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On the modelling of diffraction line profiles from nanocrystalline materials

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Abstract. Recent advances in Line Profile Analysis of powder diffraction patterns must be paralleled by increasing attention to the quality and quantity of experimental data. The analysis of simulated data with different noise levels demonstrates the importance of statistical quality to reveal fine details of interest in the analysis of nanocrystalline materials, like the crystallite shape. It is also shown how synchrotron radiation diffraction can improve data quality with respect to laboratory measurements, both in terms of statistical quality and in terms of accessible information.

Introduction

Powder diffraction Line Profile Analysis (LPA) is frequently used in the study of nanocrystalline materials, to estimate the size of crystalline domains and the presence of lattice defects. While the very basic ideas of LPA are quite well established and explained in many textbooks on diffraction theory and practice (e.g., see [1,2]), the subject is still the object of methodological studies [3,4].

One of the major developments in the recent past has been the introduction of full pattern analysis methods. Nowadays, most Rietveld refinement codes include some LPA, usually performed by interpreting width and shape parameters of the chosen profile functions in terms of mean size of the coherently scattering domains (crystallites) and lattice distortions (microstrain) [4,7]. Still belonging to full pattern methods, although substantially different, the Whole Powder Pattern Modelling (WPPM) is based on a fully convolutive approach [4,8]: the line profile of each peak in the powder pattern is modelled by a theoretical expression resulting from the convolution of instrumental factors and physical phenomena related to the microstructure of the studied material. This allows modelling the experimental data directly in terms of physical parameters, like e.g. mean and variance of the distribution of crystallite sizes (with several possible shapes) or type and density of lattice defects (including dislocations, planar defects, stoichiometry fluctuations, etc.) [8-11].

The flexibility, ease of application and robustness of full pattern methods like WPPM should not shadow the importance of quality and quantity of the available experimental data. The increasing performance of LPA methods must be paralleled by the upmost care in collecting high statistical quality data, with a sufficiently large number of peak profiles to properly support the reliability of a detailed LPA. Some of those issues are discussed in this short paper, the topic being still of interest for future developments of this discipline.

Effect of the statistical data quality on LPA

One of the most striking and less considered issues in LPA is data quality. The problem is of course much more general in all fields of powder diffraction, but it can be surprisingly important in the study of nanocrystalline systems, which produce intrinsically broad and weak peaks overlapping with the background signal.

Although the effects of counting statistics and background are described in textbooks [1,12], it is not so obvious how those effects influence the reliability of LPA. To discuss this point we consider

one of the major tasks of LPA applied to nanocrystalline patterns: the determination of crystallite size and shape. Starting data were simulated using the PM2K code implementing the WPPM algorithm [13], considering a system of lognormally-distributed cerium oxide spherical crystallites (mean size 4.3 nm) and a single X-ray wavelength corresponding to Cu $K\alpha_1$. Simulated data were then added different levels of random noise, generated according to the Poisson statistics of X-ray emission [1], so to produce data of different quality. Data quality is conveniently described by the following indicators (the higher the better): PB=maximum peak intensity/background and PN=maximum peak intensity/noise standard deviation. The standard deviation (SD) was referred to the difference between the data with a given noise level and the simulation without added noise.

