Method $FW\frac{1}{5}/\frac{4}{5}M$ of determination of the Grain Size Distribution from a Peak Profile of the Powder Diffraction Pattern

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Abstract

Manual on how to use new $FW\frac{1}{5}/\frac{4}{5}M$ method of determination of the Grain Size Distribution from a X-Ray diffraction peak profile is presented.

Introduction - existing methods

Equation and Scherrer constant for polidisperse powders

Scherrer equation:

$$FWHM = K\frac{2\pi}{< R >}$$

constraints diffraction peak width $FWHM$ and average size of crystallites $< R >$ in the powder by the constant K, known as a Scherrer constant. It has been found that peak width, thus Scherrer constant, depends on dispersion of crystallite sizes of the powder [1]:

$$\begin{aligned} FWHM(< R >, \sigma) &= K\frac{2\pi}{< R >} \\ &= \frac{2 < R >}{\sigma^2} 0.000585 \\ &\quad +0.004636 \cdot ctg\left[0.002288 + 0.00135\left(\frac{< R >^2}{\sigma^2} - 1\right)\right] \end{aligned} \tag{1}$$

Figure 1 shows Scherrer constant's dependence on normalized Grain Size Distribution width $K(\frac{<R>}{\sigma})$. In practice, one may estimate lowest value of K as c.a. 0.5 since it corresponds to $\frac{<R>}{\sigma} < 1$, which means dispersion σ larger than average grain size $< R >$. Highest value of K corresponds to the powder containing grains of identical sizes (mono-dispersive).

Sense of the Fig. 1 may be summarized as follows: **value of the Scherrer constant depends on normalized Grain Size Distribution width**. Moreover, **in real cases this dependence is very strong**. E.g. nanocrystalline powders of SiC after synthesis

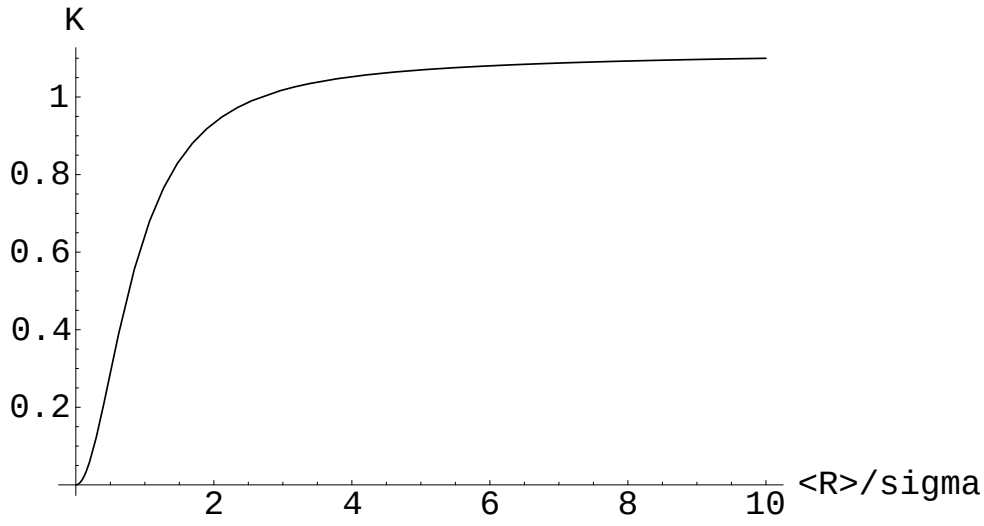

Figure 1: Scherrer constant K dependence on $\frac{<R>}{\sigma}$ of the Grain Size Distribution $K(\frac{<R>}{\sigma})$. For narrow GSDs (higher $\frac{<R>}{\sigma}$ ratio) Scherrer constant approaches value of 1.10665425 corresponding to a powder without size distribution. I.e. SiC nanocrystals have $\frac{<R>}{\sigma} \in 1 \div 1.4$. Due to variable K, crystallite size measurement may lead to errors up to 100%.

