

Simulation Tools and References for the Analysis of Nanomaterials

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Summary

A series of analytical tools have been developed to analyze and characterize nanomaterials by powder diffraction methods. These tools are embedded software in the PDF-4 relational database family. The tools include algorithms to help in phase identification, crystallite size and distribution measurements, and measuring molecular orientation. In addition to these tools, a flexible interface has been developed to perform diffraction pattern simulations. The simulations can be applied to X-ray, neutron, electron and synchrotron diffraction data. A series of four different algorithms are used so that all reference materials (currently >890,000), independent of source and data type, can be expressed as a digital powder pattern nanomaterial. The expression of all references as nanomaterials enables a variety of total pattern analysis methods to use the references for the analysis of complex multicomponent mixtures. For non-crystalline materials or systems of mixed crystallinity, the ICDD (International Centre for Diffraction Data) has developed experimental full digital patterns. These patterns can also be used in whole pattern fitting methods. Reference collections targeted for experimental full digital patterns include polymers, clays, amorphous pharmaceuticals and nanomaterials where the reference patterns may contain both coherent and incoherent scattering contributions. This tool set encompasses the analysis of crystalline materials, non-crystalline materials, amorphous materials and modulated structures.

Introduction

X-ray, neutron, and electron diffraction methods are well suited for studying nanomaterials due to the nanometer wavelengths that are of the same scale as the materials being studied. Diffraction methods are sensitive to the degrees of order and disorder in solid state materials and experts use both the coherent and incoherent scatter to understand nanomaterial structures. The ICDD has worked with its international membership of scientists to develop a series of software tools and simulations to study and characterize nanomaterials. Simultaneously, the ICDD has developed reference data and editorial procedures for experimental nanomaterials as well as amorphous materials. PDF-4 products now contain both amorphous and nanomaterial references. Methods have been developed that are generically grouped under the title of “Total Pattern Analyses”, whereby the entire digital profile of a diffraction pattern is used to study degrees of order, domains sizes, and contributions from scatter and background in order to extract information about all of the materials present in the solid state independent of their crystallinity. The ability to simulate digital patterns for reference materials on the same scale as the material being analyzed allows us to study crystallite size (Scardi et. al., 2006), molecular orientation and

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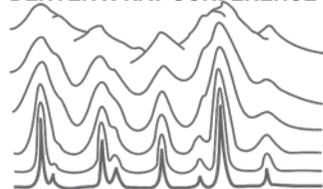
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various instrumental and specimen contributions to the coherent and incoherent scatter, allowing for the analysis of crystallinity. Digital simulation tools are used to make the analysis radiation independent so that we can use experimental X-ray, neutron, electron (Reid et. al., 2008) or synchrotron diffraction data (Kaduk and Reid, 2011) for the analyses. Multiple examples of nanomaterial analyses using X-ray powder diffraction data are shown.

Experimental

Many of the tools are now utilized as a suite of interrelated software in the Powder Diffraction File™ family of PDF-4 products. These tools were developed over a period of approximately ten years as part of a development platform in the PDF-4 relational database. Individual components have been described and published previously and the ICDD is indebted to the many international scientists who have contributed to this project. Some of the key components are described below, with details provided in the cited references.

Profile fitting and crystallite size – The software utilizes five separate profile fitting algorithms in PDF-4. Four of the profile algorithms, Lorentzian, Gaussian, Pseudo-Voigt and Modified Thompson-Cox-Hastings Pseudo-Voigt were implemented with the original PDF-4 program suite (Kabekkodu et. al., 2002). This suite included digital pattern calculations that could be modified by various instrumental profiles. In 2006 another profile function was added (Scardi et. al., 2006) that was specifically developed for the analysis of nanomaterials. This crystallite size algorithm is the preferred tool for the analysis of nanomaterials because of its accuracy and ability to use both a mean and a distribution variance based on gamma populations. As originally developed and described (Scardi et. al. 2005 and 2006) this method is optimum for the analysis of 1-10 nm crystallites where crystallite size profile measurements are in degrees and the instrumental contributions are minimal (centidegrees). The user can analyze various distributions through a user defined variance. If the crystallite size is larger than 10 nm, the software enables a selection of other profile fitting algorithms as well as the ability to input an instrument parameter file in one of several known formats (i.e. GSAS, FullProf). The design of the profile fitting module offers the user a selection of easy to use software tools that have been validated in field applications. The profile fitting modules can determine crystallite sizes, distributions and various instrumental contributions. The fitting analyses do not include considerations for other known profile contributions such as stress, strain, vacancies and dislocations and other software should be used if one is studying these line broadening effects. Since crystallite size, specimen and instrumental contributions are considered the major contributors to peak breadths and distributions, the software is an appropriate first approximation and screening tool.