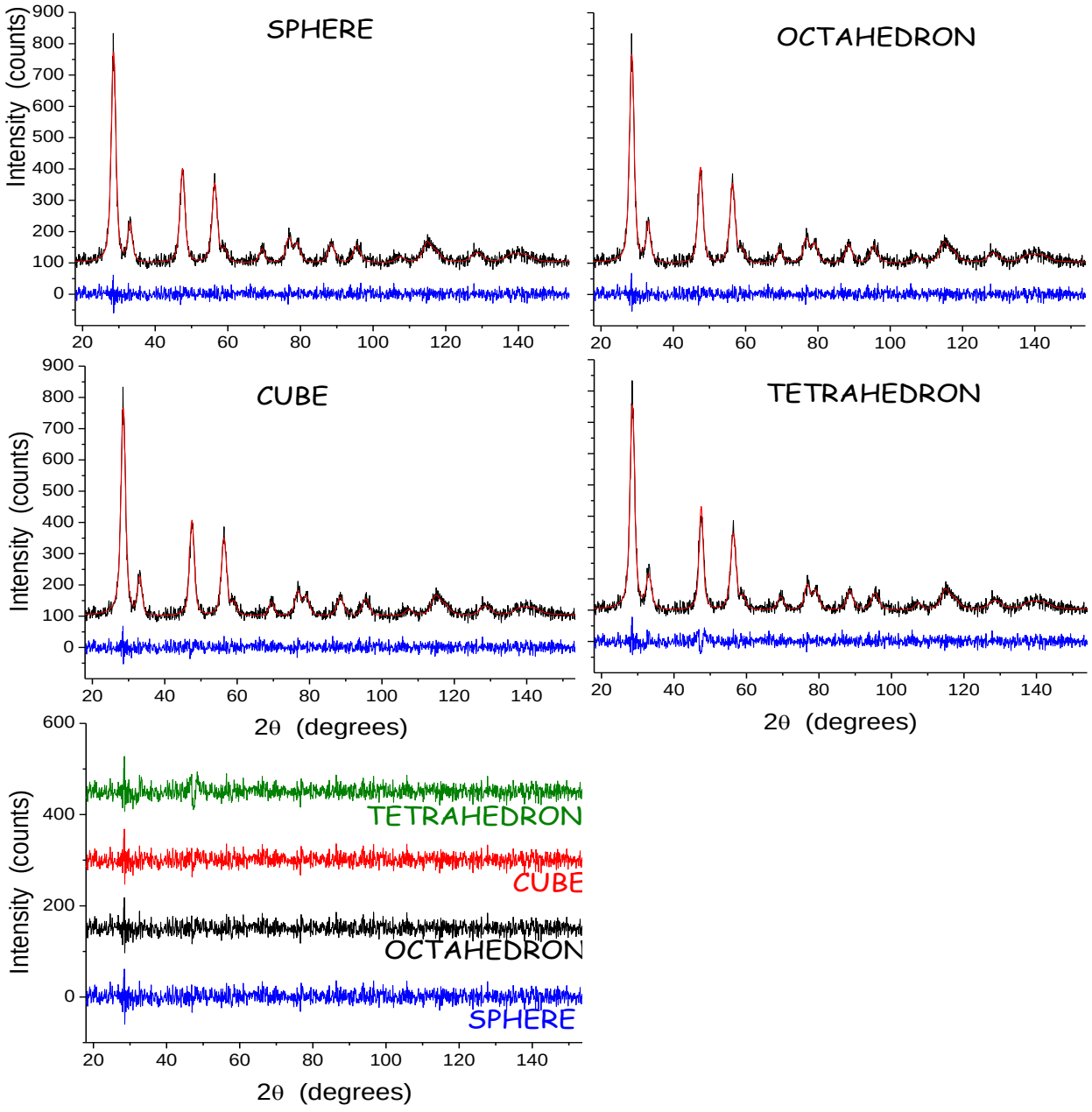

Fig. 1. Results of PM2K modelling using different crystallite shapes. Data were simulated for a powder of spheres with lognormally distributed diameters (lognormal mean μ=1.4 and lognormal variance σ=0.35), adding Poisson noise (PB=8.3, PN=72, noise SD=11.5, see text for details). Residual are also compared on a higher magnification scale (bottom left).

