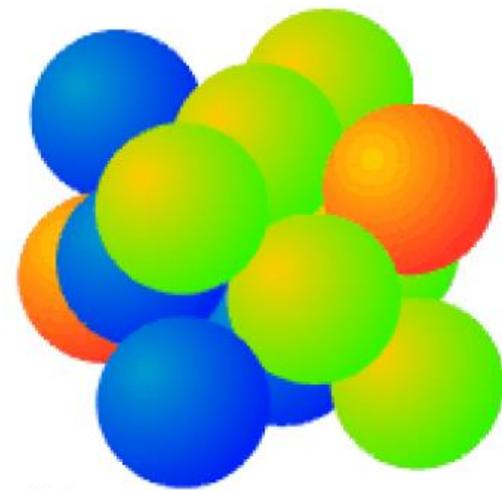
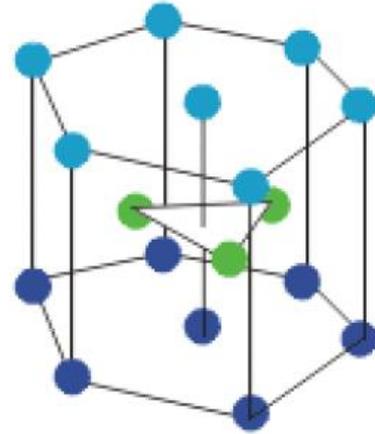
(a)



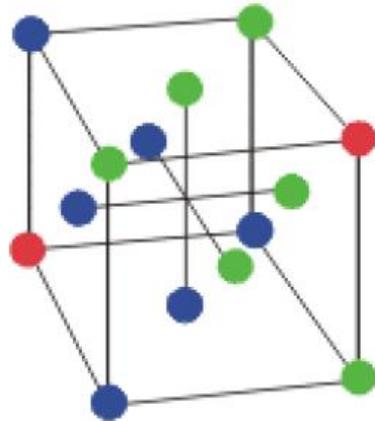
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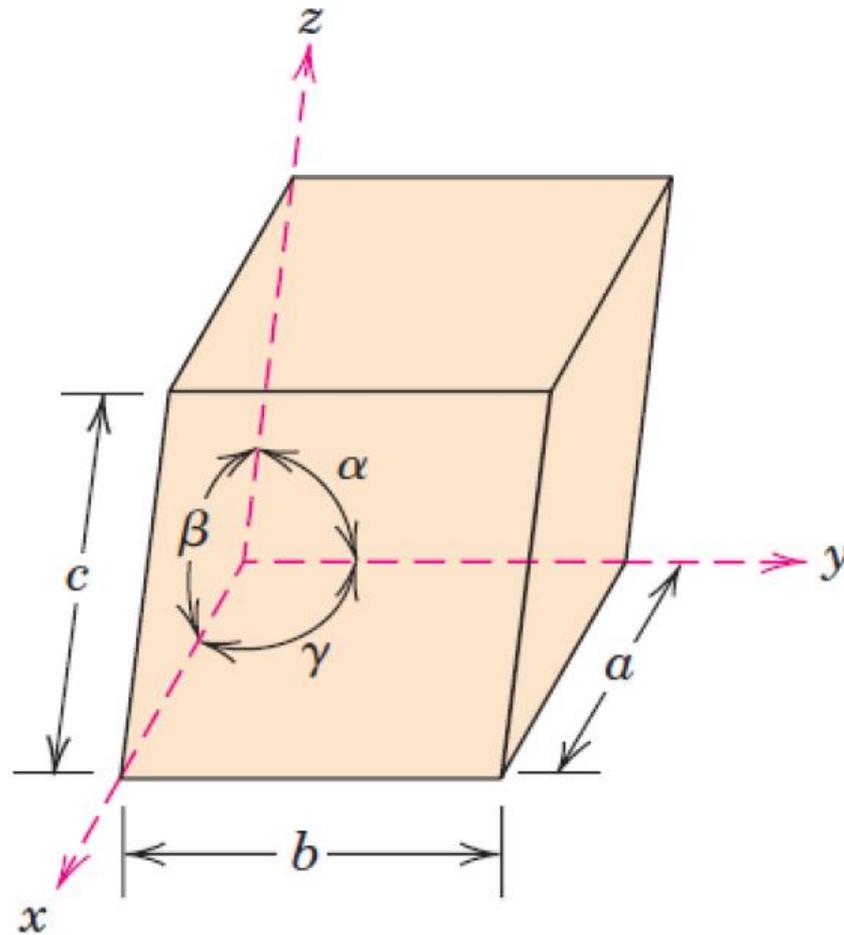
(a)

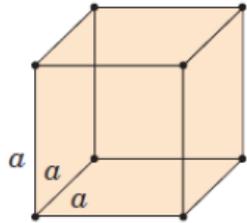
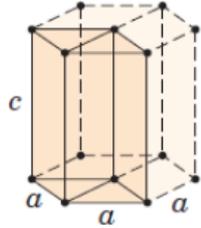
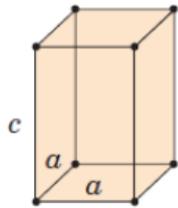
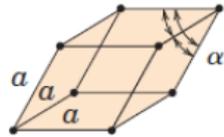


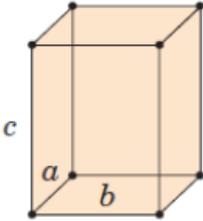
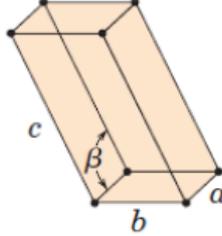
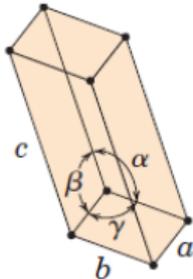
(b)



Sistemas Cristalinos



<i>Crystal System</i>	<i>Axial Relationships</i>	<i>Interaxial Angles</i>	<i>Unit Cell Geometry</i>
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	

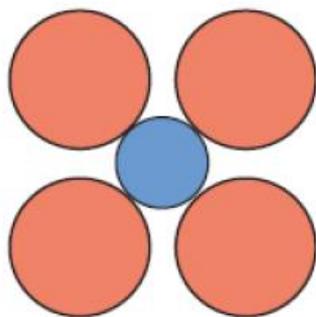
<i>Crystal System</i>	<i>Axial Relationships</i>	<i>Interaxial Angles</i>	<i>Unit Cell Geometry</i>
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

- Parâmetros de cela: $a, b, c; \alpha, \beta, \gamma$
- Coordenadas pontuais q, r, s
- Planos cristalográficos (h, k, l)

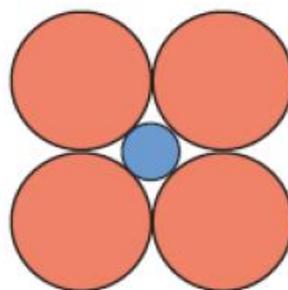
https://www.youtube.com/watch?v=4ZRTxQOJ_7U&t=25s

- Mas normalmente não temos apenas um tipo de átomo na estrutura.
- Como fica?

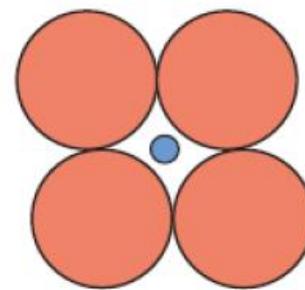
Relação de raios



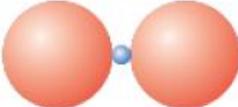
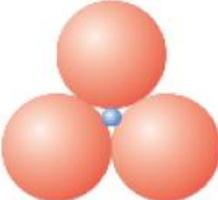
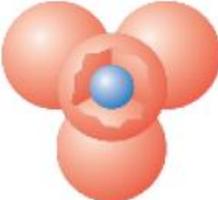
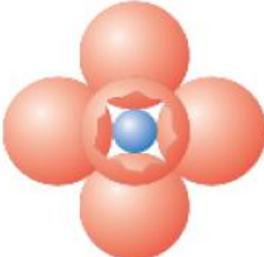
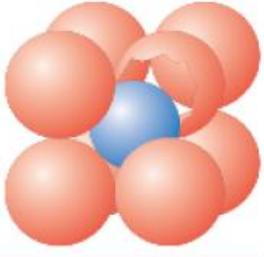
Stable



Stable



Unstable

<i>Coordination Number</i>	<i>Cation-Anion Radius Ratio</i>	<i>Coordination Geometry</i>
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

Source: W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

Alguns tipos de estruturas

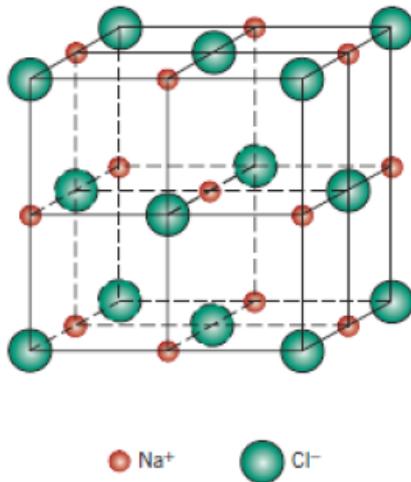


Figure 12.2 A unit cell for the rock salt, or sodium chloride (NaCl), crystal structure.

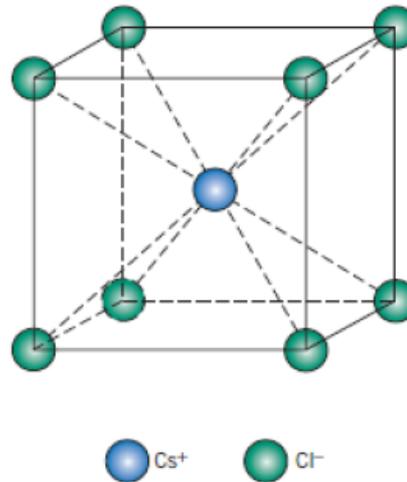


Figure 12.3 A unit cell for the cesium chloride (CsCl) crystal structure.

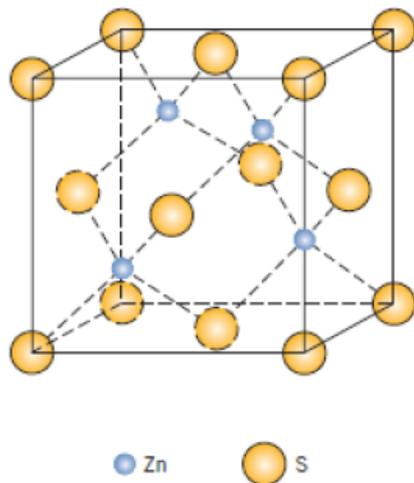


Figure 12.4 A unit cell for the zinc blende (ZnS) crystal structure.

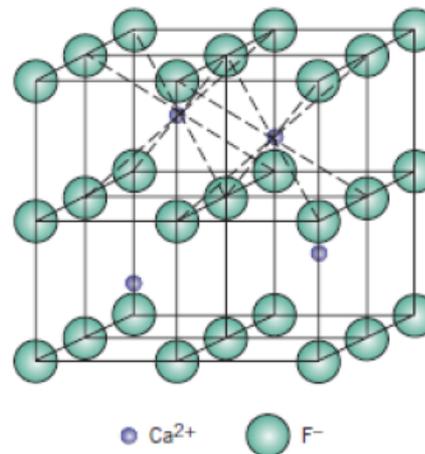


Figure 12.5 A unit cell for the fluorite (CaF₂) crystal structure.