(with no segregation applied) have ratio $\frac{<R>}{\sigma}$ in range of $1 \div 1.4$, which belongs to the region of the steepest slope at Fig.1. Ratio $\frac{<R>}{\sigma}$ maintains its value for the materials of the same origin, disregarding actual size of the crystallites synthesized. This ratio changes after intentional segregation only.

Let's imagine we have synthesized a crystalline powder having some distribution of sizes. Using a system of sieves we segregate entire powder into fractions with more and more precisely defined crystal sizes. Simultaneously, using powder diffraction and Scherrer equation we want to determine average grain size in subsequent fractions. Unfortunately, it turns out that we need to use a different Scherrer constant for each fraction: lower at the beginning of the segregation (while the powder is still a mixture of small and big crystals, say $K = 0.5$), higher at the end (for mono-dispersive fractions, say $K = 1.1$), since K depends on *width* of the Grain Size Distribution.

Attempts of *precise* determination of the grain size using this method are questionable as for calculation of *exact* $< R >$ value one needs to know *exact* value of K, which depends on width of Grain Size Distribution that is the quantity we're actually looking for. Since K varies in wide range from c.a. 0.5 to c.a. 1.1, so as much as two times, this is the possible deviation of the average grain size obtained.

It must be stressed that aside from errors of order - typically - tens of %, Scherrer method is certainly the best existing, the simplest and most elegant. However, the difficulties described show that it would be nice to have a method of determination *both* parameters of the Grain Size Distribution: it's average and dispersion. Not only to reduce deviation of $< R >$ but mostly for determination of dispersion of crystallite sizes.

Method $FW\frac{1}{5}/\frac{4}{5}M$ of determination of Grain Size Distribution from a Diffraction Line Profile

Quantity of $FWHM$(*Full Width at Half Maximum*) is a commonly used crystallographic parameter, mainly due to clear definition and ease of determination. In case of crystalline powders containing grains of same size (mono-dispersive), there exists a simple relation between $FWHM$and the grain size, called Scherrer equation. In a more realistic case of polidisperse powders, single parameter $FWHM$ is not sufficient to determine both properties of Grain Size Distribution: it's average $< R >$ and dispersion σ. In order to derive two unknowns, two equations are needed - that's why determination of full Grain Size Distribution requires two line widths to be used: $FW\frac{1}{5}M$ and $FW\frac{4}{5}M$ - measured at $\frac{1}{5}$ and $\frac{4}{5}$ of line maximum, respectively.

Detailed derivation of $FW\frac{1}{5}/\frac{4}{5}M$ method is skipped here and can be found in [1].

We assume gamma Grain Size Distribution of crystallites:

$$GSD(R, < R >, \sigma) = \frac{R^{\frac{<R>^2}{\sigma^2}-1}\left(\frac{<R>}{\sigma^2}\right)^{\frac{<R>^2}{\sigma^2}}}{e^{\frac{R<R>}{\sigma^2}}\Gamma\left(\frac{<R>^2}{\sigma^2}\right)}, \tag{2}$$

We present **expressions that can be readily used in order to obtain average size**[1] **of the grain in a powder and dispersion of the** GSD **as a function of measured values of** $FW\frac{1}{5}M$ **and** $FW\frac{4}{5}M$:

$$\begin{aligned} < R > &= \frac{2BC}{FW\frac{4}{5}M} \\ \sigma &= \frac{2B\sqrt{C}}{FW\frac{4}{5}M}, \end{aligned} \tag{3}$$

where auxiliary variables A, B and C are:

$$\begin{aligned} A &= arcctg\left[277069 - 105723\frac{FW\frac{1}{5}M}{FW\frac{4}{5}M}\right] \\ B &= 0.001555 + 0.00884 \cdot ctg\left[0.002237 - 2101 \cdot A\right] \\ C &= -0.6515 - 463695 \cdot A \end{aligned}$$

