

Europe 600

Crystallite size estimation of nanopowders

Introduction

Polycrystalline materials contain imperfections affecting the intensity, shape and position of Bragg peaks: this departure from ideal structure, known as *microstructure*, can profoundly influence their properties. Nanocrystalline materials are characterized by a magnified “non ideal structure” on purpose, in order to get new tailored functional properties.

Nowadays, interest in nanocrystalline materials keeps growing enormously. Catalysts, nanoceramics, and nanocrystalline heat-resisting alloys are produced on an industrial scale and are widely used in the different fields of science and technology¹.

The study of microstructure by XRD, through Line Profile Analysis (LPA), is thus fundamental to understanding its relationship with the desired functional properties.

The physical broadening of diffraction lines can be roughly divided into diffraction-order-independent (size) and diffraction-order dependent (strain) broadening in reciprocal space.

Size broadening depends on the size of coherent diffracting domains (crystallites): it is not limited to grains but may include effects of stacking/twin faults too.

Strain broadening is caused by any lattice imperfection, i.e. dislocations and point defects.

It must be pointed out that crystallite size and strain are usually dispersed according to a distribution, thus the term “average” when referring to results of peak broadening analysis.

LPA has been in development since Scherrer's work on relationship between diffraction line broadening (breadth) and crystallite size (1918). Available methods can be divided in Integral Breadth (IB) and Warren-Averbach types (WA): the latter is based on peak profile Fourier coefficients and is considered the least constrained one for separation of size-strain broadening, even if it has some drawbacks and limitations related to peak overlaps. After Whole Pattern Fitting (Rietveld) analysis spread, IB method gained new appeal, due to its easy implementation in the code together with the Voigt profile function². However, it is well known that Voigtian profile fails in some circumstances: peak profiles generated directly from simple crystallite shape and size distributions have thus been proposed as a simple physically-sound alternative by Scardi and Leoni³.

Actually, current research efforts are focused on Whole Powder Pattern Fitting and Modelling (WPPF, WPPM), where a microstructural analytical model constrains analytical profile parameters in the previous, while it is directly compared and refined against experimental data in the latter⁴.

In this note, the average apparent crystallite size of a mixture of nanostructured Anatase and Rutile powders is determined first by Scherrer formula and then by microstructural calculation routine of Fullprof Rietveld program⁵. Results are compared with those from the BREADTH free software by Balzar and Ledbetter⁶

¹ E.J. Mittemeijer and P. Scardi, *Diffraction Analysis of The Microstructure of Materials*, Springer-Verlag.

² D. Balzar in *Microstructure Analysis from Diffraction*, edited by R. L. Snyder, H. J. Bunge, IUCr 1999; D. Balzar et al., *J. Appl. Cryst.* (2004) 37, 911-924

³ P. Scardi, M. Leoni, *Powder Diffraction* 21 (4), December 2006

⁴ P. Scardi et al, *Eur. Phys. J. B* 18, 23-30 (2000); *Acta Cryst.* (2002) A58, 190-200

⁵ J. Rodríguez Carvajal and T. Roisnel. *Materials Science Forum* 443-444, 123-126 (2004).

⁶ D. Balzar and H. Ledbetter, *J. Appl. Cryst.* 26 (1993) 97-103.

Summary

Nanocrystalline materials are currently an active field of research: the possibility of tailoring their functional properties, by modifying their microstructure, makes them very appealing. XRD is an effective technique to study their defective microstructure through Line Profile Analysis: Europe 600 benchtop diffractometer equipped with Celerix linear detector allows to perform Rietveld refinement with extraction of microstructural parameters in a fast and easy way.

Theoretical overview

Diffraction line profile $h(x)$ is broadened by both instrument $g(x)$ and specimen $f(x)$, so that the observed profile $h(x)$ is a convolution:

$$h(x) = g(x) * f(x)$$

In order to get information on the microstructure, the physical broadened profile must be extracted from the observed one. First, the instrumental profile must be determined for the current experimental setup either by measuring a suitable standard (e.g. NIST LaB₆) or by Fundamental Parameters Approach (FPA) simulation. Once $g(x)$ is available, either deconvolution process or fitting with a suitable analytical function/model provide $f(x)$.

