

Received 19 September 2015
Accepted 2 March 2016

Edited by K. Tsuda, Tohoku University, Japan

Keywords: Scherrer equation; powder diffraction; X-ray diffraction; dynamical theory.

The Scherrer equation and the dynamical theory of X-ray diffraction

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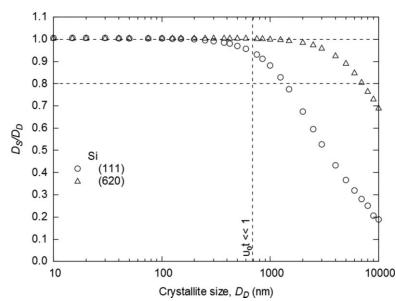
The Scherrer equation is a widely used tool to determine the crystallite size of polycrystalline samples. However, it is not clear if one can apply it to large crystallite sizes because its derivation is based on the kinematical theory of X-ray diffraction. For large and perfect crystals, it is more appropriate to use the dynamical theory of X-ray diffraction. Because of the appearance of polycrystalline materials with a high degree of crystalline perfection and large sizes, it is the authors' belief that it is important to establish the crystallite size limit for which the Scherrer equation can be applied. In this work, the diffraction peak profiles are calculated using the dynamical theory of X-ray diffraction for several Bragg reflections and crystallite sizes for Si, LaB₆ and CeO₂. The full width at half-maximum is then extracted and the crystallite size is computed using the Scherrer equation. It is shown that for crystals with linear absorption coefficients below 2117.3 cm⁻¹ the Scherrer equation is valid for crystallites with sizes up to 600 nm. It is also shown that as the size increases only the peaks at higher 2θ angles give good results, and if one uses peaks with 2θ > 60° the limit for use of the Scherrer equation would go up to 1 μm.

1. Introduction

The properties of polycrystalline materials depend, among other things, on the crystallite size. This fact has led in the past few decades to research in nanomaterials, for example; it is therefore very important to measure with accuracy the crystallite size of a polycrystalline sample. A widely used tool to perform this operation is X-ray powder diffraction combined with the Scherrer equation (Azároff, 1968; Burton *et al.*, 2009; Holzwarth & Gibson, 2011; Klug & Alexander, 1974; Langford & Wilson, 1978; Patterson, 1939; Vives *et al.*, 2004):

$$\text{FWHM} = (k \times \lambda) / (D \times \cos \theta), \quad (1)$$

in which FWHM is the full width at half-maximum of the diffraction peak, k is a shape constant (James, 1962), D is the crystallite size and θ is the Bragg angle. This equation is obtained based on the assumption that each atom (scattering centre) scatters the incoming radiation independently, and once scattered the radiation does not interact with the other atoms. The derivation for this equation can be seen for example in Klug & Alexander (1974) and it does not depend on the type of atoms inside the crystal, the structure factor of the reflection or the linear absorption coefficient. Cullity & Stock (2001) argue that this equation is valid only for crystallite sizes up to 200 nm. This limit, however, is related to the resolution of the diffractometer. The purpose of this work is to assess the limit of equation (1) based on diffraction theory, and we propose that it is still valid for crystallite sizes up to 1 μm.



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Table 1

List of hkl planes of LaB_6 , used in this work, along with their respective 2θ angles for $\text{Cu } K\alpha_1$ radiation ($\lambda = 1.540598 \text{ \AA}$).

The structure factors (F) were calculated using the atomic form factors given by Waasmaier & Kirsch (1995) with the anomalous correction, f' and f'' given by Cromer (1970), which for $\text{Cu } K\alpha_1$ radiation are $f'(\text{La}) = -1.41534$, $f''(\text{La}) = 9.12962$, $f'(\text{B}) = 0.00934416$ and $f''(\text{B}) = 0.00398772$. The FWHMs, given here in 2θ , were measured directly in the calculated rocking curves using the angle positions where the intensity is half the maximum on either side of the peak.