Simulated data were then modelled by PM2K assuming a lognormal size distribution of one of the four simple crystallite shapes: sphere, octahedron, cube, and tetrahedron. As shown in Fig. 1,

when the noise level is high (PB=8.3, PN=72) virtually any shape can reproduce the data with a sufficiently good match. By reducing the noise level, i.e. by increasing the data quality (as it would happen in practice by, e.g., using longer counting time and/or brighter X-ray sources), differences start to appear. Fig. 2 shows the same modelling on data with better statistics (PB=677, PN=1167, SD =58): the differences between the various crystallite shapes are quite evident, and the modelling clearly points out that spherical crystallites are far more appropriate to reproduce the data.

Results are summarized in Fig. 3a-b, where the Goodness of Fit (GoF), defined as sum of squared weighted difference between data and model intensity, divided by the degrees of freedom (Number of data - Number of model parameters) [14], is shown as a function of the different crystallite shapes used in the modelling, for powder patterns with three different quality levels.

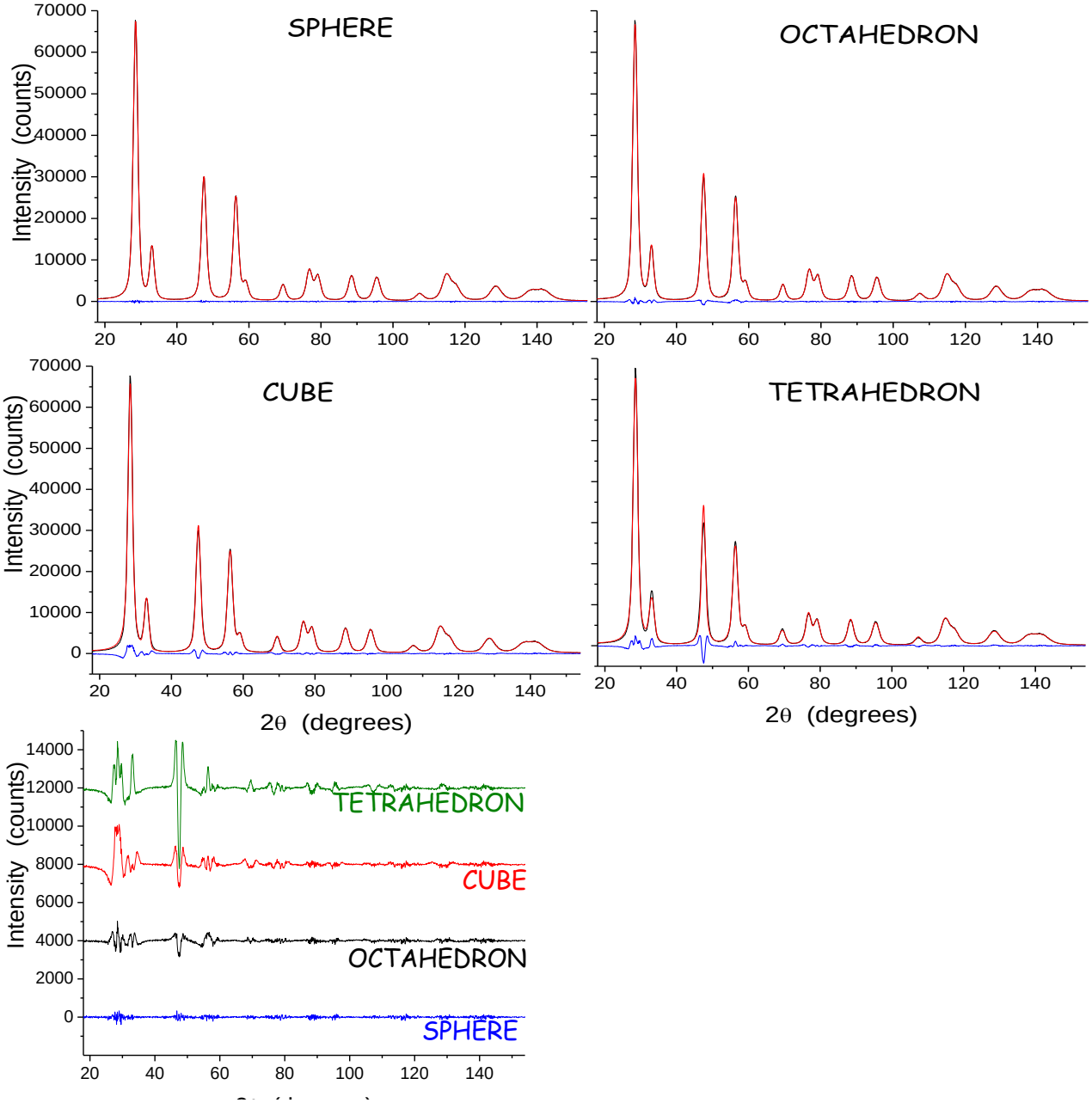

Fig. 2. Results of PM2K modelling using different crystallite shapes. Same data as Fig.1, but lower noise (PB=677, PN=1167, noise SD=58, see text for details). Residual are also compared on a higher magnification scale (bottom right).