Digital pattern calculations – Four algorithms are used to calculate digital powder patterns. The selection of a specific algorithm is performed automatically and depends on the type of information contained in a reference data set. The four algorithms correspond to the use of d-spacings/intensity lists, scattering factors, atomic coordinates and modulated atomic coordinates as fundamental content in the calculations. Calculations using d-spacing and intensities are typically applied to older data sets and non-crystalline systems where other information is not available. The algorithm developed by Faber (Kabekkodu et. al, 2002) utilizes an instrument function to create a profile and the instrument function can be adjusted and customized for instrumental and specimen corrections. Calculated patterns using scattering factors or atomic

coordinates use the program POWD as a computational platform (Smith, 1963, Smith et. al., 1987). This program has been updated, revised, and rewritten with 50 years of continuous usage and annual revisions by the ICDD editorial staff based on millions of pattern calculations. A custom version called SlimPOWD is used for on-the fly calculations within the PDF-4 databases. These programs are significantly different from the original platform since they have been modified and optimized by decades of practical use and have been repeatedly tested and authenticated using ISO 9001:2001 certified procedures. Many additional modules have been added to this program to examine data quality and improve accuracy. With the addition of modulated structures to the database, the ICDD collaborated with the research team of Prof. Vaclav Petricek to develop a calculation method based on the published JANA 2006 software (Petricek et al, 2014) and integral with ICDD's editorial and quality analysis system. The programs are also cross tested and evaluated for self consistency. For example, recent neutron diffraction pattern calculations in the database used multiple programs to evaluate the accuracy of the calculations.

Identification – The fundamental similarity index algorithms and historic development of this index are described in the publication by Faber and Blanton (Faber and Blanton, 2008). Adjustments were made in 2011 to optimize the algorithm which resulted in the Normalized R-Index. The adjustments were based on experimental optimization of the algorithm. This index can be used with individual references, collections of references, or in combination with the Search and Identification program SIEve+, by having the program available through different menus within the database. The advantage of using this identification method is that the method itself does not depend on crystallinity or peak positions; it is a basic pattern recognition algorithm based on a point by point comparison between the diffraction pattern of the material being analyzed and the reference. There are other pattern identification algorithms and match evaluation methods in the associated SIEve/SIEve+ software that have been described previously (Faber and Blanton, 2004). The identification algorithms use a modified classic search and identification method originally developed by Hanawalt and coworkers, Fink, and a modification of the Fink Index, Long8 (ICDD, 2014). Match evaluation methods include the similarity index, GOM (goodness-of-merit) and Pattern GOM. The GOM calculations are based on crystalline peak positions and intensities.

Wavelength and Instrumental Corrections – A user “Preferences” menu has been created to enable users to select experimental and instrumental conditions so that they can match simulations to their experimental data. By selecting various menus, the user can specify the conditions for an individual reference or apply them to a collection of references. We have previously discussed the profile and crystallite size selection. The digital pattern calculation is not a user preference and is automatically calculated based on the appropriate data in the database. The simulated profile “Preferences” menu is shown in Figure 1 and also includes selection of wavelength, radiation type (neutron, X-ray, electron), input instrument functions, optical geometry and calculation ranges and step size. Default instrumental functions for synchrotron and neutron diffraction cases are made from averaged published and experimentally determined functions for worldwide synchrotron and neutron facilities as described by Reid and Kaduk (2011) and Faber et al. (2014).