hkl	2θ (°)	F	$ F $	FWHM (°)		
				10 nm	100 nm	1000 nm
100	21.359	(36.4, 9.1)	37.5	0.796	0.080	0.010
110	30.386	(48.1, 9.1)	48.9	0.810	0.081	0.009
111	37.443	(48.2, 9.1)	49.0	0.826	0.083	0.010
200	43.508	(46.8, 9.1)	47.7	0.842	0.084	0.010
210	48.959	(40.0, 9.1)	41.1	0.859	0.086	0.009
211	53.991	(32.3, 9.1)	33.6	0.878	0.088	0.009
220	63.221	(33.5, 9.1)	34.7	0.918	0.092	0.010
221	67.550	(41.6, 9.1)	42.6	0.941	0.094	0.010
300	67.550	(24.7, 9.1)	26.3	0.941	0.094	0.010
310	71.748	(39.0, 9.1)	40.1	0.965	0.097	0.010
311	75.847	(32.4, 9.1)	33.6	0.991	0.099	0.010
222	79.873	(24.3, 9.1)	25.9	1.020	0.102	0.010
320	83.848	(28.3, 9.1)	29.7	1.051	0.105	0.011
321	87.795	(30.0, 9.1)	31.3	1.085	0.109	0.011
400	95.675	(37.0, 9.1)	38.1	1.165	0.117	0.012
410	99.646	(26.2, 9.1)	27.8	1.212	0.121	0.012
322	99.646	(31.7, 9.1)	33.0	1.212	0.121	0.012
411	103.664	(27.8, 9.1)	29.2	1.265	0.127	0.013
114	103.664	(27.8, 9.1)	29.2	1.265	0.127	0.013
330	103.664	(36.8, 9.2)	37.9	1.265	0.127	0.013
331	107.753	(24.3, 9.1)	26.0	1.326	0.133	0.013
420	111.937	(29.3, 9.1)	30.7	1.397	0.140	0.014
421	116.248	(29.8, 9.1)	31.1	1.481	0.148	0.015
332	120.727	(29.3, 9.1)	30.7	1.581	0.158	0.016
422	130.413	(22.4, 9.1)	24.2	1.865	0.186	0.019
430	135.805	(19.8, 9.1)	21.8	2.079	0.208	0.021
500	135.805	(22.9, 9.1)	24.7	2.079	0.208	0.021

The assumptions made to derive the Scherrer equation are very close to the ones made in the kinematical theory of X-ray diffraction, used for crystals with appreciable defects or of small size (Zachariasen, 1945). For large and perfect crystals, the kinematical theory cannot (always) be assumed and the dynamical theory of X-ray diffraction should be applied instead. This theory treats the crystal as a three-dimensional complex dielectric constant and uses Maxwell's equations to describe the interactions between incident and diffracted beams, and all waves inside the crystal (Zachariasen, 1945; Batterman & Cole, 1964; Authier, 2001). This means that the waves scattered by each atom (or atomic plane) are subsequently scattered by other atoms (or atomic planes) giving rise to distinct phenomena that do not appear in the kinematic theory, such as the Darwin width (Authier & Malgrange, 1998), primary extinction (Authier & Malgrange, 1998) and the Borrman effect (Batterman & Cole, 1964). The Darwin width is the smallest possible width of a diffraction peak even in an infinitely large crystal. The primary extinction happens when the diffracted beam is diffracted again in the direction of the primary beam while inside the crystal, therefore decreasing the energy transferred to the diffracted beam. The Borrman effect is the anomalous transmission of X-rays through a thick crystal, which should be completely absorbed

but are not because the X-ray wavefield is in fact forward diffracted.

As the amount of defects in the crystalline lattice decreases and the size of the crystal increases, the kinematical theory loses its accuracy and the dynamical theory becomes necessary. The kinematical theory is then considered a good approximation to the dynamical diffraction when the crystal is small and imperfect.

Several works in the literature, such as the ones by Caticha (1993) and by Wilkins (1978), show the agreement of experimental diffraction beam intensities with kinematical and dynamical diffraction theory. Other works modify the dynamical diffraction theories to work with deformed crystals or crystals of intermediate quality (Sawada *et al.*, 2006; Pavlov & Punegov, 2000).

In the same way that there is a limit to the application of the kinematical theory, one can suppose there is also a limit to the validity of the Scherrer equation. Taking into account also the constant improvement of the crystal growth methods of polycrystalline materials in which the obtained crystals may present crystallite sizes in the order of micrometres and with high lattice perfection, it becomes necessary to pinpoint the limit of validity of the Scherrer equation.