Perovskitas

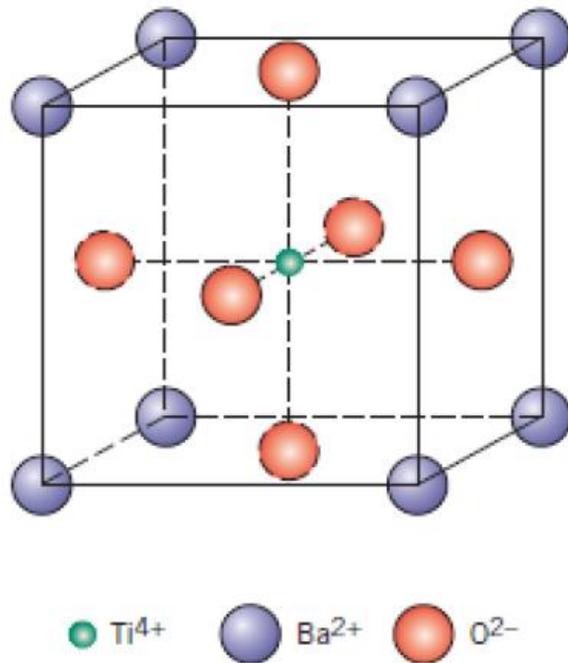
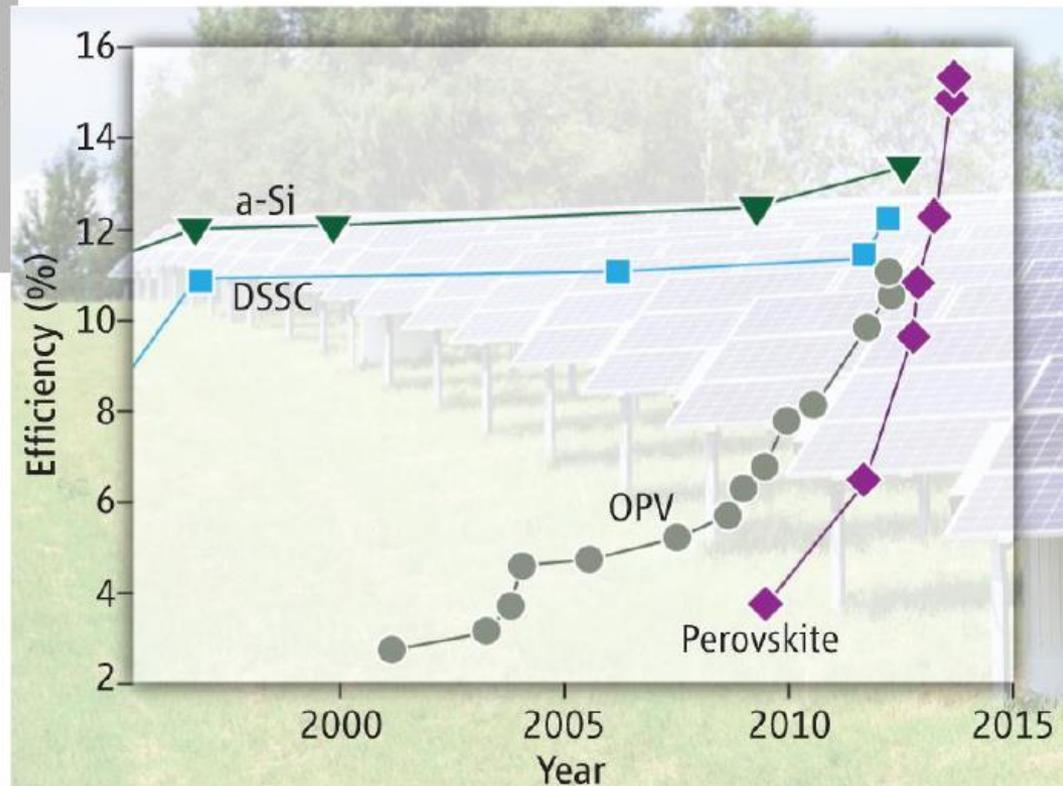
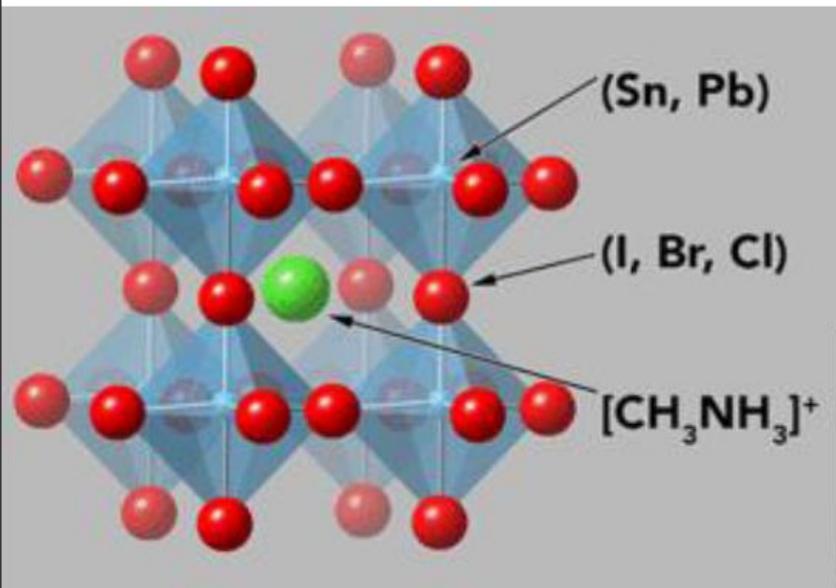
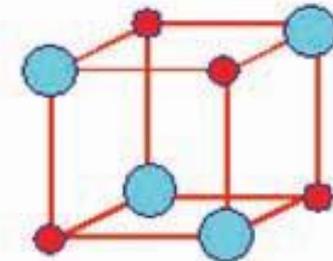
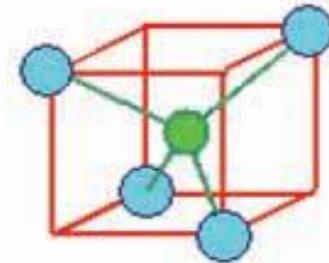
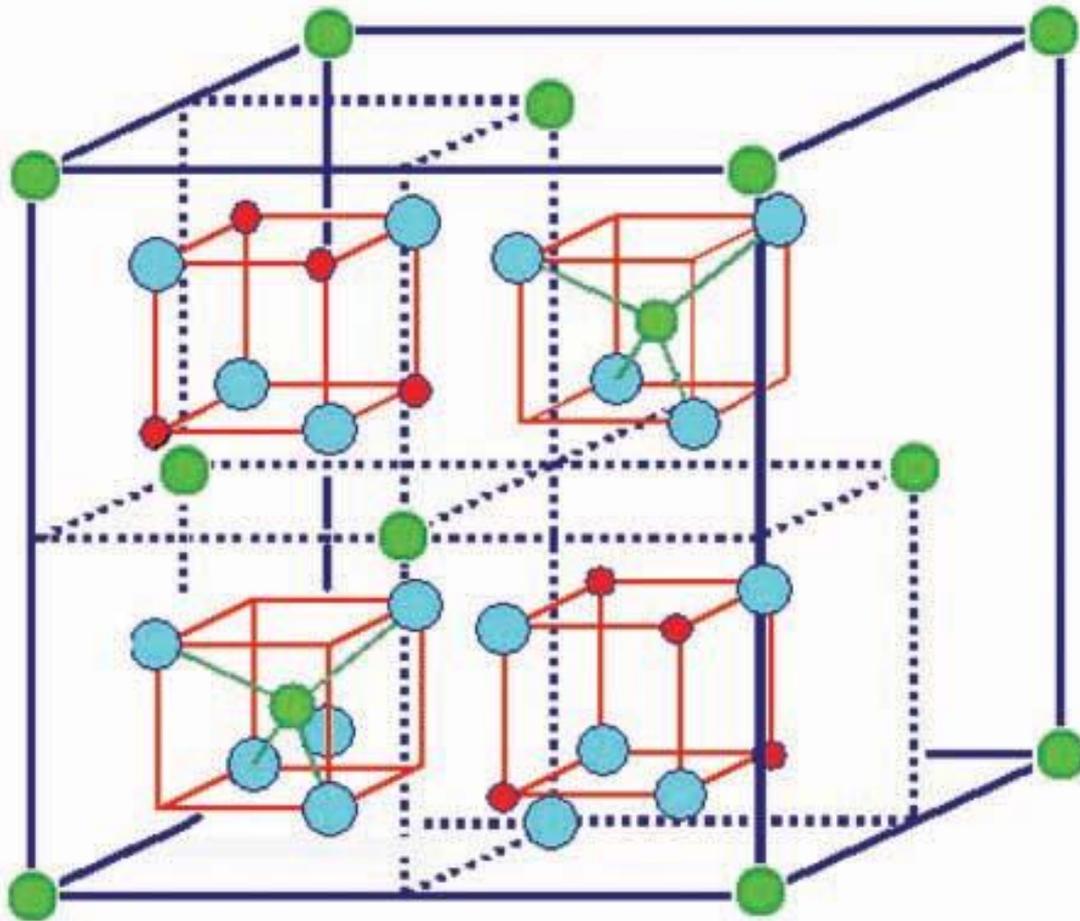


Figure 12.6 A unit cell for the perovskite crystal structure.

Celulas Solares de Perovskita



Espinélio, AB_2O_4



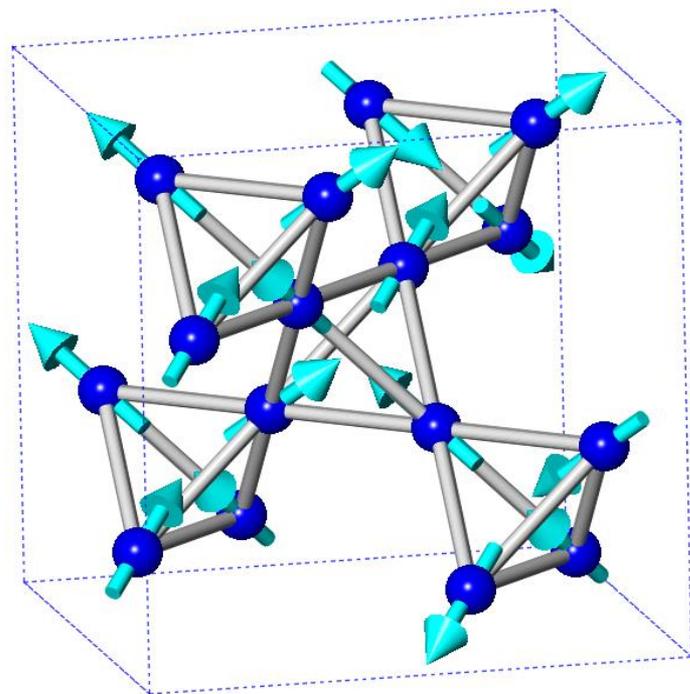
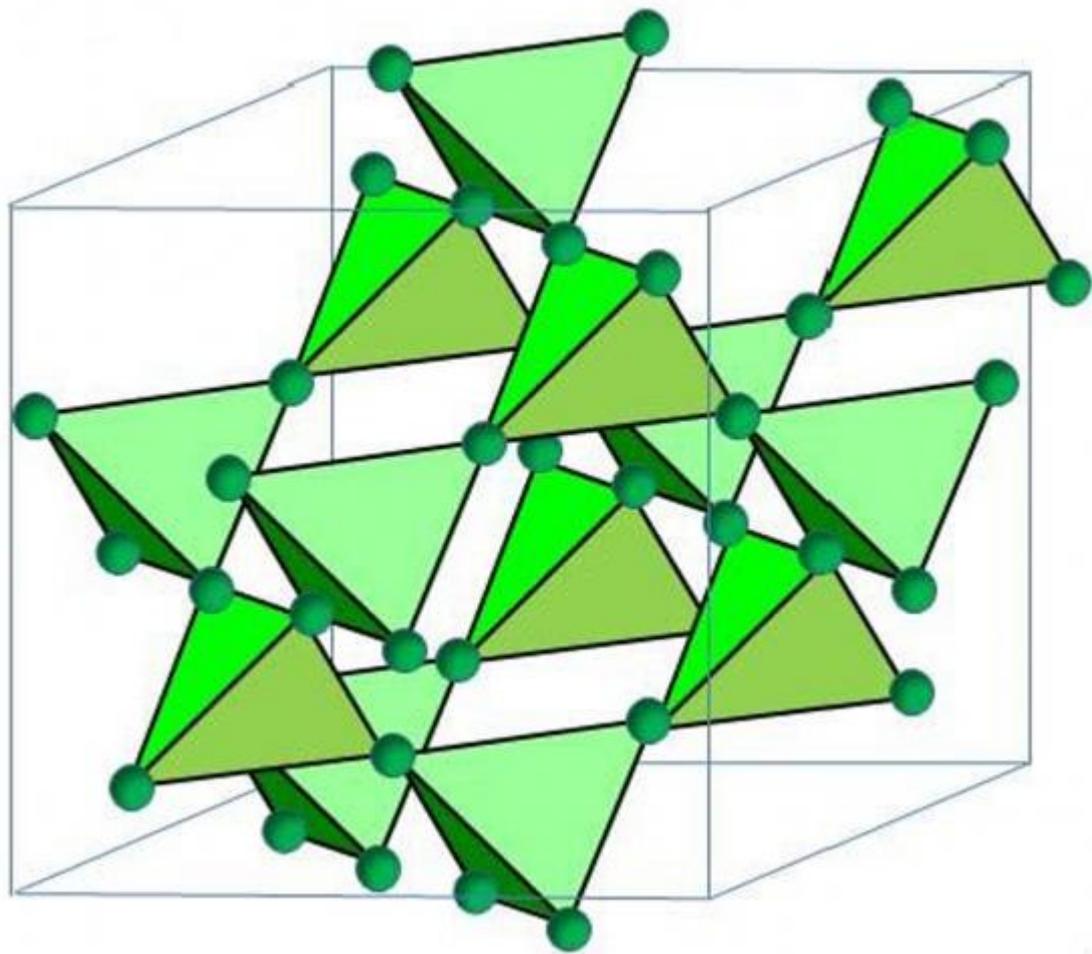
● Oxygen