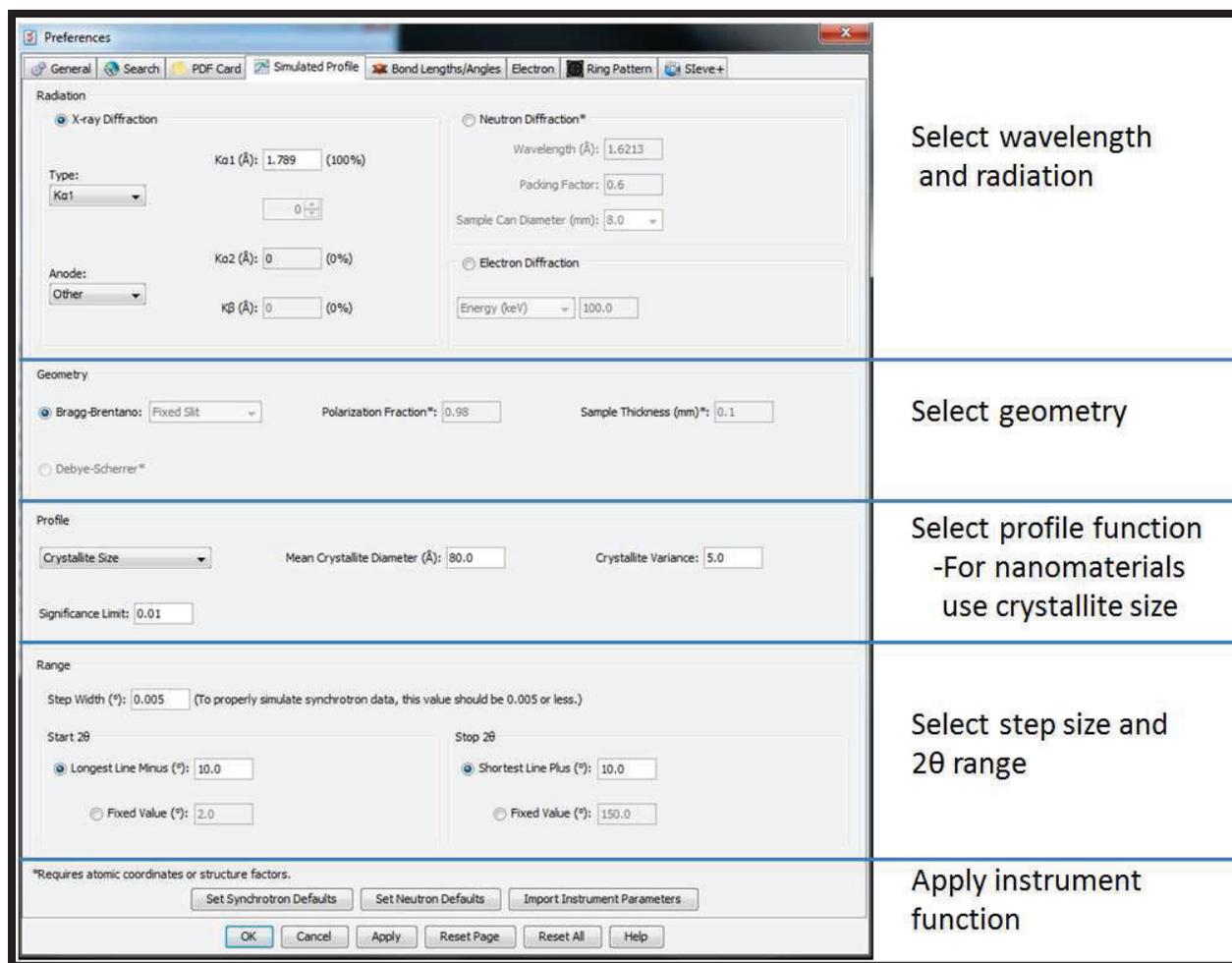


Figure 1. User's preferences for digital pattern simulations. There are 5 major sections with a general description shown on the right of the figure.

Results and Discussion

Identification – The identification of nanomaterials is made more difficult because of crystallite size effect on diffraction peak broadening. With nanomaterials in the size range of 1-10 nanometers, the broadening can occur over several degrees two theta for each indexed reflection. The net result of crystallite size broadening is that peak profiles will merge and the background will appear to rise. Both of these effects are shown in Figure 2, a nanocrystalline malachite, particularly in the region of 25-50 degrees two theta. Automated background programs will often remove intensity, mistaking crystallite size broadening for other types of background contributions. Both peak merging and increases in background means that the basic quantities of peak location and intensity are not in their specified ranges for identification processes for nanomaterials. Depending on the severity of peak overlap, this problem could be minor or debilitating to the phase identification process. For the malachite diffraction pattern shown in Figure 2, the problem would be considered moderate since there are isolated high intensity

singlet peaks even for this nano sized material. However, any mixtures containing nanomaterials would face additional overlap issues due to multiple phases.