In this work, we calculate the diffraction peak profiles using the dynamical theory of X-ray diffraction for several Bragg reflections and crystallite sizes of three crystals; Si, LaB_6 and CeO_2 . Then, we extract the FWHM and obtain the crystallite size using the Scherrer equation. We show that for crystals with linear absorption coefficients below 2117.3 cm^{-1} the Scherrer equation is valid for crystallites with sizes up to 600 nm. We also show that as the size increases only the peaks at higher 2θ angles give good results, and if one uses peaks with $2\theta > 60^\circ$ the limit for use of the Scherrer equation would go up to 1 μm .

2. Materials and methods

To obtain the diffraction peak profiles based on the dynamical theory of X-ray diffraction, the Zachariasen formulation was used [Zachariasen, 1945, equation (3.139)], given below for the symmetric Bragg case and π -polarized incident wave:

$$I_H/I_0 = |\psi_H|^2 (\sin^2 av + \sinh^2 aw) / \left[|q + z^2| + (|q + z^2| + |z|^2) \sinh^2 aw - (|q + z^2| - |z|^2) \sin^2 av + \frac{1}{2} \left| (|q + z^2| + |z|^2)^2 - |q|^2 \right|^{1/2} \sinh |2aw| + \frac{1}{2} \left| (|q + z^2| - |z|^2)^2 - |q|^2 \right|^{1/2} \sin |2av| \right], \quad (2)$$

in which I_H is the diffracted wave intensity, I_0 is the incident wave intensity and $z = \psi_0 - \alpha/2$. ψ_0 is a function related to the polarizability per unit volume for the (000) reflection and α is associated with the angular deviation from the exact Bragg position, $\alpha \simeq 2(\theta_B - \theta) \sin(2\theta_B)$. The quantity q depends on the structure factor through polarizability: $q = -\psi_H \psi_H^*$,

$\psi_H = -4\pi e^2 F_H / m\varpi^2 V$, in which F_H is the structure factor of the reflection, m , e and ϖ are, respectively, the mass, charge and angular frequency of the electron, and V is the volume of the unit cell. The quantities v and w are the real and imaginary parts of $(q + z^2)^{1/2}$, respectively.

The explicit dependence on crystallite size (D) is given in $a = -\pi kD / \sin \theta_B$, in which k is the wavenumber of the incident wave.

The Zachariasen equation is derived for a single crystal; on the other hand, the Scherrer equation is mostly used to obtain crystallite sizes in powder samples. These samples are composed of a mixture of crystallites of different forms and orientations. The spread crystallite orientation, for example, gives rise to an extra broadening of the diffraction peak, whereas the different forms give rise to asymmetric reflections and Laue cases, which also broaden the diffraction peak. We decided not to include all these effects in the calculations and to test the Scherrer equation only for a simple diffraction geometry. If this test fails, it is very unlikely that it will work when all the effects are taken into account. Therefore, one can think of our sample as an idealized polycrystalline material constituted of several crystallites in the form of parallel plates