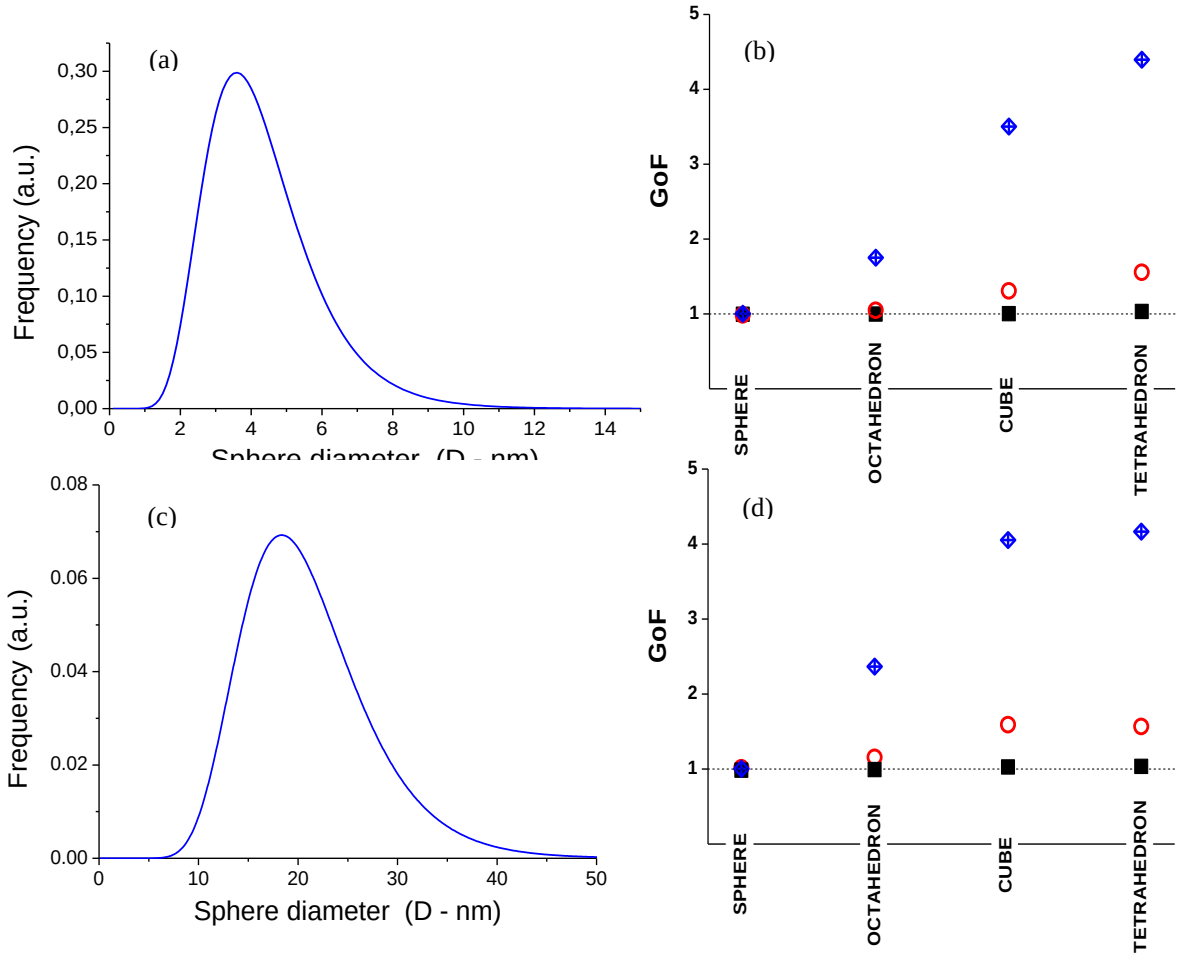

Fig. 3. Size distribution of simulated data in this study, μ=1.4, σ=0.35 (a), μ=3, σ=0.3 (c), and corresponding results (GoF) of the PM2K modelling using different crystallite shapes and data with increasing noise level (square-circle-diamond). In (b): PB=8.3, PN=72, SD=11.5 (square); PB=69, PN=330, SD=21 (circle); PB=677, PN=1167, SD=58 (diamond). In (d): PB=27, PN=223, SD=12.1 (square); PB=261, PN=1256, SD=20.8 (circle); PB=2604, PN=4849, SD=53.7 (diamond).

As discussed before, with low-quality data to the same level of agreement to the model (same GoF) is obtained, independently of the chosen domain shape. The GoF is about unity, meaning that the variance "explained" by each model is comparable with the intrinsic variance of the data. This is a statistical way to state the impossibility of distinguishing the correct crystallite shape at this noise level. Gradually improving the data quality allows one to find the optimal shape, as the modelling with the correct shape (spherical) gives a GoF ~1, distinctly lower than that obtained with other shapes. As one might expect, for a given and sufficiently low noise level the GoF decreases as a function of the number of faces of the polyhedron (tetrahedron (4) → cube (6) → octahedron (8), i.e. following the trend of the shape that increasingly better approximate a sphere).

The same analysis was repeated considering larger crystallites and a much broader distribution (Fig. 3c), a condition that should be more critical - difficult to analyze by X-ray diffraction. The patterns were normalized to the previous case, so to refer to homogeneous conditions. The results proposed in Fig. 3d show that the possibility of distinguishing the correct crystallite shape is still controlled by the statistical quality of the data. This in turn means that the best shape can still be found, provided that data quality is sufficiently good.

It is interesting to evaluate the same feature – i.e. the most appropriate crystallite shape - in a real case of study. This opportunity is offered by the data of the CPD Round-Robin on a cerium oxide

nanopowder [15]. Fig. 4a shows the data modelled by a free histogram distribution of spherical domains [16]. Data quality and agreement between data and model are sufficiently good, and the size distribution matches quite well that obtained by TEM (Fig. 4b). TEM also shows that grains are single nanocrystals, with irregular shapes not too far from an average spherical shape: mean diameters are 20.9 nm by TEM and 20.1 nm by the present analysis (PM2K-WPPM).

If the same data are analyzed under the same conditions, but testing different crystallite shapes, as in the simulations shown before, results are clearly worse. As shown in Fig. 4c, the GoF of the modelling with spheres is lower that for the other shapes, the difference being once again larger the lower the number of polyhedral faces. This further confirms the validity if using an average spherical shape, and points out that data quality should be sufficient to distinguish fine details in the powder pattern related to different crystallite shapes. It is also interesting to see the comparison between the residuals obtained when using spheres and octahedra (Fig. 4d). Despite the apparently marginal difference in GoF, it is quite clear that spheres provide a better result.