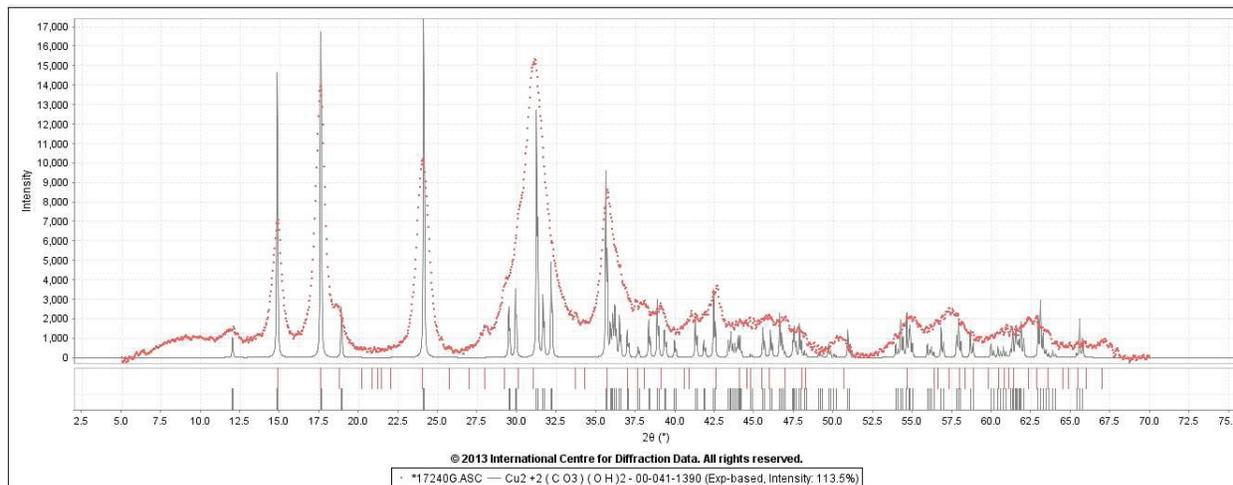


Figure 2. PDF 00-064-0862 nano malachite compared to highly crystalline malachite PDF 00-041-1390. For the nanomaterial, peaks are broadened due to crystallite size broadening. Peak overlap and broadening often results in merged profiles which can hinder automatic phase identification.

The ICDD uses three different algorithms in the identification evaluation process: A goodness-of-match (GOM), pattern goodness of match (pattern GOM) and similarity index. The first two algorithms are based on d-spacing matching (Faber et. al, 2004) producing a Goodness-of-Match (GOM). In general, the GOM will decrease with decreasing crystallite size due to the peak merging issues, where the experimental peak maxima have contributions from more than one d-spacing. The third algorithm uses a similarity type index, the Normalized R-index, which matches profiles and is independent of crystallinity, d-spacings or crystallite size. If the nanomaterial is the major phase in a diffraction pattern, the similarity index often provides the best results (Figure 3). It is also the preferred matching system for amorphous materials for similar reasons.

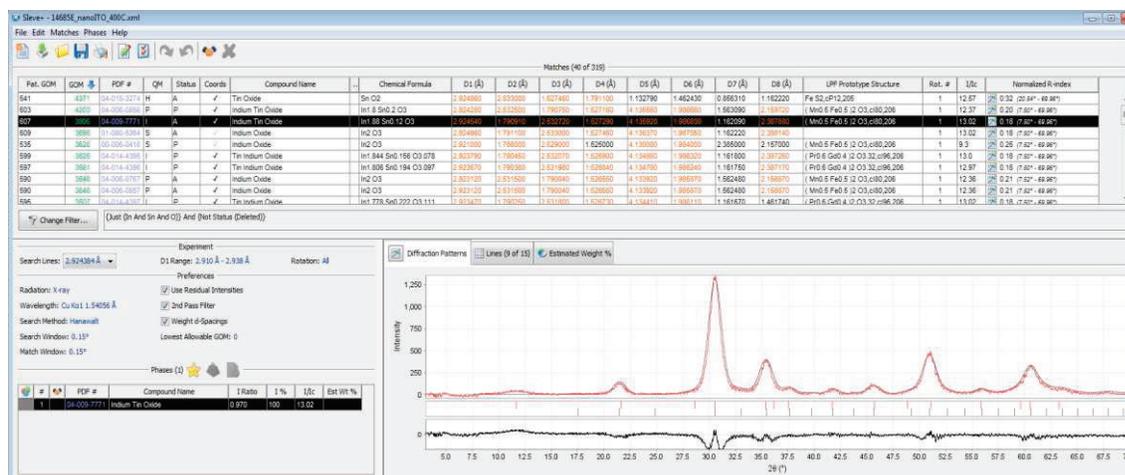


Figure 3. Diagnostic panel from the program Sieve+, demonstrating the identification of nano indium tin oxide through the use of a similarity index comparison. The pattern match between experiment and calculation is shown in the bottom right corner. The Normalized R-index calculation result is shown on the far right of the top diagnostic panel.