In case of fitting, the peak *integral breadth* is defined as the ratio between the peak area A and its height h :

$$\beta(2\theta) = \frac{A}{h} \quad \beta(s) = \beta(2\theta) \frac{\cos \theta}{\lambda}$$

$$s = \frac{1}{d_{hkl}} = 2 \frac{\sin \theta}{\lambda}$$

Scherrer formula defines the size broadening contribution as:

$$\beta_s(2\theta) = \frac{K\lambda}{\langle D \rangle_V \cos \theta} \quad \beta_s(s) = \frac{K}{\langle D \rangle_V} \quad (1)$$

Where $\langle D \rangle_V$ is the volume weighted apparent crystallite size, which is converted to the physical one by K , if the crystallite shape is known.

Stokes and Wilson added the strain contribution to peak broadening:

$$\beta_D(2\theta) = 4e \tan \theta \quad \beta_D(s) = 2es = 4e \frac{\sin \theta}{\lambda} \quad (2)$$

where e is the maximum strain, proportional to RMS strain in case of Gaussian strain distribution.

Due to their different dependence on scattering angle, size and strain contributions can be separated, usually through Williamson-Hall⁷ plots. Integral breadth is plotted versus $s=1/d$: linear fit is performed and resulting intercept and slope provide apparent size and maximum strain, respectively. The Voigt function, a convolution

between a Lorentzian (L) and a Gaussian (G), has proven to be effective for fitting XRD peak profiles. The instrumental profile broadening can be removed from the experimental one by just a subtraction involving L and G components:

$$\beta_{L,f} = \beta_{L,h} - \beta_{L,g} \quad \beta_{G,f}^2 = \beta_{G,h}^2 - \beta_{G,g}^2$$

Its numerically-fast-to-calculate version, pseudo-Voigt, is implemented in almost Rietveld codes through TCH formula⁸:

$$\beta_L(s) = (X \sin \theta + Y) \frac{\pi^2}{360\lambda} = \beta_{L,D}(s) + \beta_{L,S} \quad (3)$$

$$\beta_G^2(s) = \left(U \frac{\sin^2 \theta}{\lambda^2} + \frac{I_G}{\lambda^2} \right) \frac{\pi}{\ln 2} \left(\frac{1}{2} \frac{\pi}{180} \right)^2$$

$$= \beta_{G,D}^2(s) + \beta_{G,S}^2 \quad (4)$$

where size (S) and strain (D) components are easily identified for both Lorentzian (L) and Gaussian (G) breadth.

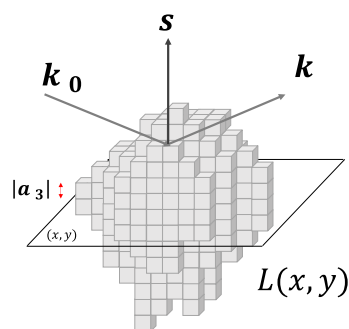
Finally, integral breadth for Voigt function is calculated as:

$$k_j = \beta_{L,j}(s) \left(\sqrt{\pi} \beta_{G,j}(s) \right)^{-1}$$

$$\beta_j(s) = \beta_{G,j}(s) (\exp k^2 \operatorname{erfc}(k))^{-1}$$

with $j=S,D$ and erfc is the complementary error function.

According to Bertaut⁹, each domain (crystallite) can be represented by columns of cells along the \mathbf{a}_3 direction normal to the diffracting planes (00l). The length between a pair of cells along \mathbf{a}_3 is $L = n|\mathbf{a}_3|$, with $n>0$.



⁷ Williamson, G. K. and Hall, W. H. Acta Met. 1, 22-31

⁸ FullProf user manual, page 21.

⁹ Bertaut, E. F. C. (1949). R. Acad. Sci. 228, 492-494.

The surface weighted column length distribution is related to the corresponding volume one by:

$$p_V(L) = \frac{L}{\langle D \rangle_S} p_S(L)$$

$$\langle D \rangle_V = \int_0^\infty L p_V(L) dL \quad \langle D \rangle_S = \int_0^\infty L p_S(L) dL$$

The Warren Averbach approach decomposes the Fourier coefficients $A[L]$ of $f(x)$ in size and strain dependent terms:

$$\ln A[L, s] = \ln A_S[L] + \ln A_D[L, s]$$

$$\ln A[L, s] \sim \ln A_S[L] - 2(\pi s L)^2 \langle \varepsilon^2(L) \rangle$$

with

$$\varepsilon(L) = \frac{\Delta L}{L}$$

representing the strain averaged over cell separation L . It is thus possible to determine A_D and A_S by plotting $A[L]$ as a function of s^2 .