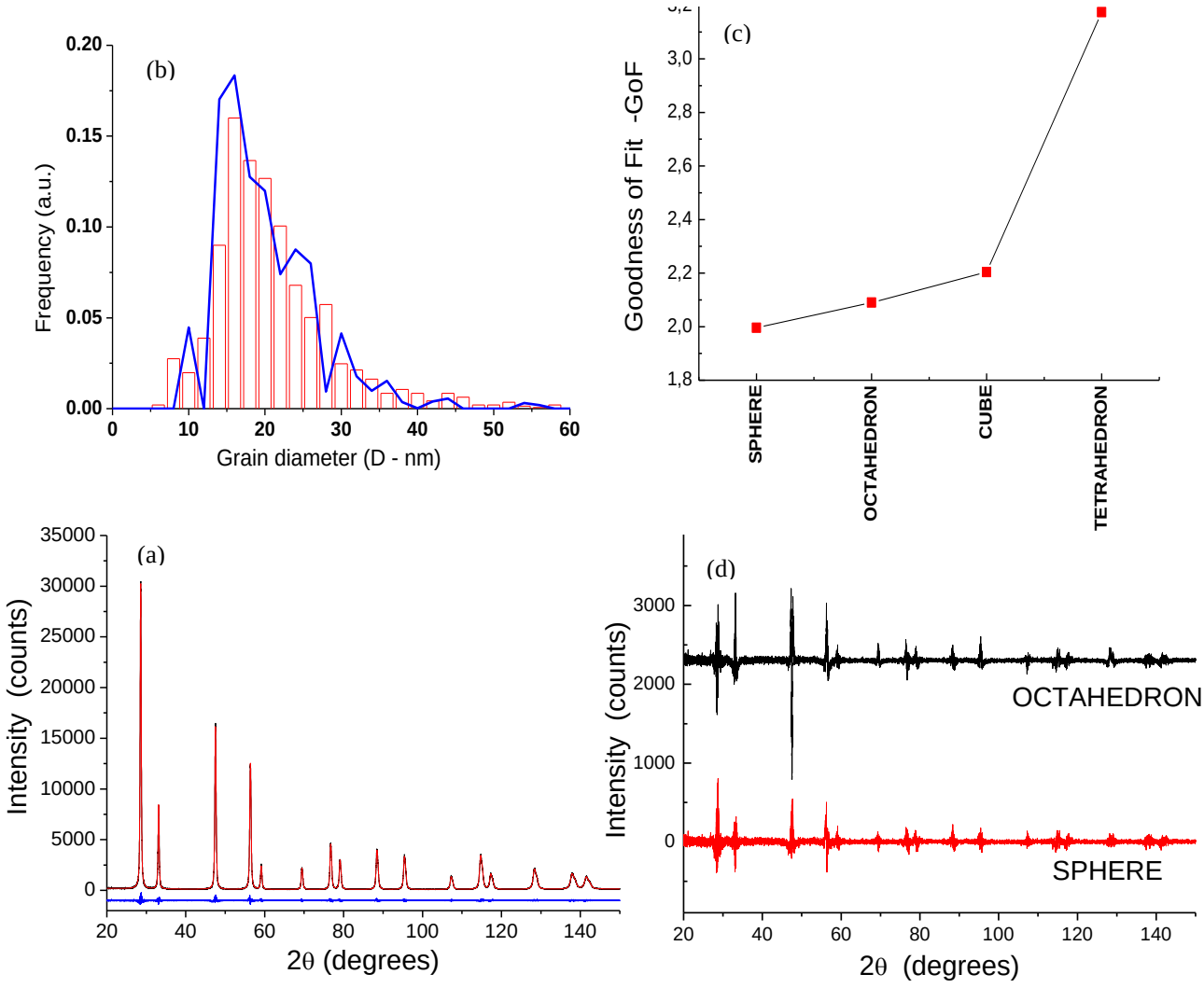

Fig. 4. PM2K results for the CPD Round-Robin ceria [15] using a free histogram distribution of diameters of spherical crystallites (a); the distribution is shown in (b) (line) together with the TEM data (column) [17] (a); GoF of PM2K modelling using spheres, octahedra, cubes or tetrahedra (c) and comparison between residuals of PM2K modeling using spheres and octahedra (d).