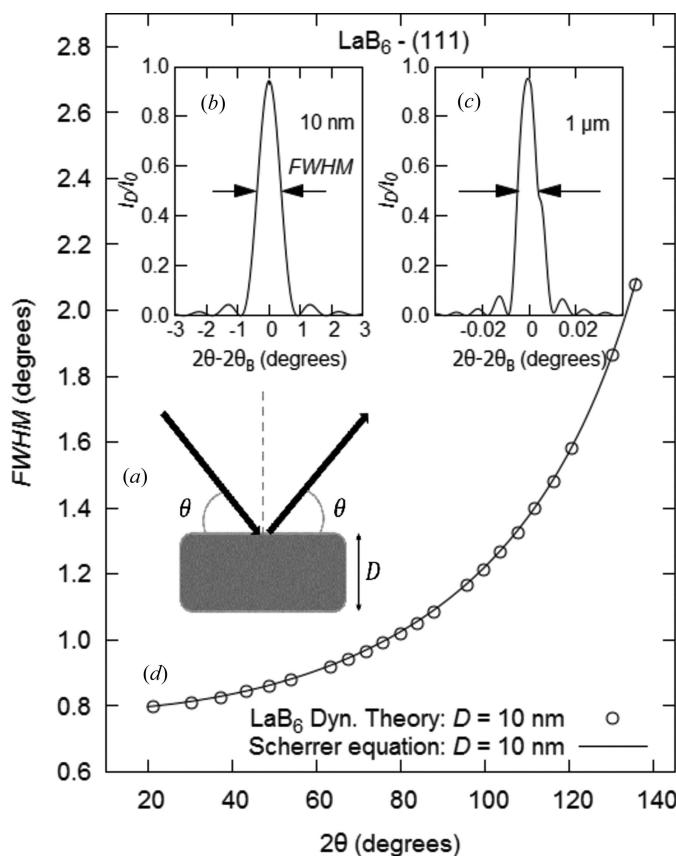


Figure 1

(a) Diffraction geometry used in the dynamical theory calculations; symmetrical Bragg diffraction. (b), (c) Examples of rocking curves obtained with dynamical theory for two crystallite sizes, 10 nm and 1 μm . I_D and I_0 are the diffracted and incident beam intensities, respectively. (d) Comparison of the FWHM extracted from the dynamical diffraction rocking curves and the FWHM obtained using the Scherrer equation for $D = 10$ nm.

with thickness D (crystallite size). All of these plates are oriented parallel to the surface of the sample and, within them, the diffraction planes are oriented parallel to their surfaces.

The dynamical theory peak profiles were obtained for three crystal structures: Si (space group $Fd\bar{3}m$), LaB_6 ($Pm\bar{3}m$) and CeO_2 ($Fm\bar{3}m$). $\text{Cu } K\alpha_1$ radiation ($\lambda = 1.540598 \text{ \AA}$) was used and the incident wave was π -polarized. Table 1 shows the list of hkl planes of LaB_6 , used in this work, along with their respective 2θ angles for $\text{Cu } K\alpha_1$ radiation ($\lambda = 1.540598 \text{ \AA}$). It also shows the respective structure factors (absolute value and complex form) and the FWHMs for three different crystallite sizes, 10 nm, 100 nm and 1 μm .

The diffraction peaks of this idealized polycrystalline sample are all due to symmetrical Bragg cases (see Fig. 1a), and asymmetric reflections, Laue cases and broadening due to particle orientation spread within the powder are neglected.

It is common to use an analytical function to fit the diffraction peak in order to obtain the FWHM, such as Lorentzians, Gaussians or their convolution. In this work, however, we simply retrieve the angle positions in which the intensity is half the maximum because we believe that doing so will not introduce any systematic error due to fit inaccuracies. In laboratory experiments, it is often not possible to perform this simple extraction because of the presence of the $k\alpha_2$, which is usually not resolved, and which gives rise to peak overlaps, resulting in a systematic error. An example of the calculated peak profiles using the dynamical theory of X-ray diffraction [equation (3.139) of Zachariasen, 1945], with an indication of the FWHM, is shown in Figs. 1(b) and 1(c).

3. Results and discussion

Fig. 1(d) shows the plot of the dynamical diffraction FWHM versus 2θ obtained for LaB_6 in the 2θ range of $20\text{--}140^\circ$, in what we call a Scherrer plot, and the calculated Scherrer FWHM with $k = 0.89$. The agreement between the two theories is very good. It is interesting to note that although the calculated value of the Scherrer constant given by James is between 0.98 and 1.3 for crystallites with cube, sphere, tetrahedron and octahedron shapes, the value we obtained, 0.89, is sufficient to achieve a good fit. This value is in agreement with the derivation given by Klug & Alexander (1974), which assumes a cubic shape.

The excellent agreement between the Scherrer equation and the dynamical diffraction theory presented in Fig. 1(d) is expected since it considered a very thin crystal slab (thickness = 10 nm). Zachariasen (1945), starting from equation (2), developed an approximation for the FWHM for thin crystals where the absorption is negligible (equation 3.159), namely

$$\text{FWHM} = 4 \left(\frac{\ln 2}{\pi} \right)^{1/2} \frac{\lambda |\gamma_H|}{D \sin(2\theta_B)}, \quad (3)$$

in which γ_H is the direction cosine of the diffracted wave and the 4 in front of the square root term is to give the full width in 2θ and from one side to the other side of the peak. For the

symmetric Bragg case, $|\gamma_H| = \sin \theta_B$, equation (3) reduces to the usual form of the Scherrer equation (1).