Moreover,

$$\left[\frac{dA_S[L]}{dL} \right]_{L \rightarrow 0} = -\frac{1}{\langle D \rangle_S} \quad p_V(L) \propto \frac{d^2 A_S[L]}{dL^2}$$

Balzar and Ledbetter⁶ showed the equivalence of WA method with their "Double Voigt" one, if the distribution $\varepsilon(L)$ is Gaussian for each L . Average apparent size is simply given by:

$$\langle D \rangle_S = (2\beta_{L,S})^{-1} \quad \langle D \rangle_V = (\beta_S)^{-1}$$

where integral breadth related to size and strain components can be determined by fitting Gaussian and Lorentzian breadth as a function of s^2 :

$$\beta_L(s^2) = \beta_{L,D}(s^2) + \beta_{L,S} ; \quad \beta_G^2(s^2) = \beta_{G,D}^2(s^2) + \beta_{G,S}^2$$

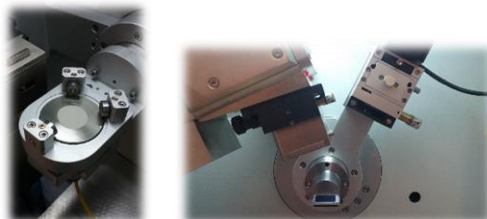
Independently of the approach, maximum detectable crystallite size by XRD peak broadening is reported to be below 200 nm¹⁰.

Product Specifications



Europe 600 is a benchtop X-Ray Powder Diffractometer for qualitative and quantitative XRD analysis of polycrystalline materials. It is available in both Theta-2Theta and Theta-Theta configurations. Its compact size and robust design enable installation and operations in a small space, with low cost of ownership and maintenance.

Thanks to the wide offer of configurations and accessories, such as high-speed detector, scintillation counter, secondary monochromator, spinner and multiple sample holder, EUROPE is a cost-effective instrument for fast-paced routine industrial quality assurance analysis and for teaching XRD at academic level.



¹⁰ A. Guinier, X-Ray Diffraction in Crystals, Imperfect Crystals and Amorphous Bodies, W.H. Freeman and Company

Experimental

Configuration:	Theta-Theta		
Goniometer radius [mm]:	160	Detector slit [mm]	5
X-Ray Source:	Cu FF	Soller slit [°]	2.3
Power settings[kV, mA]	40, 15	Filter[mm]:	Nickel 0.02
Divergence slit[°]:	0.5	Detector:	Celerix 640 1D
Soller slit [°]	2.3	Active area[°]:	2
Anti-scatter slit [°]:	0.5	Scan speed [°/min]:	1.8

NIST SRM 660 (LaB₆)¹¹ and NIST 1898¹² were chosen as standard and sample, respectively. The former is suited to determine the instrumental profile $g(x)$ (instrumental resolution function), being its contribution to peak broadening almost absent, while the latter is a mixture of nanocrystalline Anatase and Rutile (TiO₂).

Both standard and sample were hand pressed on a back-loading sample holder and then mounted on the diffractometer.

Results

The collected diffractograms were analyzed with Match! program linked to ICDD PDF 4+ Database (Courtesy of ICDD): after peak searching, profile was fitted with the built-in function to extract integrated intensity and FWHM values.

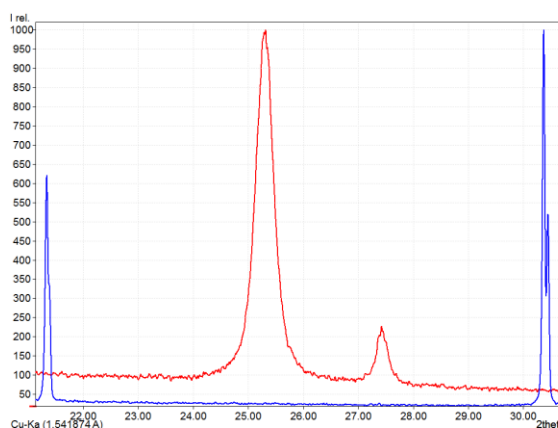


Figure 1. Detail of LaB₆ (blue) and nanocrystalline powder (red) diffractograms: the peak broadening for the latter is apparent.