● B atoms – octahedral positions

● A atoms – tetrahedral positions

AB_2O_4 spinel

Pirocloros, $A_2B_2O_7$

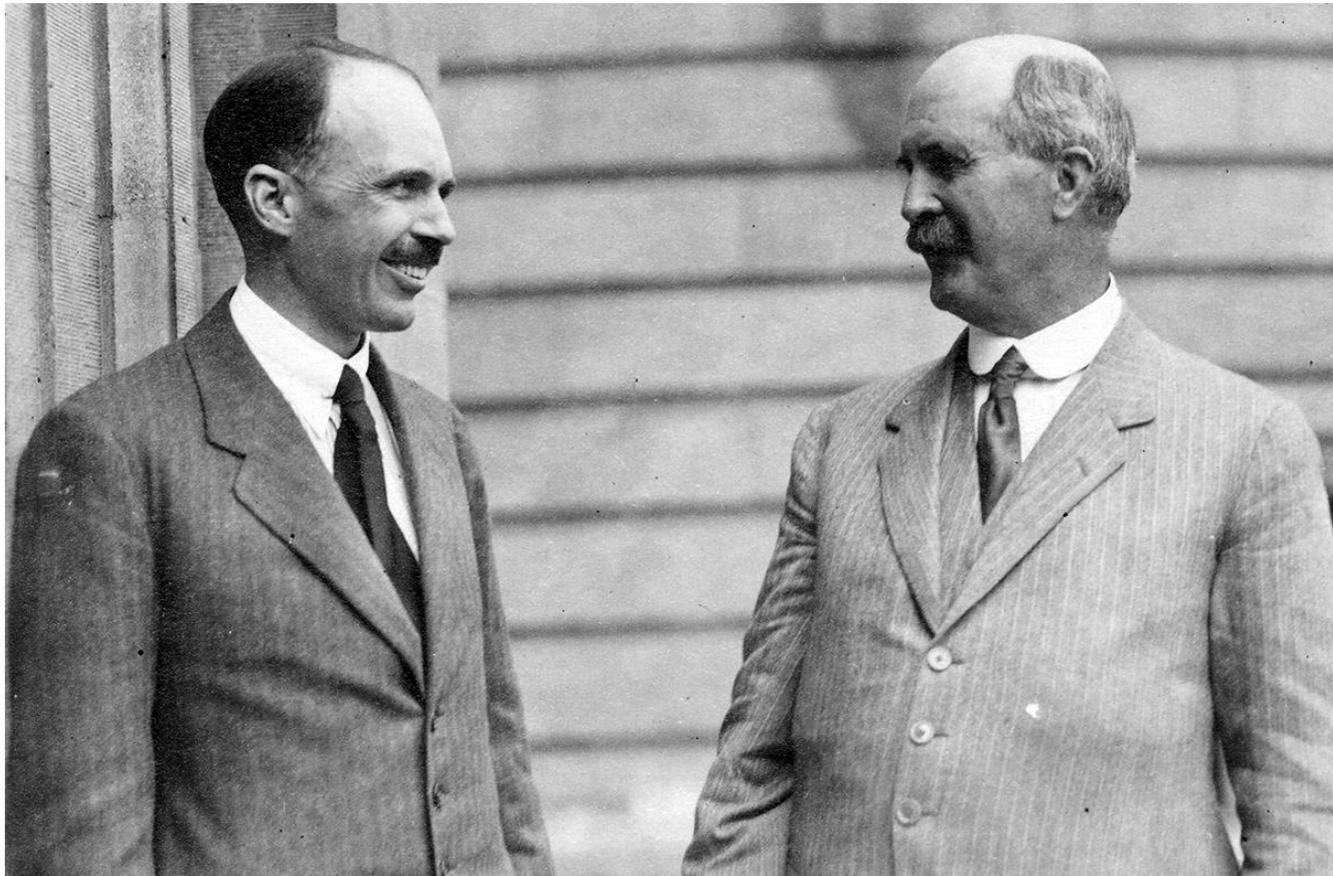


Monocristais vs policristais

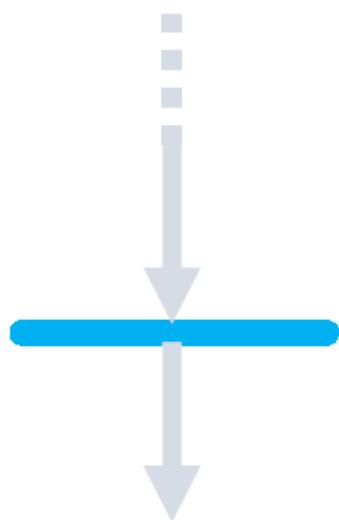


Figure 3.17 Photograph of a garnet single crystal that was found in Tongbei, Fujian Province, China. (Photograph courtesy of Irocks.com, Megan Foreman photo.)

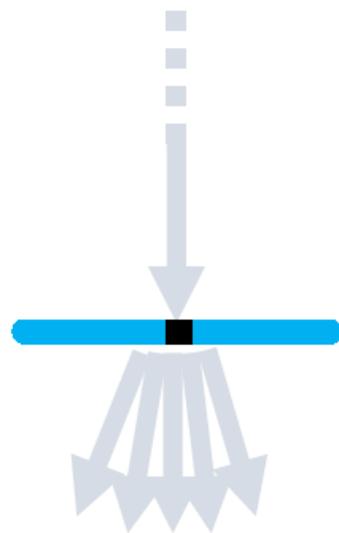
Interação dos raios X com a matéria: difração



A luz e a matéria



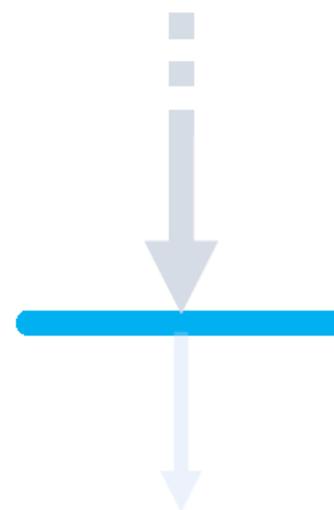
Transmissão



Difração

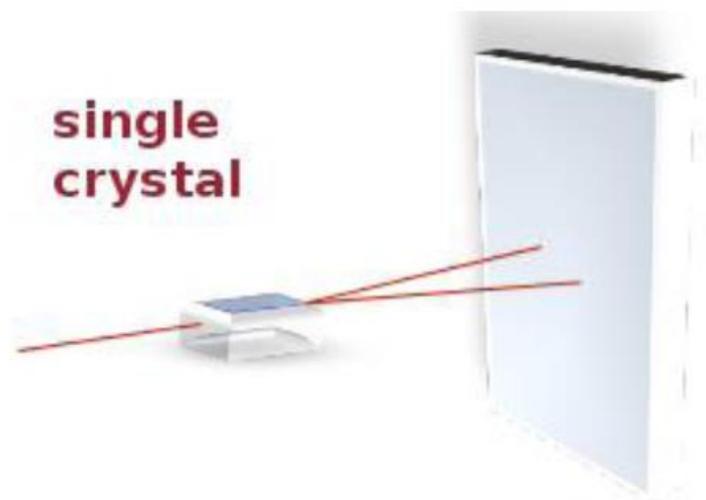


Reflexão

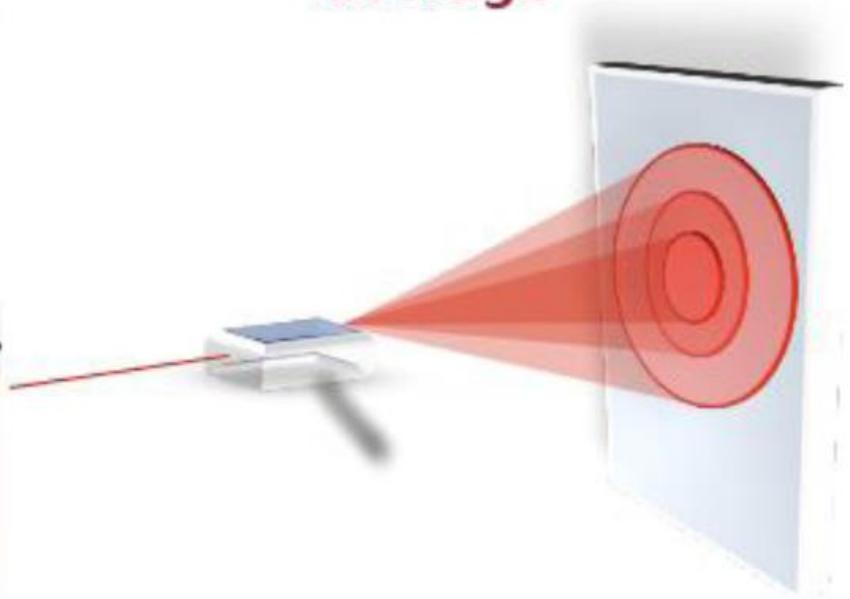


Absorção

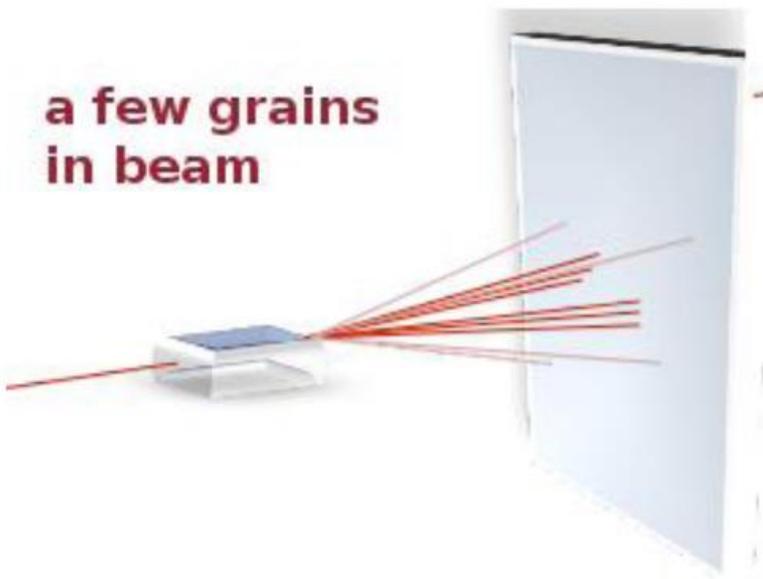
**single
crystal**

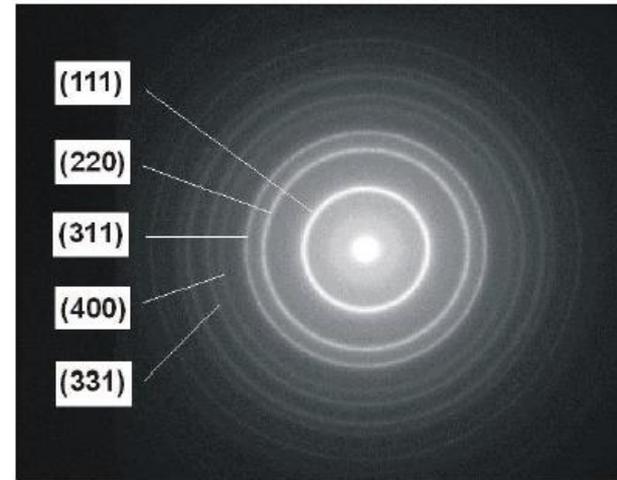
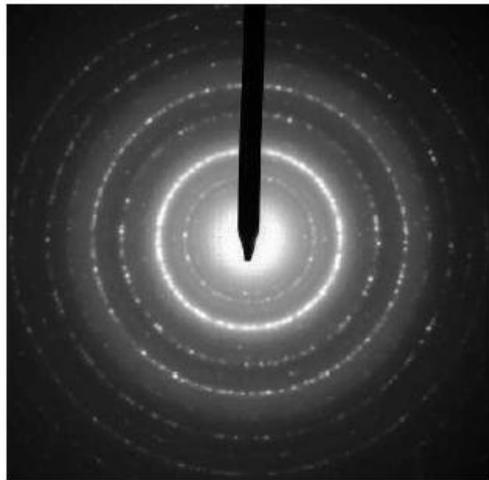
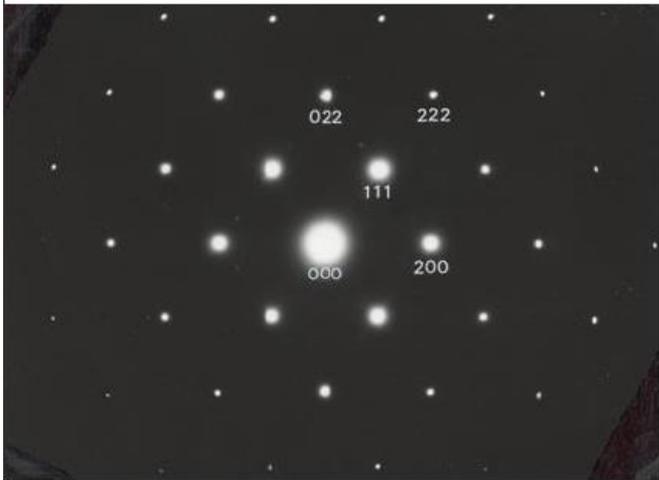