Figure 2 shows examples of Grain Size Distribution determinations performed for *ab initio* calculated diffraction patterns. Theoretical diffraction patterns were obtained with log-normal Grain Size Distribution assumed. After background subtraction, widths of (111) and (113) lines have been measured at $\frac{1}{5}$ and $\frac{4}{5}$ their maximum. Then expressions 3 have been used in order to obtain GSD parameters $< R >$ i σ. Having parameters $< R >$ i σ

[1]Remainder: in this manual we operate exclusively in a scattering vector units $q = \frac{4\pi \sin\theta}{\lambda}$. Line widths $FW\frac{1}{5}M$ and $FW\frac{4}{5}M$ are expressed consequently in q, so in Å^{-1}. Respectively, quantities related to sizes in real space (e.g. $< R >$ and σ) are given in Å.

we have drawn Grain Size Distribution (2) obtained seen on right-hand side of the Fig. 2 (red curve) together with original GSD used during *ab initio* calculations of the diffraction pattern (black curve). Fig. 2 shows that gamma distribution of sizes used in derivation of the $FW\frac{1}{5}/\frac{4}{5}M$ method well reflects shape of log-norm distribution, however differs from the latter in mathematical properties, and is certainly sufficient for evaluations of experimental data. One has to state, however, that every quantitative analysis of the diffraction profile, including $FW\frac{1}{5}/\frac{4}{5}M$ method, is sensitive to any deformation of line, e.g. resulting from stacking faults or lattice strains.

Another example of usage of the $FW\frac{1}{5}/\frac{4}{5}M$ is given on Fig.3. It shows standard GSD evaluation for BN nanocrystals from profile of (111), (220) and (311) diffraction lines. Standard deviations do not exceed 1% for average sizes determined and 4% for dispersions. Such a small deviations are due to good quality of diffraction data (smooth experimental curves).

In next section a practical supplement to the $FW\frac{1}{5}/\frac{4}{5}M$ method is presented. It allows for direct application of parameters obtained during fitting Pearson7 curve to the experimental peak profile. Curve Pearson7 is commonly used in popular crystallographic software.

Application of function Pearson7 for $FW\frac{1}{5}/\frac{4}{5}M$ method

Presented $FW\frac{1}{5}/\frac{4}{5}M$ method of GSD determination is only as precise as measurements of both widths $FW\frac{1}{5}M$ and $FW\frac{4}{5}M$. This precision can be raised by fitting an analytical curve to the experimental data being evaluated, then measurement of widths of the analytical (instead of experimental) curve. One of possible choices could be popular function Pearson7:

$$P7(q,a_0,a_1,a_2,a_3) = \frac{a_0}{\left[1+4\left(\frac{q-a_1}{a_2}\right)^2\left(2^{1/a_3}-1\right)\right]^{a_3}}, \tag{4}$$

where a_0 is line intensity, a_1 - line position, a_2 i a_3 are line widths. Putting $a_0 = 1$ and $a_1 = 0$ and comparing expression (4) to $h = \frac{1}{5}$ and $h = \frac{4}{5}$ we obtain equation for the width of Pearson7 curve at $\frac{1}{5}$ and $\frac{4}{5}$ of maximum:

$$\frac{1}{\left[1+4\left(\frac{\Delta q}{a_2}\right)^2\left(2^{1/a_3}-1\right)\right]^{a_3}} = h \tag{5}$$

Interesting solutions of above equation are:

$$FW\frac{1}{5}M(a_2,a_3) = 2\Delta q = 2\frac{a_2\sqrt{-1+5^{1/a_3}}}{\sqrt{-4+2^{2+1/a_3}}} \tag{6}$$

$$FW\frac{4}{5}M(a_2,a_3) = 2\Delta q = 2\frac{a_2\sqrt{-1+\left(\frac{5}{4}\right)^{1/a_3}}}{\sqrt{-4+2^{2+1/a_3}}} \tag{7}$$