¹¹ <https://www-s.nist.gov/srmors/certificates/660c.pdf>

¹² <https://www-s.nist.gov/srmors/certificates/1898.pdf>

Scherrer formula analysis

LaB₆ FWHMs for K α ₁ were stored in the corresponding *Instrumental Broadening Standard* of the *Crystallite Size estimation* routine; sample FWHMs were then processed in order to get volume weighted apparent crystallite size according to Scherrer formula, with FWHM taken as breadth¹³:

$$\langle D \rangle_V = \frac{K_w \lambda}{FWHM(2\theta) \cos \theta}$$

Results are reported in Table 1. A comparison is performed with information values reported in the NIST 1898 certificate note b page 5, where $K_w = 1$ and FWHM was uncorrected. Taking into account the roughness of estimation, the agreement is quite good for 200 and 111 directions.

Table 1. Results of Scherrer analysis for selected peaks

Apparent crystallite size [nm]				
Phase	Peak	Match!	Match! Uncorrected	Certificate Information Value
Anatase	(200)	23.6	23.3	23.6
Rutile	(111)	48.6	39.3	44.1

Converting to integral breadth, the resulting crystallite size would be 20 nm and 37 nm for Anatase and Rutile, respectively.

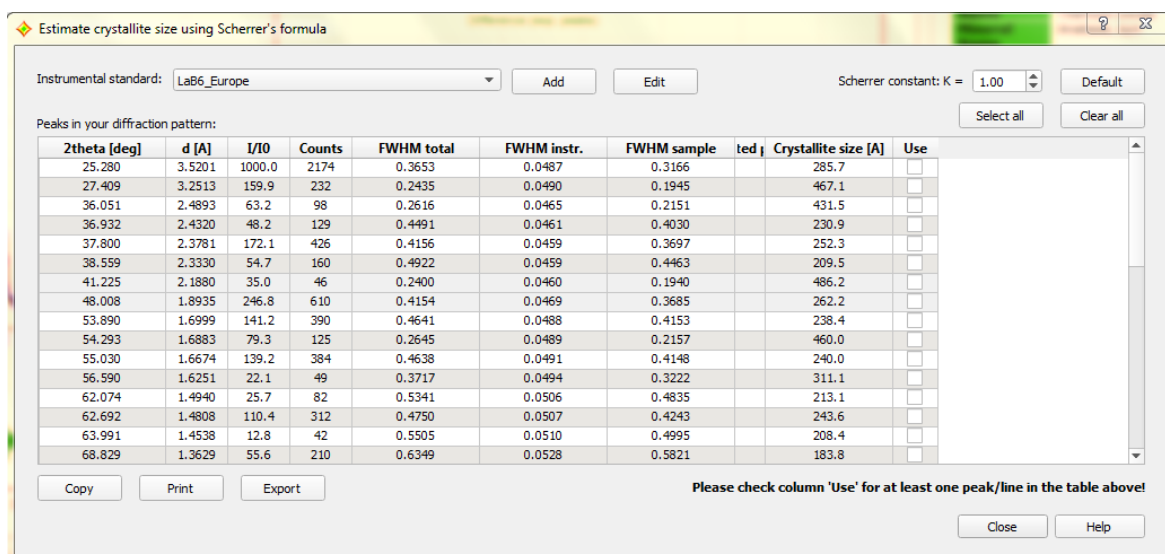


Figure 2. Match! Crystallite size routine window

Rietveld analysis

After phase identification, Match! allows to either perform directly Rietveld refinement or export the input file for exploiting all FullProf capabilities. Rietveld refinement plot is shown in Figure 3. The software takes into account the instrumental broadening provided by LaB₆ when calculating the sample one: instrumental FWHM as a function of scattering angle is reported in Figure 5. Results provided by microstructural routine are reported in Table 2.

Williamson-Hall plots can be displayed¹⁴ in Lorentz-Lorentz approximation² too, as in Figure 5. The agreement with Certificate information values is good: moreover, the same results for Microstructural routine and W-H plot suggest a minimal contribution from Gaussian component. No estimated uncertainty is provided.