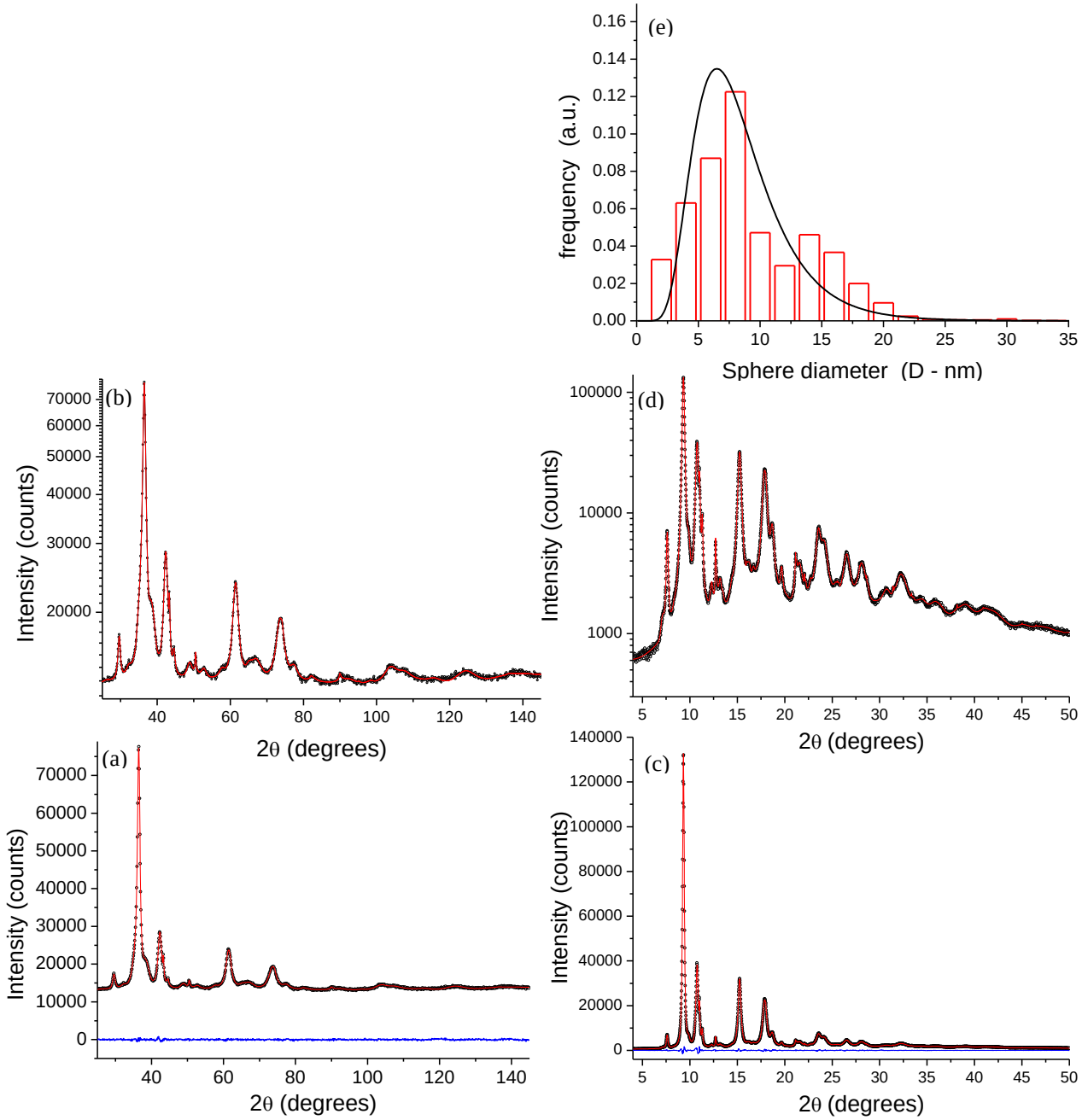

Fig. 5. PM2K results for a Cu_2O powder after extensive mechanical grinding. Data collected on a laboratory diffractometer (a, b in log scale) and at a high resolution synchrotron radiation beamline (c, d in log scale) [18]: data (point) model (line) and residual (line below). Lognormal (line) and free histogram (column) distribution of sphere diameters from synchrotron data (e).