**full powder
average**

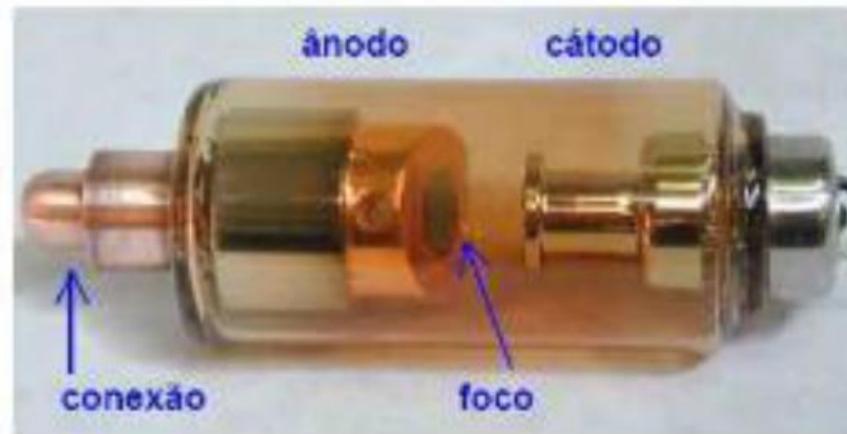


**a few grains
in beam**





Fontes de Raios X

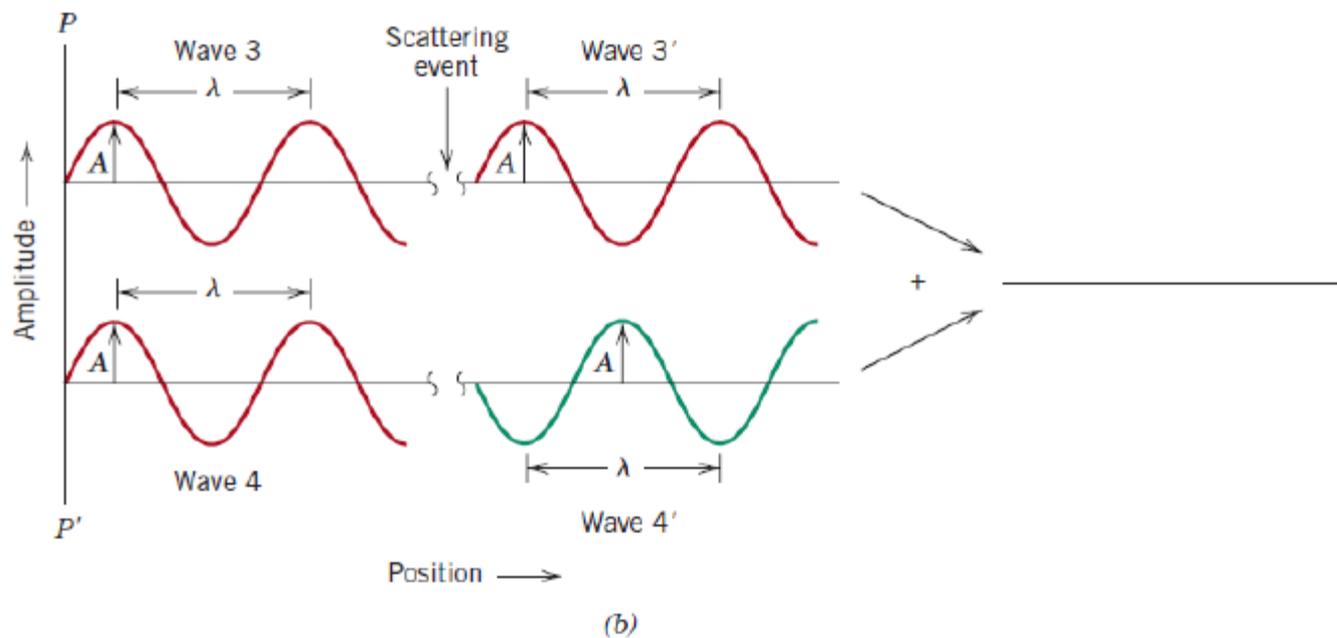
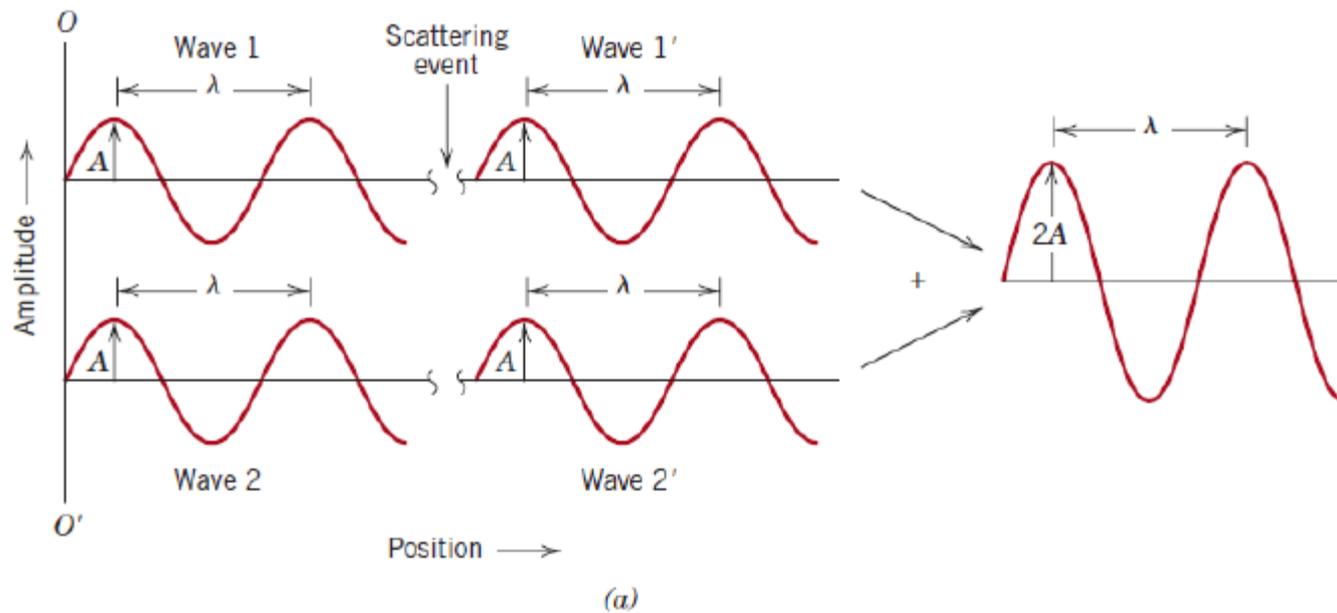


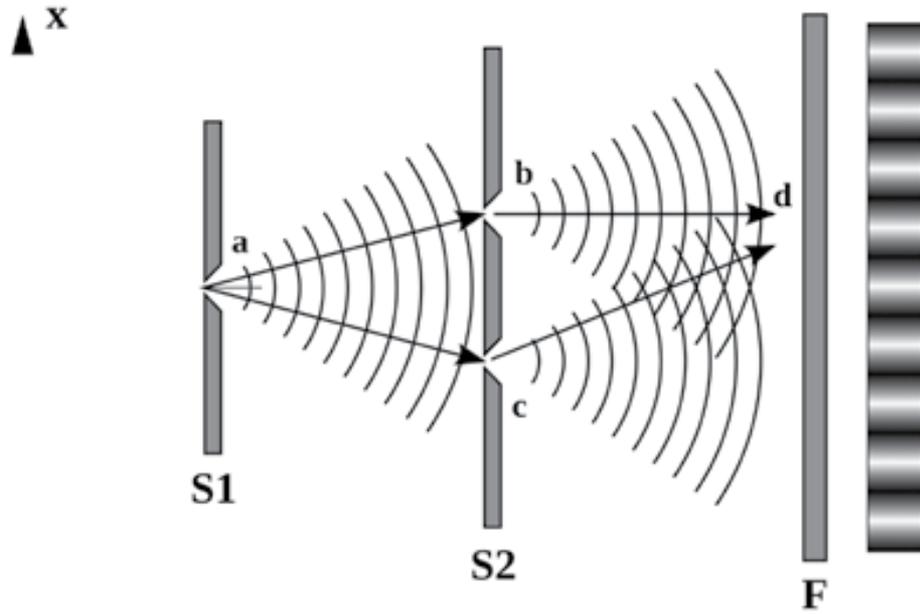
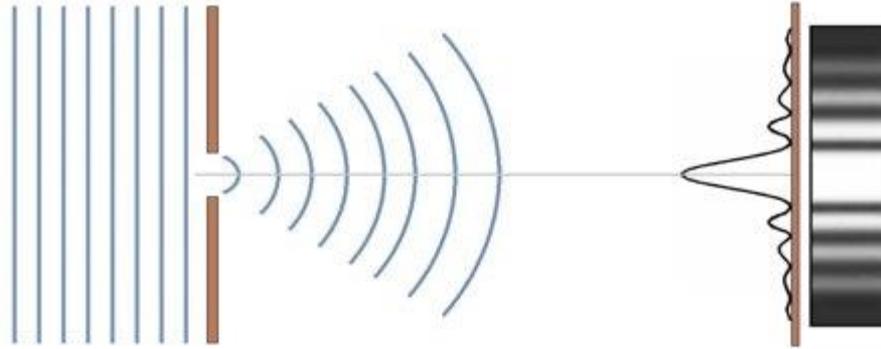
Relação dos raios X com a matéria

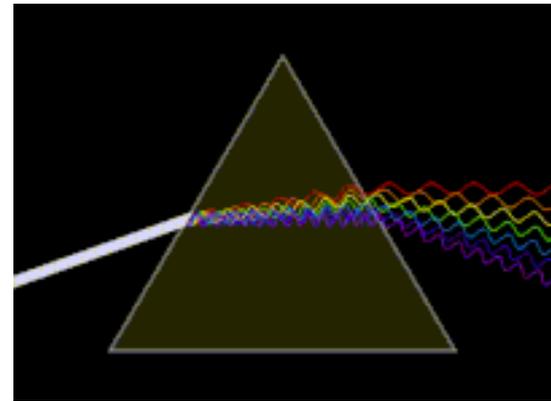
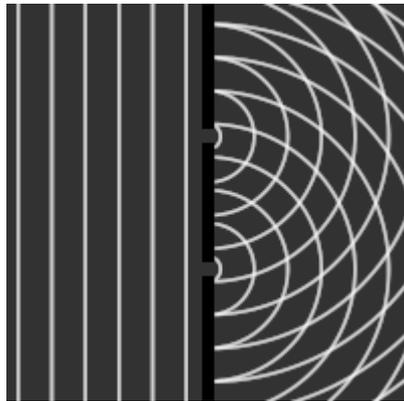
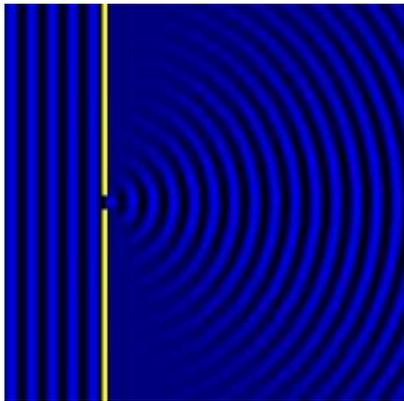
Fenômeno de difração ocorre quando a distância das franjas de difração possui a mesma ordem de grandeza do comprimento de onda.

Resolução da luz visível: 10^2 nm

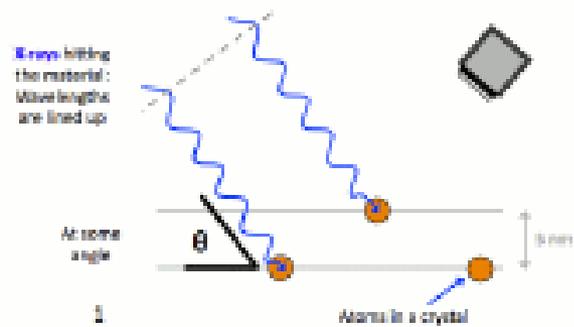
Resolução dos raios X: Å







X-Ray Diffraction



<https://www.youtube.com/watch?v=LxRFwjygvU>

<https://www.youtube.com/watch?v=1FwM1oF5e6o>

<https://www.youtube.com/watch?v=oYFEWoxuB1I>

<https://www.youtube.com/watch?v=a-jE7BM902Q>

(Documentário sobre os Bragg – English only)

<https://www.youtube.com/watch?v=pc93R2u3pjE>

Uma aula de 20 minutos sobre ondas e vibrações, dada pelo Prof. Sir Lawrence Bragg em pessoa! – MUITO BOM!!!