¹³ J. I. Langford and J.C. Wilson, J. Appl. Cryst. (1978). 11,102-113

¹⁴ T. Roisnel and J. Rodríguez Carvajal, Materials Science Forum, EPDIC7, vols 378-381 (2001) pp. 118-123

Rietveld R-factors

Not corrected for background
 Rp: 4.33
 Rwp: 5.86
 Rexp: 5.91

Corrected for background:
 Rp: 12.3
 Rwp: 12.5
 Rexp: 12.62

Global user-weighted χ^2
 (Bragg contrib.): 1.08

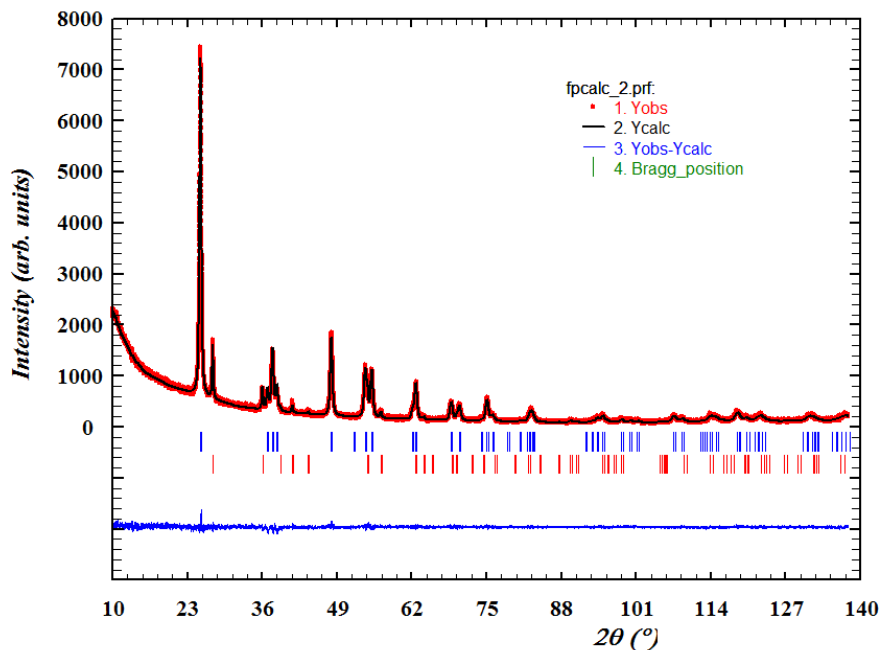


Figure 3. Rietveld refinement plot for Anatase (blue) and Rutile (red) mixture.

Table 2. Results from FullProf microstructural analysis

Phase	Volume weighted apparent crystallite size [nm]		
	FullProf	W-H Plot	Certificate Information Value
Anatase	20	20	19±2
Rutile	36	36	37±6

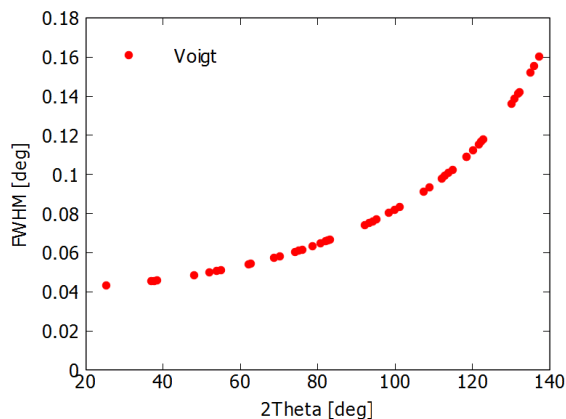


Figure 4. FWHM for LaB₆ as fitted by Match!-Fullprof

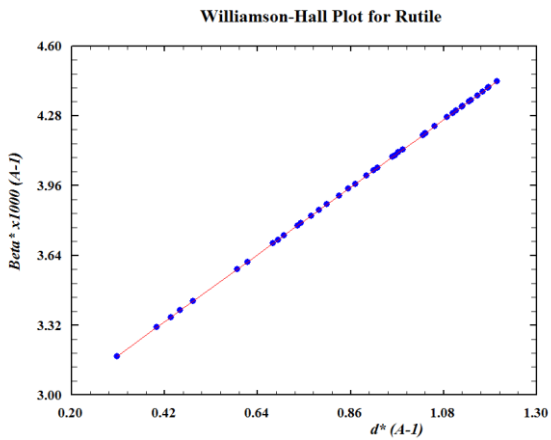
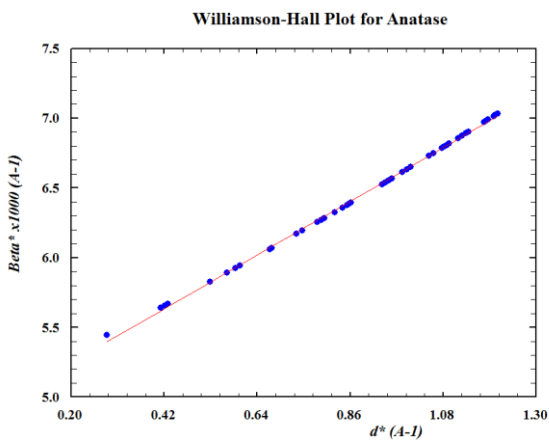