Lab versus synchrotron data

To show the effect of using data collected under drastically different experimental conditions (a traditional lab instrument vs. a high resolution powder diffraction synchrotron beamline) we consider samples of an ongoing research on semiconducting oxides for photovoltaic applications.

Cuprite nanopowders have been produced by different methods [18], with the aim of producing so-called solar inks, i.e., dispersions of fine oxide particles in a suitable medium, to be used to make semiconducting layers in thin film devices [19,20]. Cuprite nanopowders were produced by grinding in a mechanical mill (Fritsch P9), under conditions reported elsewhere [18]. Data were

collected first on a laboratory powder diffractometer (Rigaku III-D max) using Cu radiation ($K\alpha_1$ 0.1540598 nm, $K\alpha_2$ 0.15444565 nm) with a secondary graphite bent-crystal analyzer, and then reanalyzed at the European Synchrotron Radiation Facility (ESRF) ID31 beamline for high resolution powder diffraction, using X-rays of energy around 30 keV (0.03999284 nm).

PM2K results are shown in Fig. 5 for laboratory (a,b) and synchrotron (b,c) data. Grinding conditions are such that minor fractions of CuO and of metallic Cu form in addition to nanocrystalline cuprite, so the analysis must consider three phases at the same time. Details on this research are reported elsewhere [18], but here it is interesting to point out the different quality of the results.

Both data sets provide the same qualitative information, but only the much better statistical quality of synchrotron data (see the intensity scales) and the larger quantity of observed peak profiles at a higher X-ray energy provide results of the required reliability. It is also worth noting the intense background in the lab measurement (caused by inevitable Cu fluorescence), despite the long counting time (approx 24 h), and the much lower noise and nearly absent background in the synchrotron data.

Comparing the most relevant results, the mean domain size (<D>) and standard deviation of the distribution (sd) assuming lognormally distributed spherical crystallites, are <D>=8.6 (18) nm, sd=10 (4) nm from lab data and <D>=9.8 (5) nm, sd=11(1) nm from synchrotron data (estimated standard deviations (esd) referred to last digit are in parentheses). Analogous results can be found for all parameters, including the quantitative phase analysis. The effect of having esds 400% smaller when using synchrotron data is particularly evident for the Wilkens parameter, defined as the product of the effective outer cut-off radius and the square root of the dislocation density [21]. In this case Wilkens parameter is below unity, suggesting a strong dislocation interaction, as in dislocation dipoles or pile-ups. Nothing conclusive could have been said from lab data, for which this parameter had an esd close to 100%, whereas synchrotron data give an esd of less than 20%, which makes the conclusion on the dislocation interaction much more reliable. Finally, as shown in Fig. 5e, the higher quality of synchrotron data allows the refinement of a free histogram in place of the imposed lognormal distribution. Although with some different details, the histogram is not too far from the lognormal distribution.

Summary

Results shown in this paper demonstrate the importance of data quality for a reliable LPA: using low quality data cannot give detailed information, and in general takes to no conclusive answers. Risk in using noisy data is that a modelling can support any conclusion, in particular if fine details are being examined. When working with nanomaterials, long counting times are strongly recommended to collect data with sufficient statistics. Using synchrotron radiation is of course beneficial to improve counting statistics, but is also important because data can be collected with higher energy X-rays, leading to a considerable increase in the number of observed reflections.

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