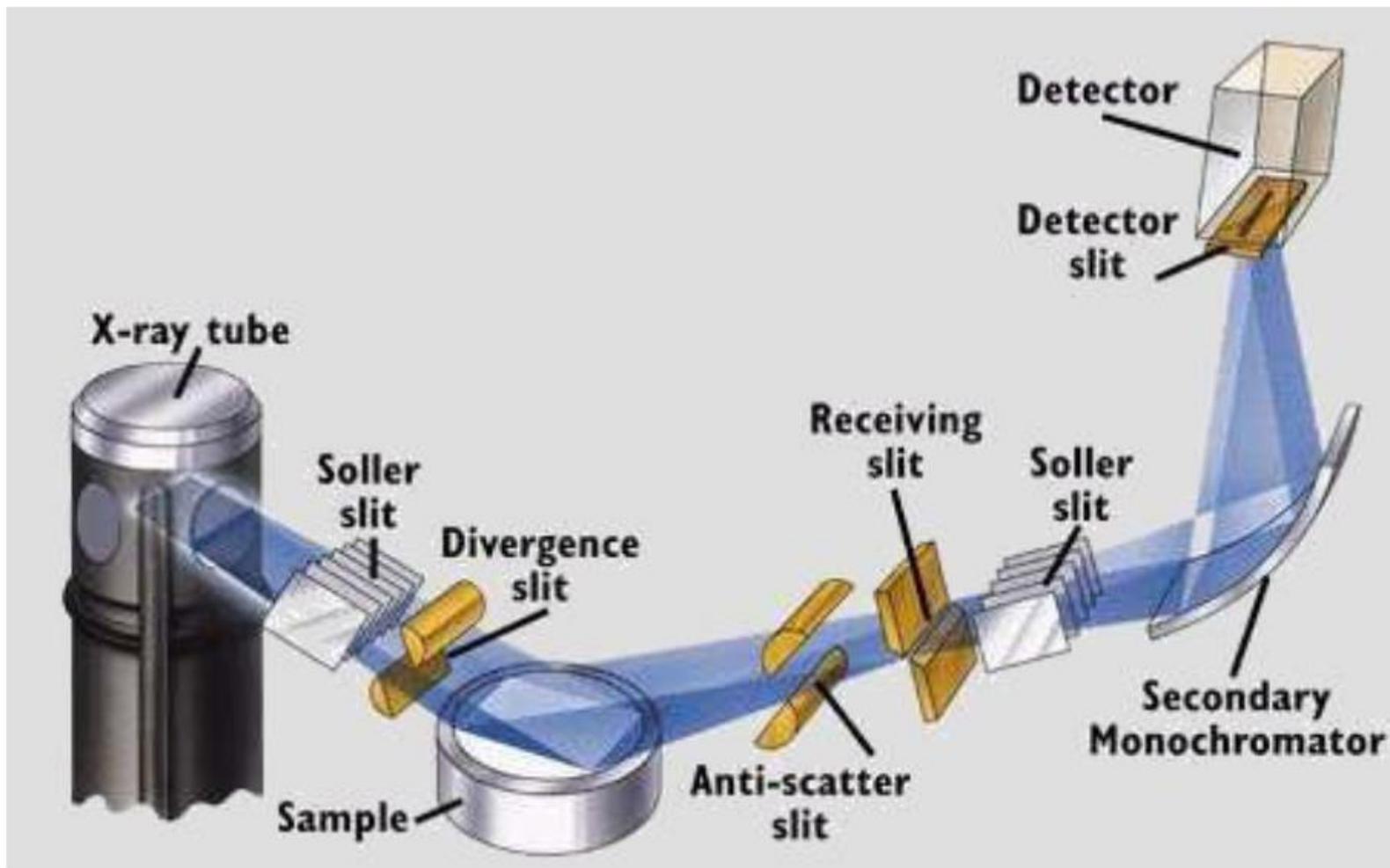
<https://www.youtube.com/watch?v=zRI06kq50hI>

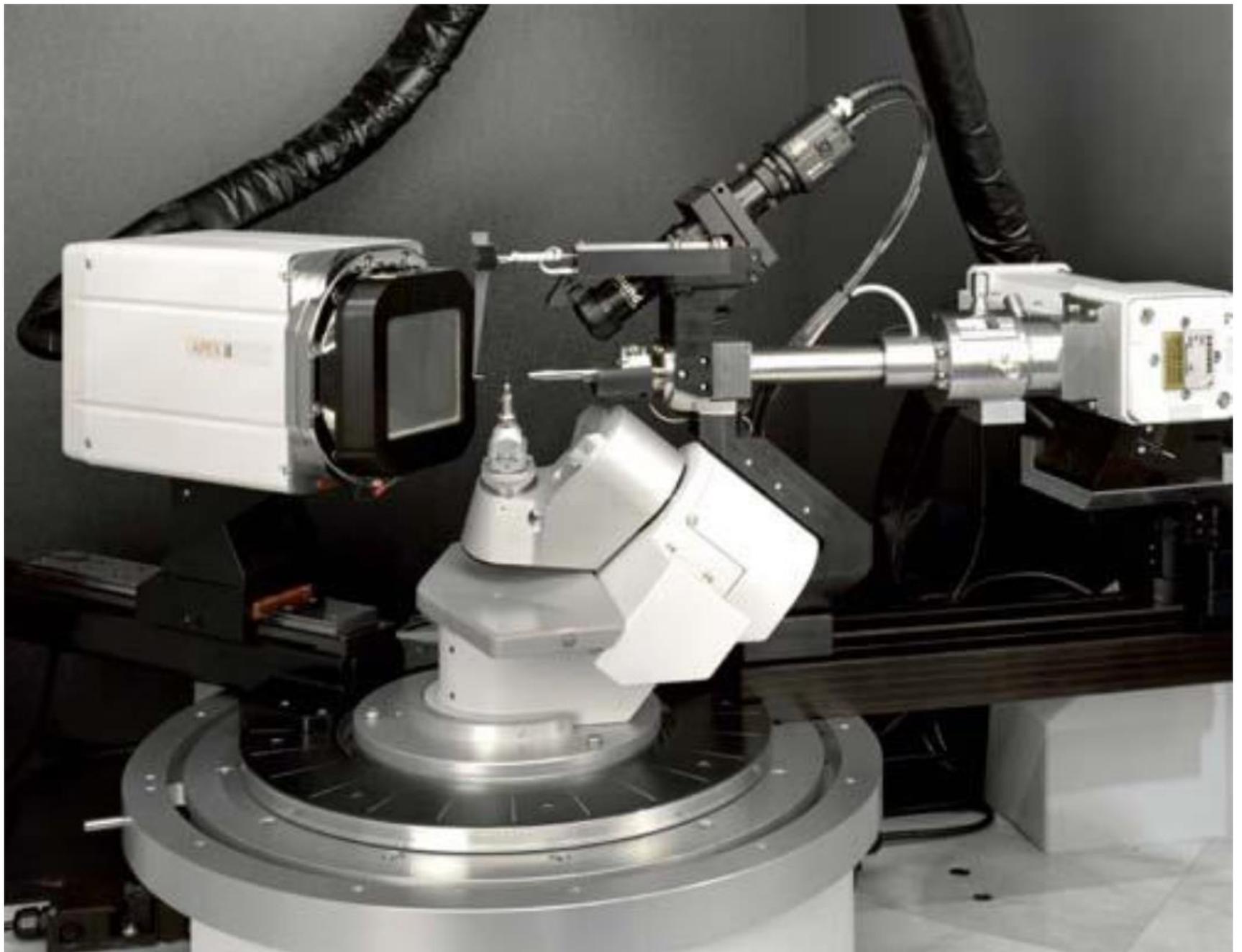
Outra aula do Prof. L. Bragg: Young e a teoria ondulatória da luz. Legendas bem ruins...)

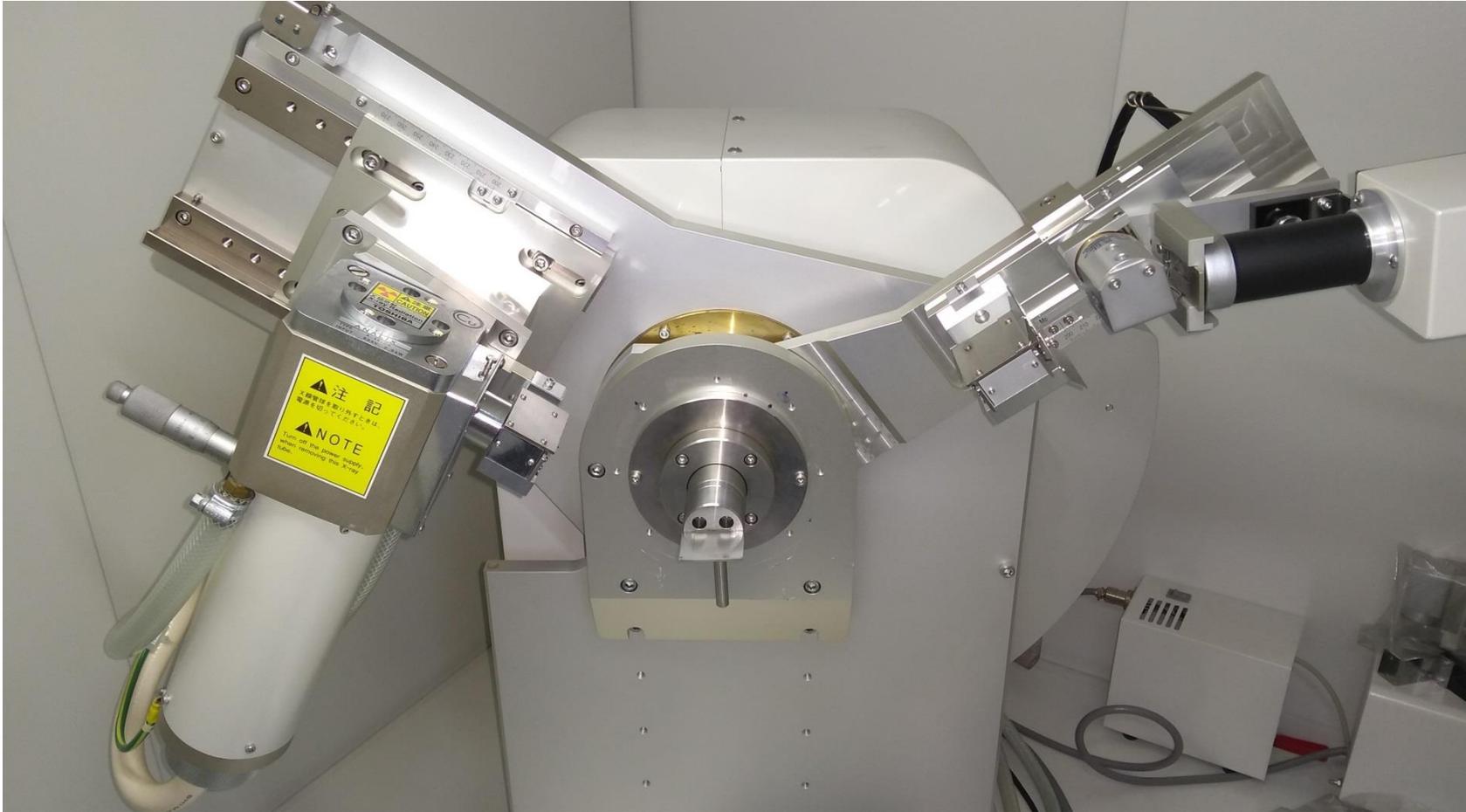
<https://www.youtube.com/watch?v=Ms-CVF540fo>