Figure 5. W-H plots for Anatase and Rutile. Lorentz-Lorentz approximation is assumed

Breadth “Double Voigt” analysis

Experimental data was analyzed with the Double Voigt approach, through Shadow Little Helper¹⁵ (SLH) and Breadth programs¹⁶. According to user manual, the LaB₆ diffractogram was fitted with a Split Pearson VII function to get instrumental profile parameters, which were then used in the convolution with a Voigt function representing the specimen contribution. The difference between synthesized profile and the experimental one is minimized through least-squares method, in order to extract the best parameters for specimen profile.

Lorentzian and Gaussian integral breadths are then passed to Breadth, which provides both column length distributions and apparent surface and volume weighted crystallite size². Results are compatible with those determined by FullProf microstructural routine and Certificate Information value.

Table 3. Results from Breadth microstructural analysis

Phase	Size [nm]		
	$\langle D \rangle_S$	$\langle D \rangle_V$	$\langle D \rangle_V$ Certificate Information Value
Anatase	14±4	20±4	19±2
Rutile	28±5	36±5	37±6

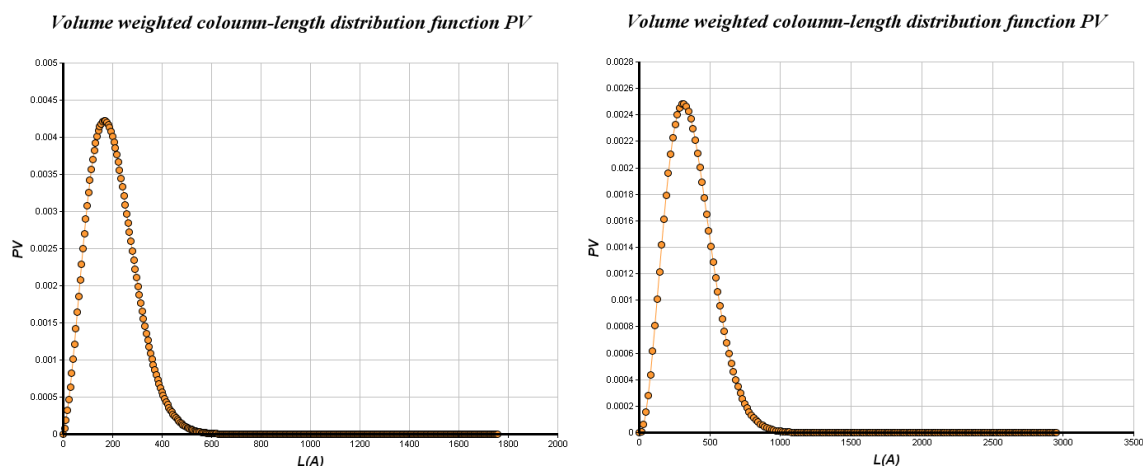


Figure 6. Anatase (left) and Rutile (right) $P_V(L)$ distribution functions

¹⁵ SLH by J. Muller, NIST Boulder, CO; Shadow program by Howard, S. A. and Snyder, R. L. (1985a). NYS College of Ceramics Technical Publication.

¹⁶ <http://mysite.du.edu/~balzar/breadth.htm>

Conclusions

Europe 600 diffractometer allowed to analyze effectively a nanocrystalline mixture of Rutile and Anatase. Apparent average crystallite size for both phases was estimated by simple Scherrer formula, integral breadth methods implemented in Rietveld refinement program and Double Voigt approach (Warren-Averbach like). Obtained results were compatible with reported information values for NIST 1898 sample.

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With 30 years of technological experience, GNR is a worldwide market manufacturer of advanced analytical instruments in Optical Emission Spectrometer and XRD / XRF domain, developing procedures of analysis for various applications, supplying the corresponding laboratory equipment and providing consulting and customer support worldwide.

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