It is also important to note that the Scherrer equation is independent of the types of atoms inside the crystal, or even the type of crystalline lattice, if one keeps the shape of the crystal constant. Therefore, applying it to LaB_6 or any other crystal gives the same result and this is one great advantage of this equation. Fig. 2 exemplifies this property, as it shows the

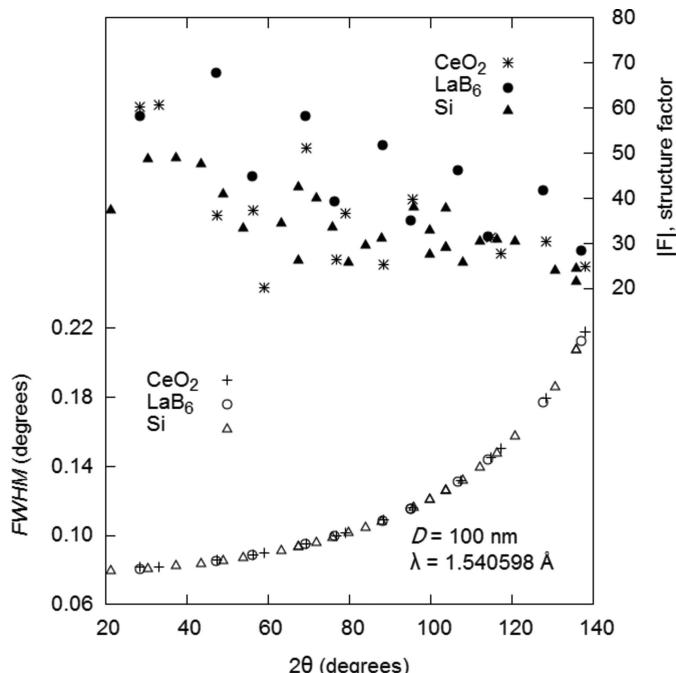


Figure 2

Top part: calculated structure factors of Si, LaB_6 and CeO_2 for $\lambda = 1.540598 \text{ \AA}$. The structure factors are very different when comparing the crystals with one another. Bottom part: the FWHM extracted from the dynamical theory calculated rocking curves for the same three crystals with $D = 100 \text{ nm}$. The FWHMs of the three crystals are the same and follow the curve given by the Scherrer equation.

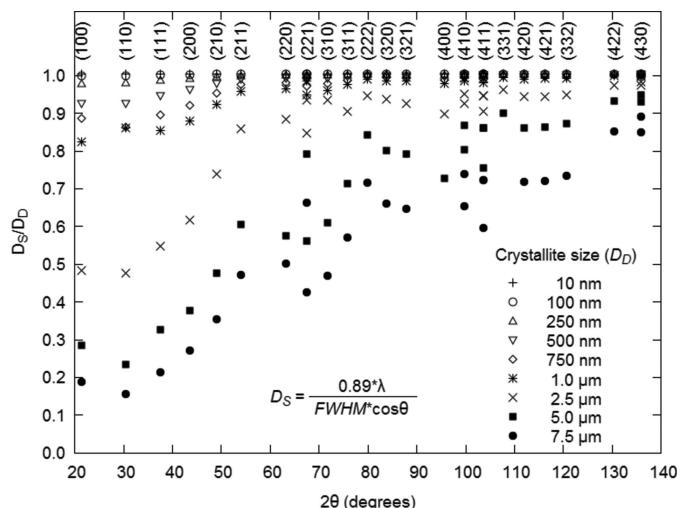


Figure 3

D_s , crystallite size obtained from the Scherrer equation; D_D , crystallite size used in the dynamical diffraction computations. This result refers to the LaB_6 crystal.

FWHM extracted from dynamical theory calculated rocking curves for three different crystals, namely Si, LaB_6 and CeO_2 . For the three crystals, the FWHMs follow the same curve given by the Scherrer equation. The top part of Fig. 2 shows the calculated structure factors and one can see that they do not have any correlation with one another. Different crystals and different structure factors produce the same FWHM.

It is safe to assume that the results shown in Fig. 2 indicate that $D = 100 \text{ nm}$ is considered small and therefore we are still in the kinematical regime. The next step is to assess this agreement for bigger crystallites. Fig. 3 shows this assessment for the LaB_6 crystal with D up to $7.5 \mu\text{m}$. In this graph we plot the ratio of the crystallite size obtained from the Scherrer equation (D_s) and the crystallite size used in the dynamical diffraction computations (D_D) against 2θ . Therefore, when the ratio D_s/D_D is equal to unity the two theories match.