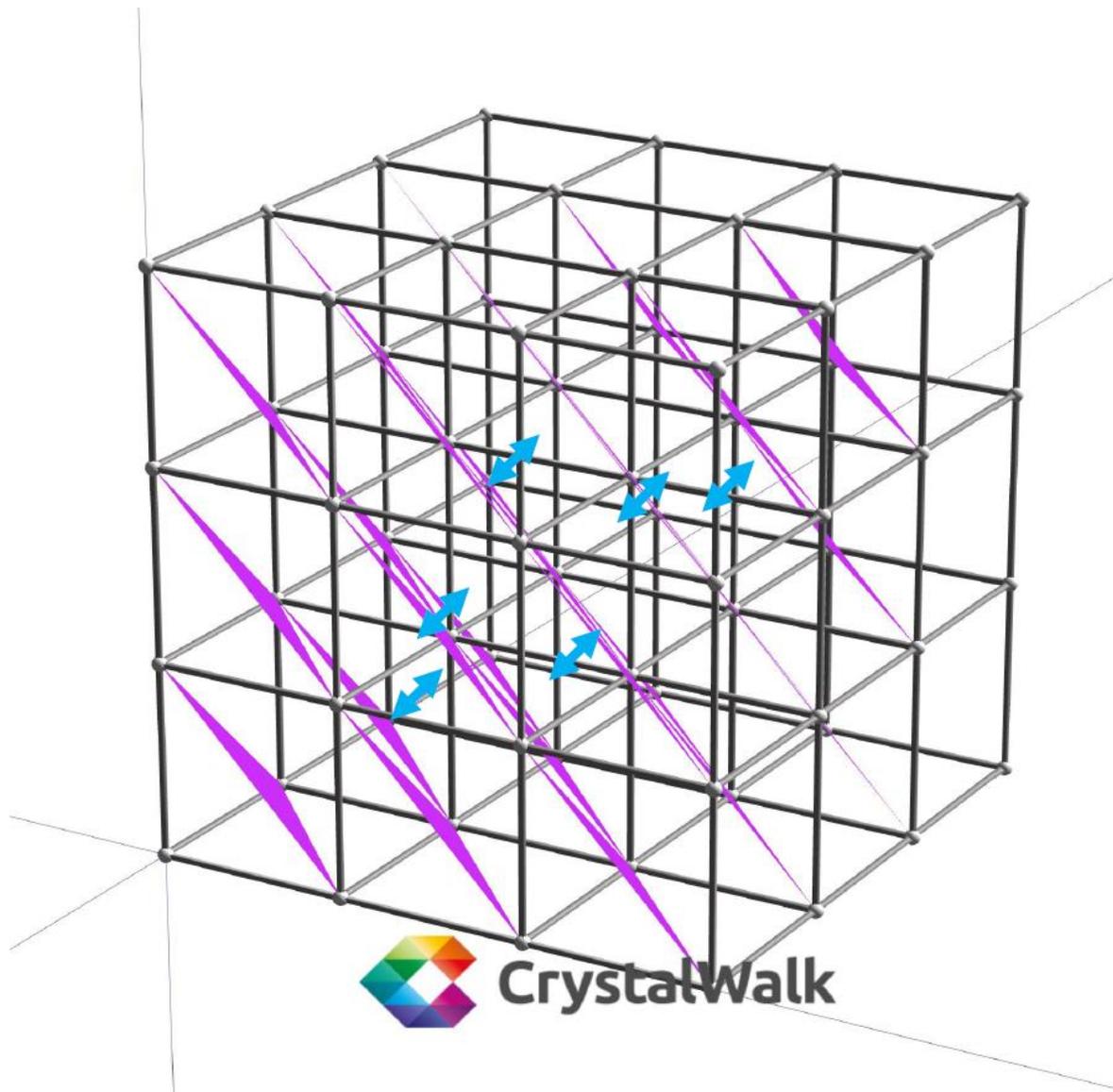
Experimento de Young, com o genial Neil deGrasse Tyson

As medidas:









CrystalWalk

Sistema cúbico

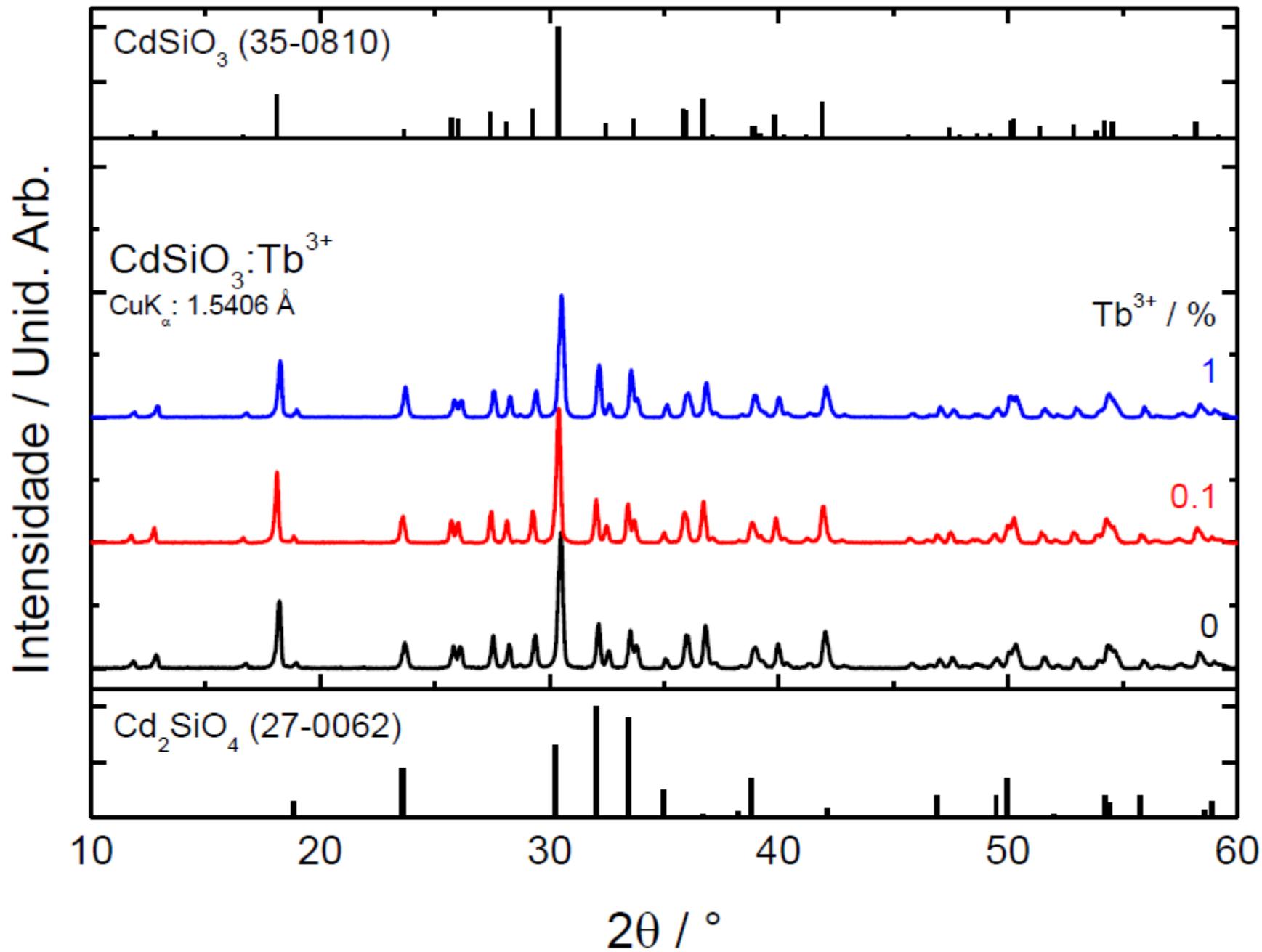
$$d_{hkl} = \frac{na}{\sqrt{h^2 + k^2 + l^2}}$$

http://www.readorrefer.in/article/Separation-between-Lattice-Planes-in-a-cubic-Crystal_6837/

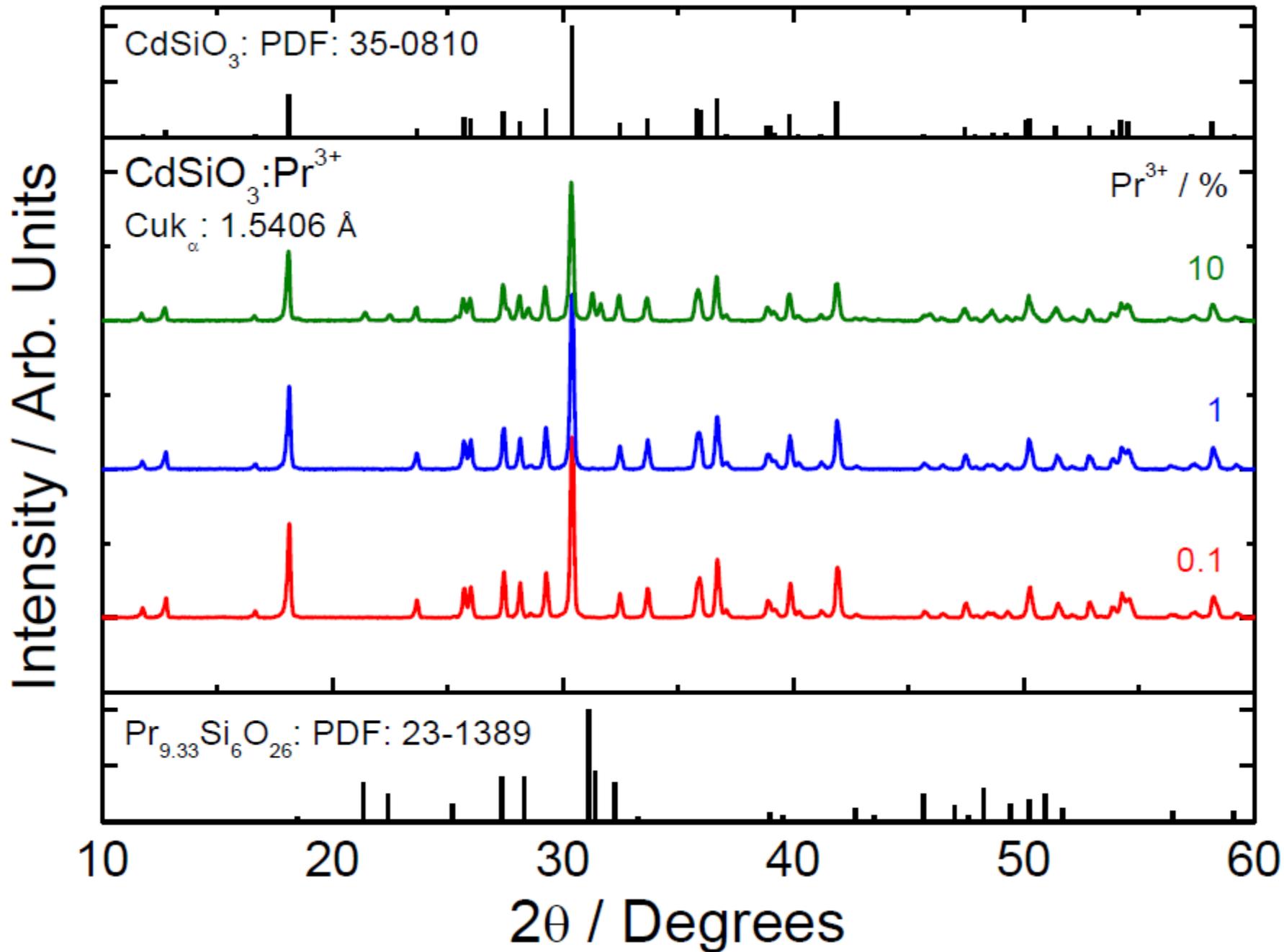
<p style="text-align: center;">Orthorhombic</p> $\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$	<p style="text-align: center;">Tetragonal</p> $\frac{1}{d_{hkl}^2} = \left[h^2 + k^2 + l^2 \left(\frac{a}{c} \right)^2 \right] \frac{1}{a^2}$	<p style="text-align: center;">Cubic</p> $\frac{1}{d_{hkl}^2} = (h^2 + k^2 + l^2) \frac{1}{a^2}$
<p style="text-align: center;">Monoclinic</p> $\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2 \sin^2 \gamma} + \frac{k^2}{b^2 \sin^2 \gamma} - \frac{2hk \cos \gamma}{ab \sin^2 \gamma} + \frac{l^2}{c^2}$		<p style="text-align: center;">Hexagonal</p> $\frac{1}{d_{hkl}^2} = \left[\frac{4}{3} (h^2 + k^2 + hk) + l^2 \left(\frac{a}{c} \right)^2 \right] \frac{1}{a^2}$
<p style="text-align: center;">Triclinic</p> $\frac{1}{d_{hkl}^2} = \left[\begin{array}{c} \left \begin{array}{ccc} \frac{h}{a} \cos \gamma \cos \beta & & \\ \frac{h}{a} & \frac{k}{b} & 1 \cos \alpha \\ \frac{l}{c} \cos \alpha & 1 & \end{array} \right + \frac{k}{b} \left \begin{array}{ccc} 1 & \frac{h}{a} \cos \alpha & \\ \cos \gamma & \frac{k}{b} \cos \alpha & \\ \cos \beta & \frac{l}{c} & 1 \end{array} \right + \frac{l}{c} \left \begin{array}{ccc} 1 & \cos \gamma \frac{h}{a} & \\ \cos \gamma & 1 & \frac{k}{b} \\ \cos \beta \cos \alpha & \frac{l}{c} & \end{array} \right \right] \cdot \left \begin{array}{ccc} 1 & \cos \gamma \cos \beta & \\ \cos \gamma & 1 & \cos \alpha \\ \cos \beta \cos \alpha & 1 & \end{array} \right ^{-1}$		
<p style="text-align: center;">Trigonal (rhombohedral)</p> $\frac{1}{d_{hkl}^2} = \frac{[(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + lh) (\cos^2 \alpha - \cos \alpha)]}{A^2 (1 + 2 \cos^3 \alpha - 3 \cos^2 \alpha)}$		

O que faço?