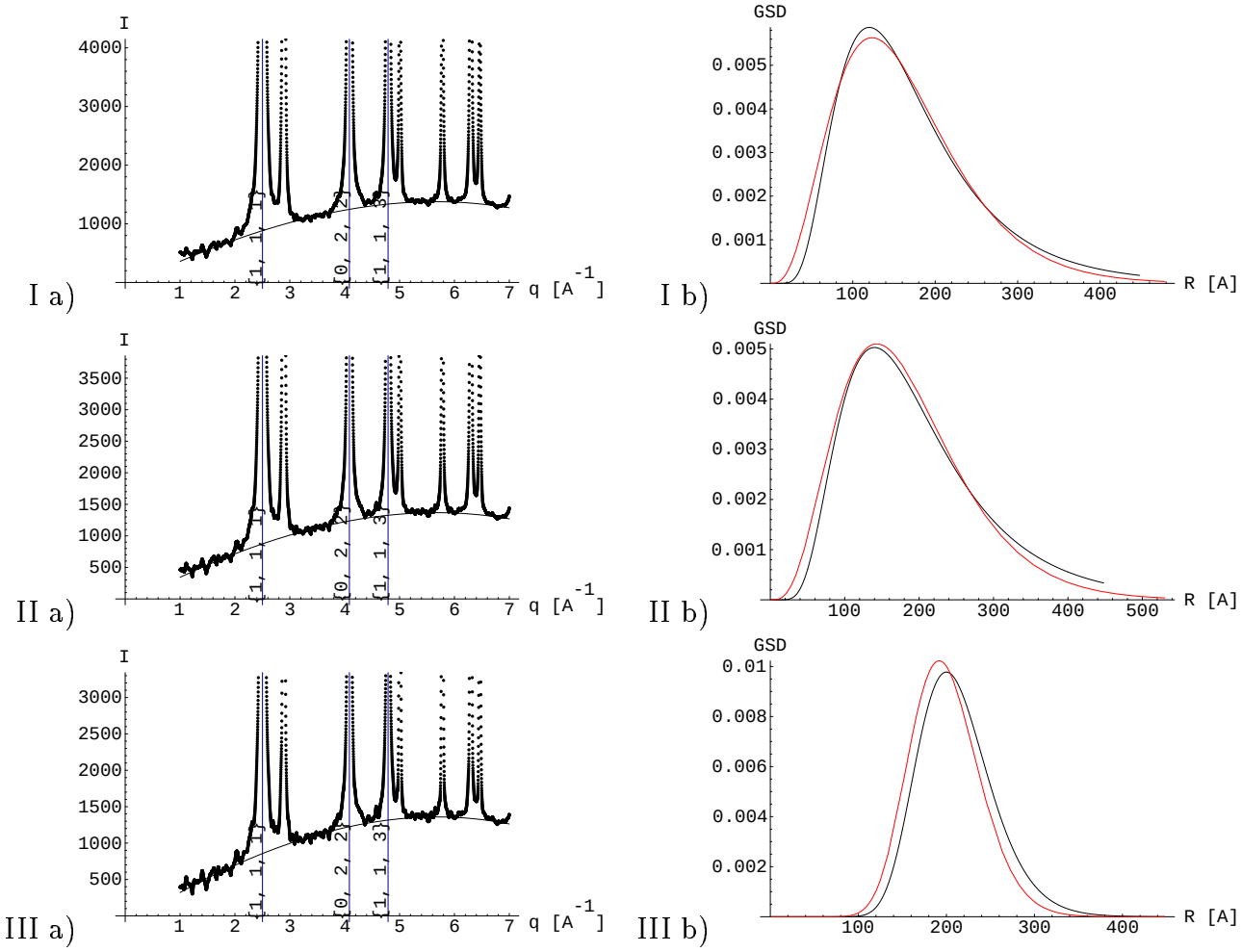

Figure 2: Examples of application of method $FW\frac{1}{5}/\frac{4}{5}M$. Powder diffraction patterns of SiC (Fig. I,II,III a) have been calculated *ab initio* for powder with log-normal Grain Size Distribution (black curve on Fig. I,II,III b). After background subtraction, widths of lines (I:(111), II:(111), III:(113)) at $\frac{1}{5}$ and $\frac{4}{5}$ of their maxima have been measured. Expressions (3) have been used to determine the GSD (red curves on Fig. I,II,III b) from the measured widths. Assumed in $FW\frac{1}{5}/\frac{4}{5}M$ method gamma distribution of crystallite sizes fairly reflects shape of log-norm distribution used for patterns calculation.