The main result from Fig. 3 is that the agreement is acceptable for thicknesses up to $1 \mu\text{m}$, with a maximum difference of less than 20% between the two theories. In fact, averaging the results over all the reflections in the interval gives an even smaller error. In this range of thicknesses, from 10 nm to $1 \mu\text{m}$, we believe that the effects of the dynamical theory are not dominant, and therefore the phenomenon of X-ray diffraction can be explained by the kinematical theory, whose assumptions are very close to the ones used to derive the Scherrer equation.

From the result shown in Fig. 3 for the LaB_6 crystal, and the result shown in Fig. 2 in which the FWHM is independent of the crystal structure, we are tempted to propose the general limit $D < 1 \mu\text{m}$ for the validity of the Scherrer equation with an acceptable systematic error. It is necessary, however, to analyse the aspect of absorption. The combination of size and the absorption determine the dominance or not of the dynamical diffraction effects. This combination is usually quantified as $\mu_0 D \ll 1$, in which μ_0 is the linear absorption coefficient of the crystal. To analyse the influence of the limit $\mu_0 D \ll 1$ on the accuracy of the Scherrer equation, we compare it to the dynamical theory in three crystals with very different absorption coefficients, namely: Si (143.0 cm^{-1}), LaB_6 (1091.6 cm^{-1}) and CeO_2 (2117.3 cm^{-1}).

Figs. 4, 5 and 6 show the comparison of the crystallite size obtained by the Scherrer equation with the one used in the dynamical diffraction computations for Si, LaB_6 and CeO_2 , respectively. The agreement between the Scherrer equation and dynamical theory is very good for $\mu_0 D \ll 1$ ($\mu_0 D = 0.01$) as expected since kinematical theory is supposed to describe the diffraction phenomenon satisfactorily in this region. If we were to allow an error in the determination of the crystallite size of about 20%, then the agreement between the two theories would go up to $1 \mu\text{m}$ for Si, $1 \mu\text{m}$ for LaB_6 and 600 nm for CeO_2 . We could summarize these results and propose that the Scherrer equation gives acceptable values of the crystallite size up to 600 nm if the linear absorption coefficient does not exceed 2117.3 cm^{-1} .

The conclusion presented above takes into account all the reflections, low and high angles. One can see in Figs. 4, 5 and 6, however, that for reflections with high 2θ angles, the Scherrer

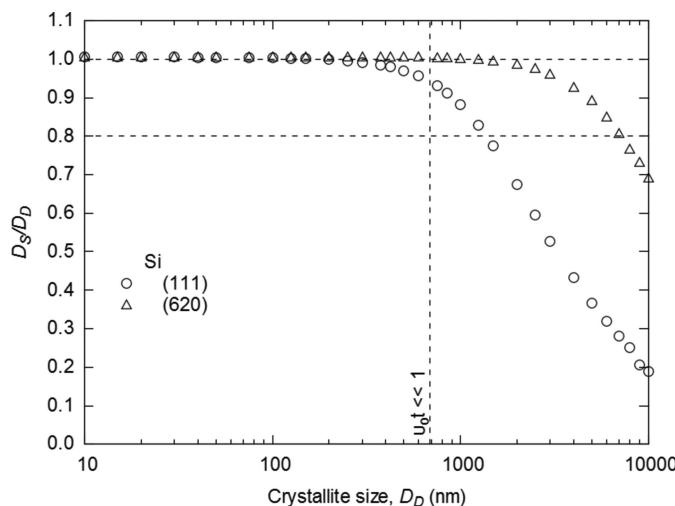


Figure 4

Comparison of the crystallite size obtained using the Scherrer equation with the one used in the dynamical diffraction computation of the rocking curves for Si. D_S , crystallite size obtained from the Scherrer equation; D_D , crystallite size used in the dynamical diffraction computations. (111): $2\theta = 28.443^\circ$, (620): $2\theta = 127.553^\circ$.