- Se o material é conhecido: Buscar um padrão
- Comparar com os seus dados
- Picos que sobram: Buscar possíveis impurezas
- Se não é conhecido: Posso ter monocristal? Sim? Perfeito
 - Não? Simule!
- BASE DE DADOS: <http://bdec.dotlib.com.br/>

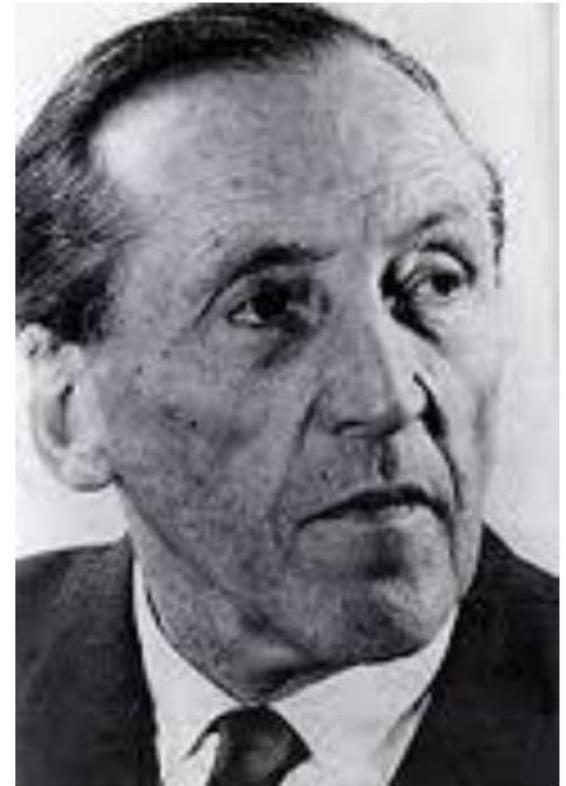


E quando há segregação de fases?



Tamanho médio de cristalito

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$



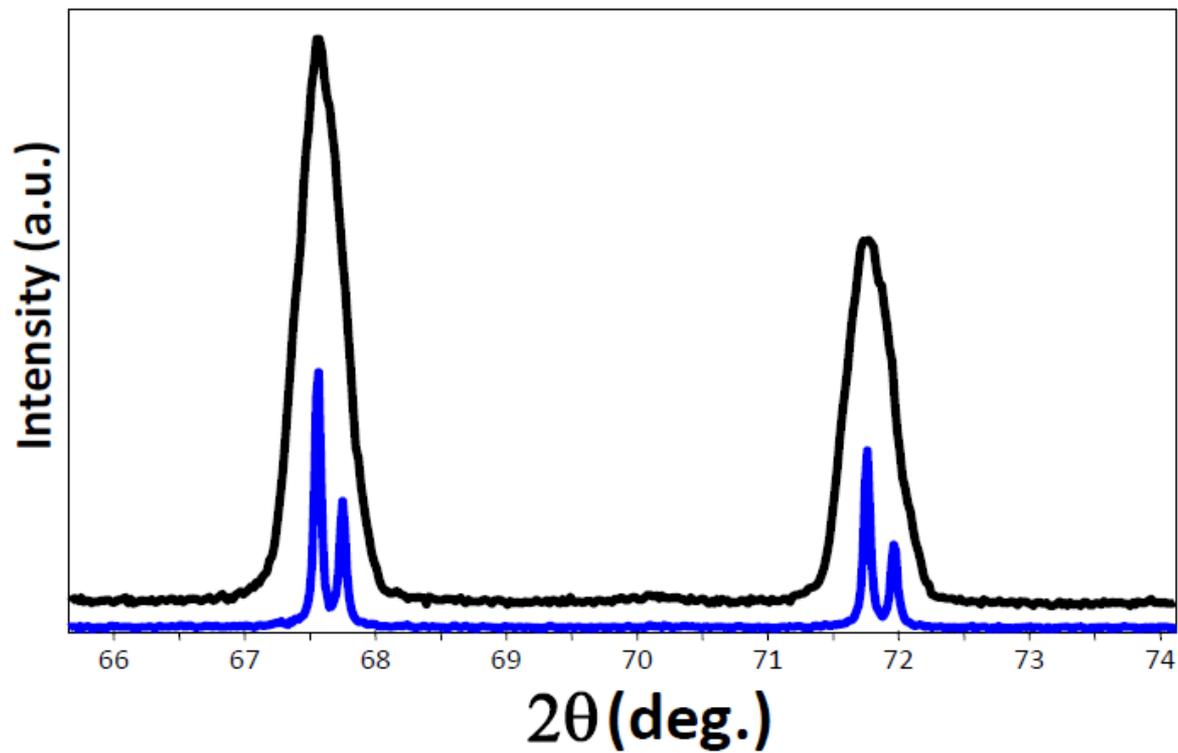
Paul Scherrer

Alguns pontos

- Largura do pico aumenta com diminuição do tamanho
- Largura aumenta com 2θ
 - Porém: Intensidade diminui com aumento de 2θ e outros alargamentos ocorrem também (exemplo stress de rede)
 - Abaixo de 30° , assimetria do pico dificulta a análise
- Melhores ângulos: entre ca. 30° e 50°
- K varia de 0,62 a 2,08, dependendo da estrutura.
 - Partículas esféricas $K = 0,94$

“Scherrer after sixty years: A survey and some new results in the determination of crystallite size,” *J. Appl. Cryst.* **11** (1978) p102-113.

Problemas



Mesma amostra

Alargamento do equipamento

$$\beta_r^2 = \beta_{exp}^2 - \beta_{ref}^2$$

Boas referências?

LaB₆

NaCl

Si

Cite this: *Nanoscale*, 2011, **3**, 792

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REVIEW

Pitfalls in the characterization of nanoporous and nanosized materials

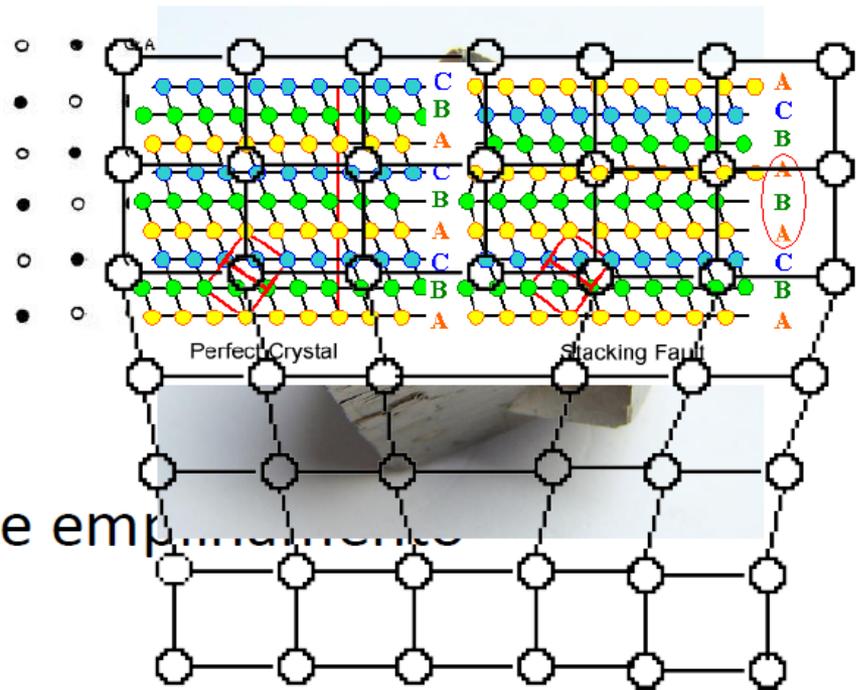
Claudia Weidenthaler*

Received 3rd August 2010, Accepted 15th November 2010

DOI: 10.1039/c0nr00561d

Alargamentos de picos devido à

- Tamanho do cristalito
- Stress
- Forma dos domínios de cri
- Distribuição de tamanho
- defeito de deslocamento
- Defeitos de macla e falhas de empilhamento
- Domínios de antifase



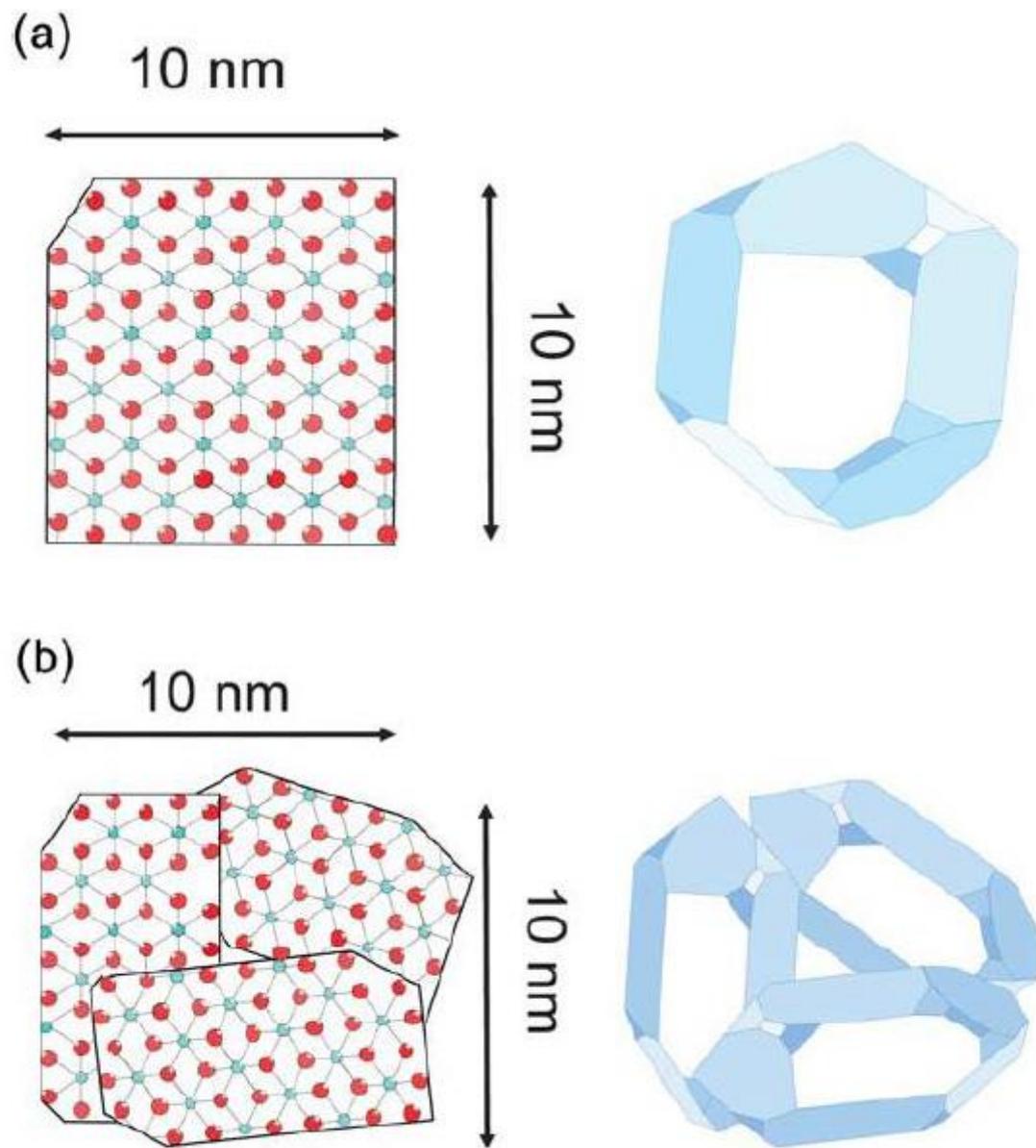


Fig. 4 (a) Single crystallite and (b) three differently oriented crystallites form an agglomerate.