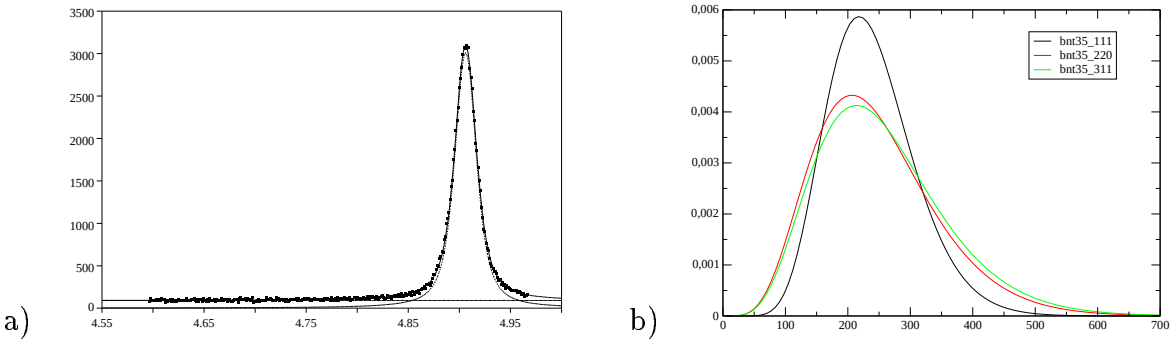

Figure 3: Examples of application of method $FW\frac{1}{5}/\frac{4}{5}M$ to the experimantal data. (a) Powder diffraction pattern of nanocrystalline BN have been evaluated (peak 220 shown). (b) Resulting Grain Size Distribution functions show anisotropy of average shape of nanocrystals evaluated. Obtained values are: $< R >_{(111)}= 238 \pm 1.5$Å, $\sigma_{(111)} = 71 \pm 3$Å, $< R >_{(220)}= 246 \pm 1$Å, $\sigma_{(220)} = 99 \pm 1.5$Å, $< R >_{(311)}= 256 \pm 1.1$Å, $\sigma_{(311)} = 104 \pm 2$Å. (a) Theoretical peak profiles calculated for obtained GSD (solid line) fits tightly corresponding experimental data (dots).

Above expressions are functions of parameters a_2 and a_3, being immediate result of fitting in a crystallographic software (e.g. PeakFit). These values $FW\frac{1}{5}M(a_2, a_3)$ and $FW\frac{4}{5}M(a_2, a_3)$ can be placed in equations (3) and we obtain a recipe how to transform Pearson7 widths to the physical quantities of $< R >$ and σ, defining Grain Size Distribution:

$$\begin{aligned} A &= arcctg\left[277069 - 105723\frac{FW\frac{1}{5}M(a_2,a_3)}{FW\frac{4}{5}M(a_2,a_3)}\right] \\ B &= 0.001555 + 0.00884 \cdot ctg\left[0.002237 - 2101 \cdot A\right] \\ C &= -0.6515 - 463695 \cdot A \end{aligned}$$

$$\begin{aligned} < R > &= \frac{2BC}{FW\frac{4}{5}M(a_2,a_3)} \\ \sigma &= \frac{2B\sqrt{C}}{FW\frac{4}{5}M(a_2,a_3)} \end{aligned} \tag{8}$$

References

[1] Roman Pielaszek, Diffraction studies of microstructure of nanocrystals exposed to high pressure, PhD thesis, Warsaw University, Department of Physics, 2003.