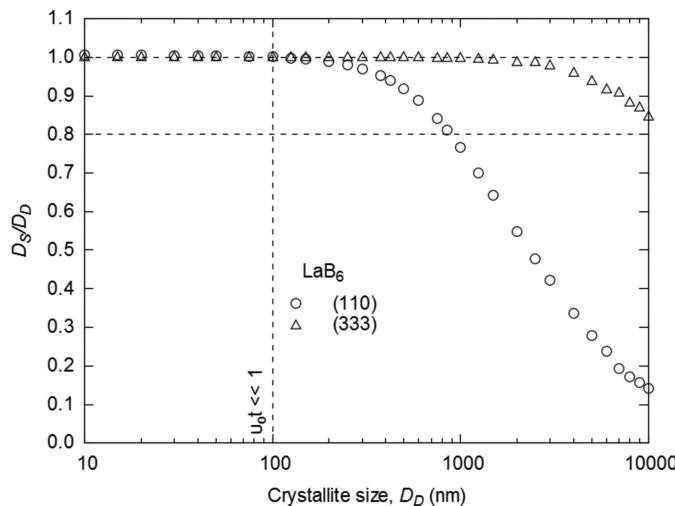


Figure 5

Comparison of the crystallite size obtained using the Scherrer equation with the one used in the dynamical diffraction computation of the rocking curves for LaB₆. D_S , crystallite size obtained from the Scherrer equation; D_D , crystallite size used in the dynamical diffraction computations. (110): $2\theta = 30.385^\circ$, (333): $2\theta = 148.432^\circ$.

equation gives better results. Therefore, we could propose that if one uses only reflections with $2\theta > 60^\circ$, the Scherrer equation gives acceptable values of crystallite sizes up to 1 μm . This limit is well above the sizes of nanomaterials, and high enough to accommodate a great number of polycrystalline materials, which could give confidence in the use of the Scherrer equation.

At this point, we would like to recall that this work was carefully designed to study only the effect of crystallite size on FWHM. Other factors which could affect the FWHM of a diffraction profile, such as apparatus resolution, wavelength spread, lattice strain and crystallite size distribution were not taken into consideration. The goal was to test the Scherrer

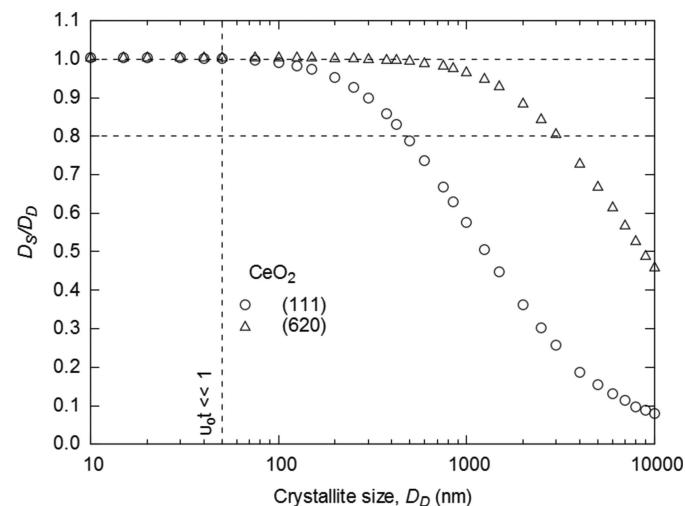


Figure 6

Comparison of the crystallite size obtained using the Scherrer equation with the one used in the dynamical diffraction computation of the rocking curves for CeO₂. D_S , crystallite size obtained from the Scherrer equation; D_D , crystallite size used in the dynamical diffraction computations. (111): $2\theta = 28.549^\circ$, (620): $2\theta = 128.408^\circ$.

equation in the simplest possible scenario to find the maximum value of crystallite size to which it can be applied. What we present is an upper limit, and experimental limits can be smaller if all the factors that affect FWHM are present.

It may not be true that the limit of application of the Scherrer equation depends only on the linear absorption coefficient. It is more important, in our opinion, to confirm that the Scherrer equation agrees with dynamical diffraction not only for $\mu_0 D \ll 1$ but also for larger values, where dynamical diffraction effects start to play a more pronounced role. Therefore, in theory, the Scherrer equation is valid for extracting crystallite size up to a certain limit.

4. Conclusions

We showed that the calculation of crystallite size using the Scherrer equation is accurate by comparing it with X-ray diffraction peaks produced by the dynamical theory of X-ray diffraction. We also established the range of validity of the Scherrer equation in terms of crystallite size and Bragg angle: for crystals with linear absorption coefficients below 2117.3 cm^{-1} the Scherrer equation is valid, with an acceptable error, for crystallites with sizes up to 600 nm. We also showed that as the size increases only the peaks at higher 2θ angles give good results, and proposed that if one uses peaks with $2\theta > 60^\circ$ then the limit for use of the Scherrer equation would go up to 1 μm .

Acknowledgements

The authors would like to thank the Brazilian funding agency CNPq for financial support (grant Nos. 306369/2014-1 and 561093/2010-5).

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