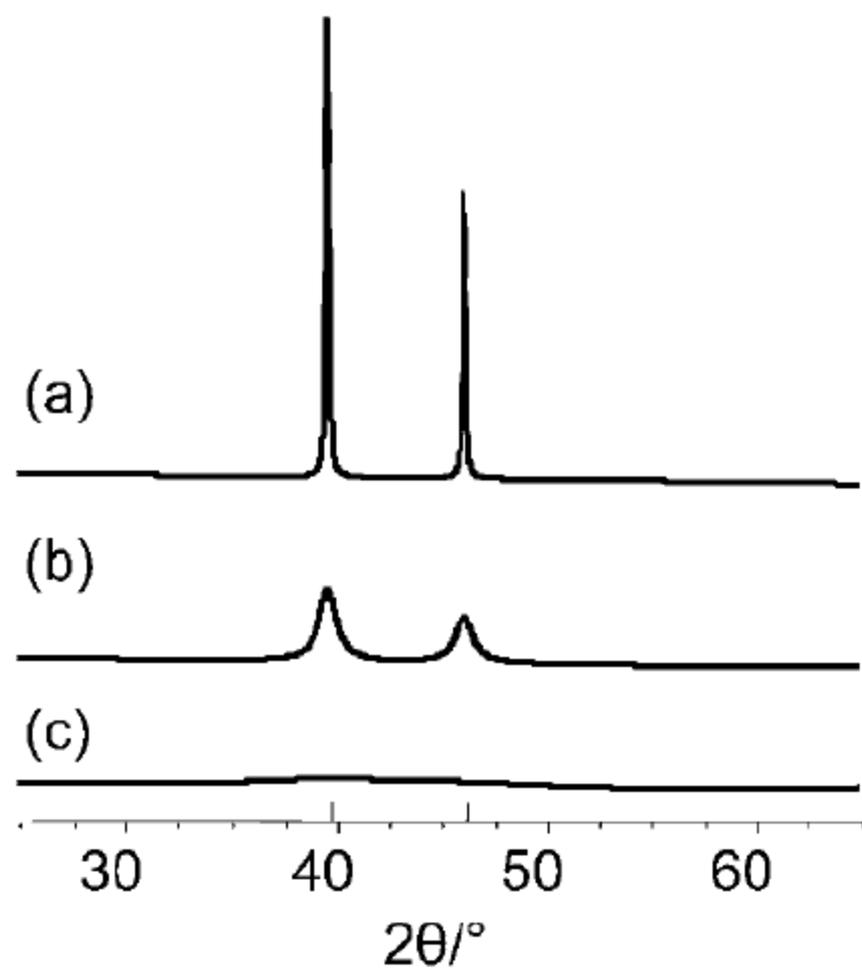


Fig. 3 Calculated powder patterns of platinum, simulated for different crystallite sizes: (a) 100 nm, (b) 10 nm and (c) 1 nm.

β vs FWHM

$$\beta = \frac{\int I d\theta}{I_{max}}$$

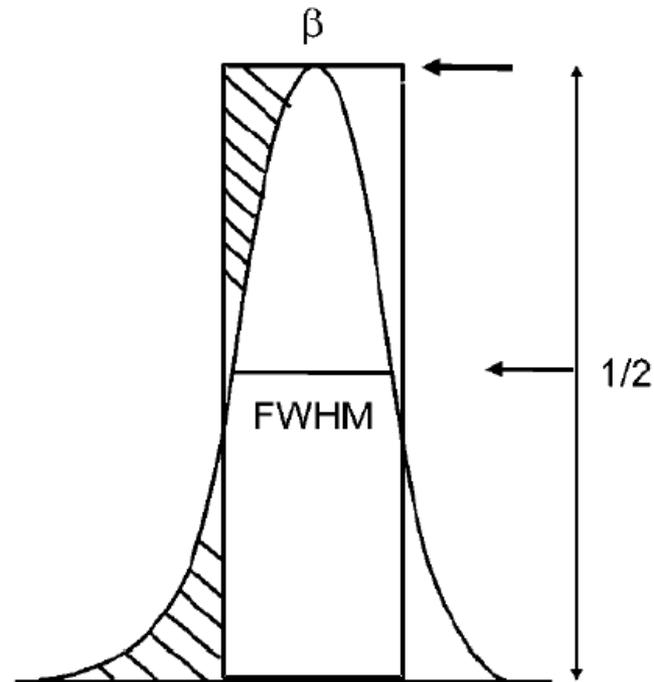


Fig. 6 FWHM: width of the peak at $\frac{1}{2}$ of its maximum intensity. Integral breadth β is defined by the width of a rectangle having the same area and the same height as the peak.

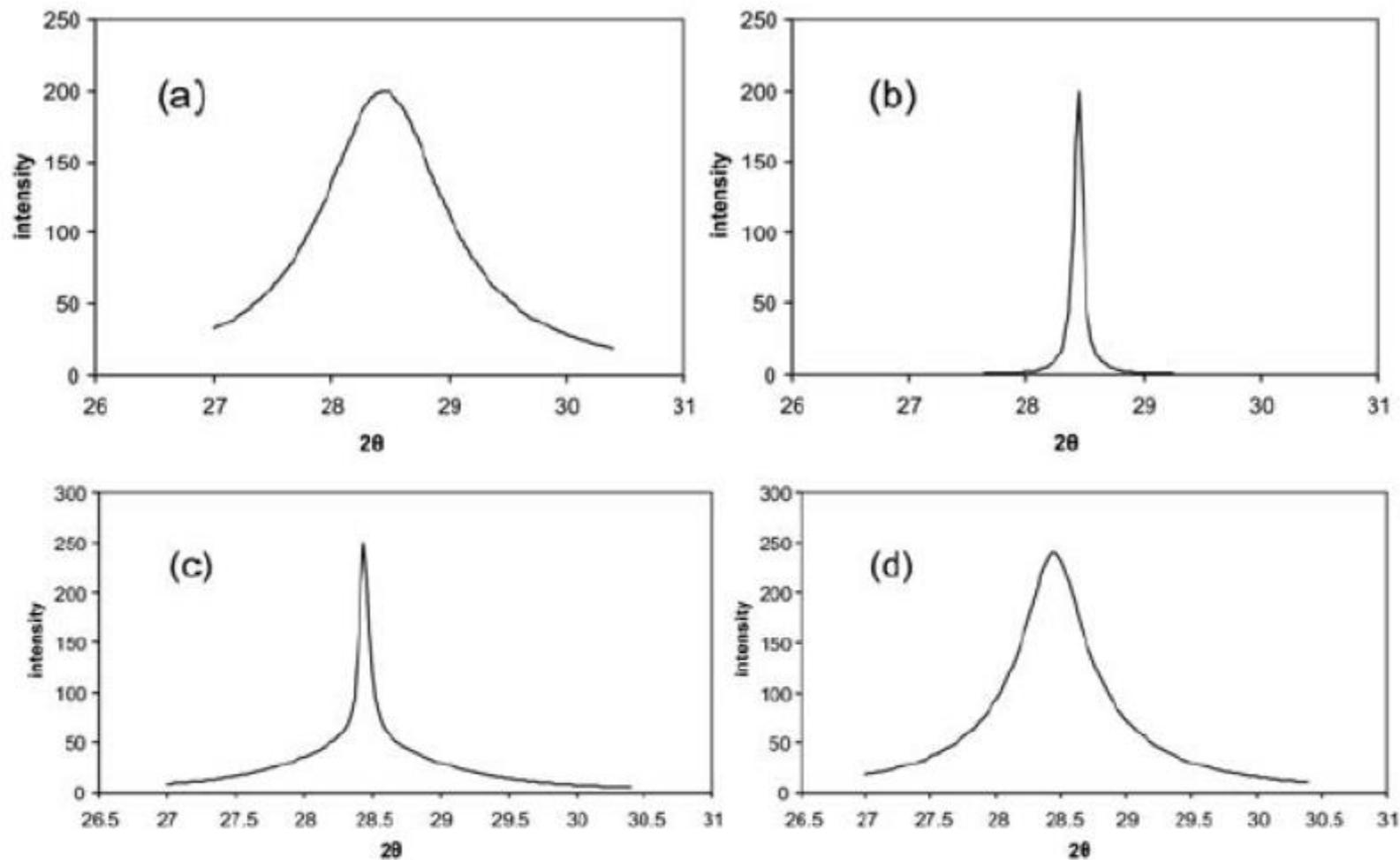


Fig. 10 (a) Monodisperse sample with crystal size of 4 nm, (b) monodisperse sample with crystal size of 65 nm, (c) polydisperse sample with a mixture of crystals of sizes 4 nm and 65 nm, and (d) polydisperse sample representing a mixture of crystals of 4 nm and 11 nm sizes.

Determinação de reflexões

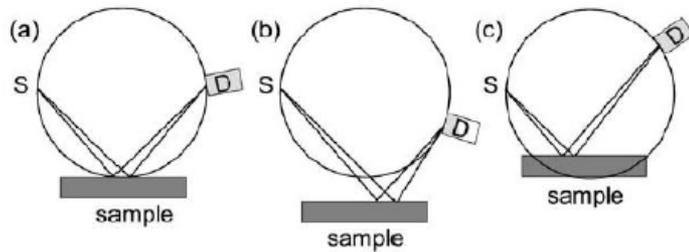


Fig. 23 (a) Sample is positioned correctly, (b) sample position is too low, and (c) sample position is too high.

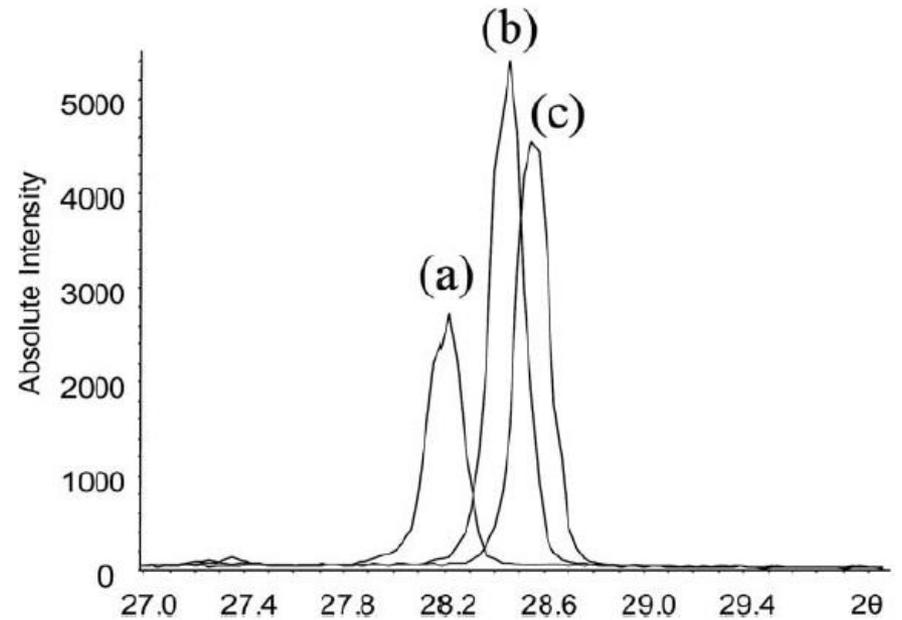


Fig. 24 Si (111) X-ray reflection measured with (a) too low sample position, (b) correct position, and (c) at too high sample position.

Refinamento Rietveld

- Método de ajuste de curva (FITTING) que minimiza a diferença entre os dados experimentais e um modelo baseado numa estrutura hipotética e parâmetros instrumentais

O que o refinamento Rietveld permite

- Parâmetros estruturais
 - Análise quantitativa de fases
 - Parâmetros de rede
 - Posição atômica e ocupação
 - Fatores térmicos (Vibrações)
- Tamanho de grão, micro-stress
- Outros defeitos lineares
- Momento magnético (difração de nêutrons)

O que eu preciso pra um refinamento?

- Conhecer previamente a estrutura
- Difração de ALTA qualidade
- Um modelo que faça sentido química e fisicamente
- Funções adequadas para os picos e fundo

$$I_i^{calc} = S_F \sum_{j=1}^{Nphases} \frac{f_j}{V_j^2} \sum_{k=1}^{Mpeaks} L_k |F_{k,j}|^2 S_j (2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

Scale Factor

S_F : beam intensity
 f_j : volume fraction
 V_j : cell volume

Structure Factor
 Multiplicity of k -th
 reflection (m_k)
 Temperature factor

Volume
 absorption

Preferred
 orientation

Lorentz--Polarization factor

- Geometry
- monochromator (angle θ)
- Detector
- beam size/sample volume
- sample positioning (angular)

i : steps

j : number of phases

k : k^{th} reflection

Cuidados

- Tenha um excelente experimento
- Saiba o máximo de sua amostra
- Não refine muitos parâmetros
- Olhe com cuidado para os picos e residuais, não faça no automático