Particle and Crystallite Size - These terms are often confused. In this paper we will describe crystallite size as the perfect crystalline domain within a particle or grain. As defined, the crystallite size is usually smaller than a grain or particle size. If the particles are agglomerated this crystallite size should not change, where the effective particle size as measured by SAXS, laser light scattering or microscopy is significantly affected by agglomeration.

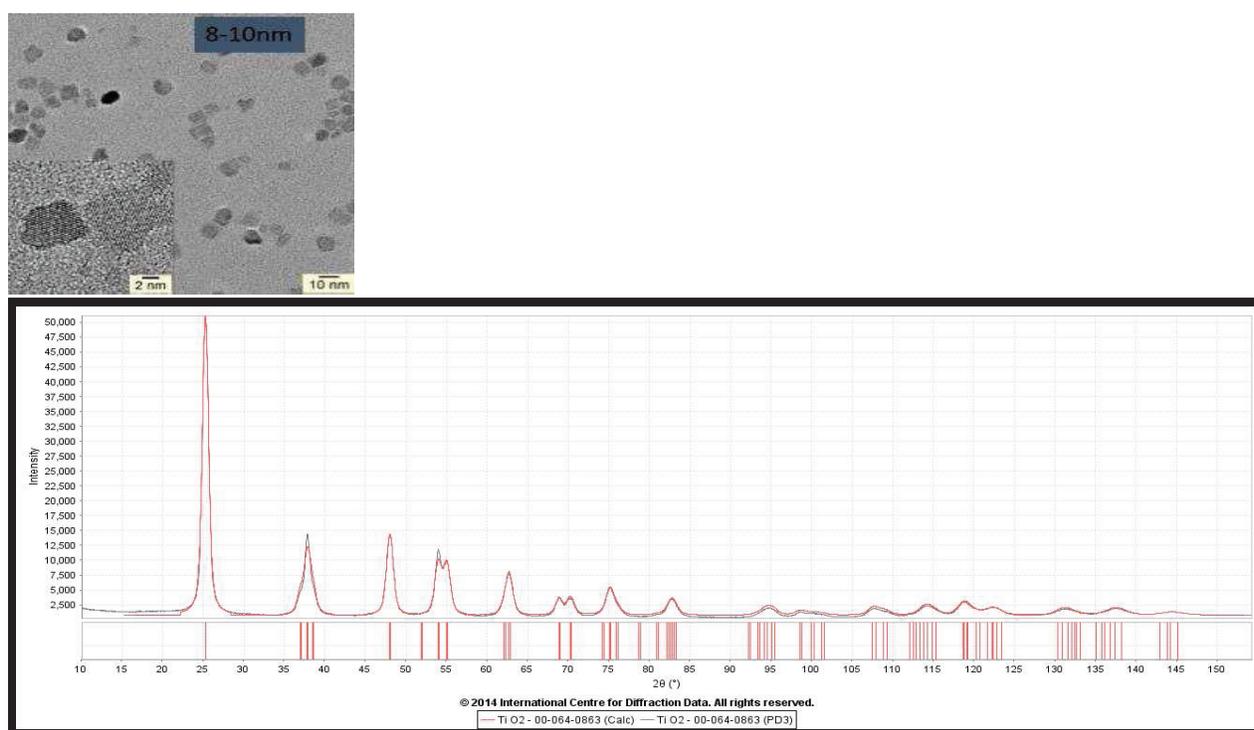


Figure 4: Comparison of experimental data (black) and 70 Å simulation (red) of anatase.

Figure 4, shows the crystallite size comparison between experiment and a 70 Å simulated X-ray diffraction pattern of anatase TiO_2 . The two patterns are nearly identical. This material exhibited a very narrow distribution as calculated by the simulation and observed by thin narrow peak top profiles. In this particular case, the anatase is of a controlled particle size as shown by TEM and dynamic light scattering results. The average crystallite size is slightly lower than the average particle size measured by TEM.

In Figure 5, we have the experimental data and crystallite size simulation for cerium oxide, CeO_2 (ceria), PDF 00-064-0737. In the data shown, a mean crystallite size of 14 Å was used with a variance of 10 Å. Caution must be used because the experimental data profiles were influenced by an appreciable low-angle background scatter from a very strong SAXS peak at 26 Å. There

was a high correlation between the background removal process and the mean crystallite size. Multiple measurements of the same data set, after background removal yielded mean sizes between 12 and 16 Å with narrow variances. This same sample is currently being analyzed by WPPF techniques (whole powder pattern fitting) that will also consider other sources of line broadening (Ungar et. al., 1999) This material is very interesting in that very small crystallites are clearly observed and measured at less than 2 nm, only a few unit cells.

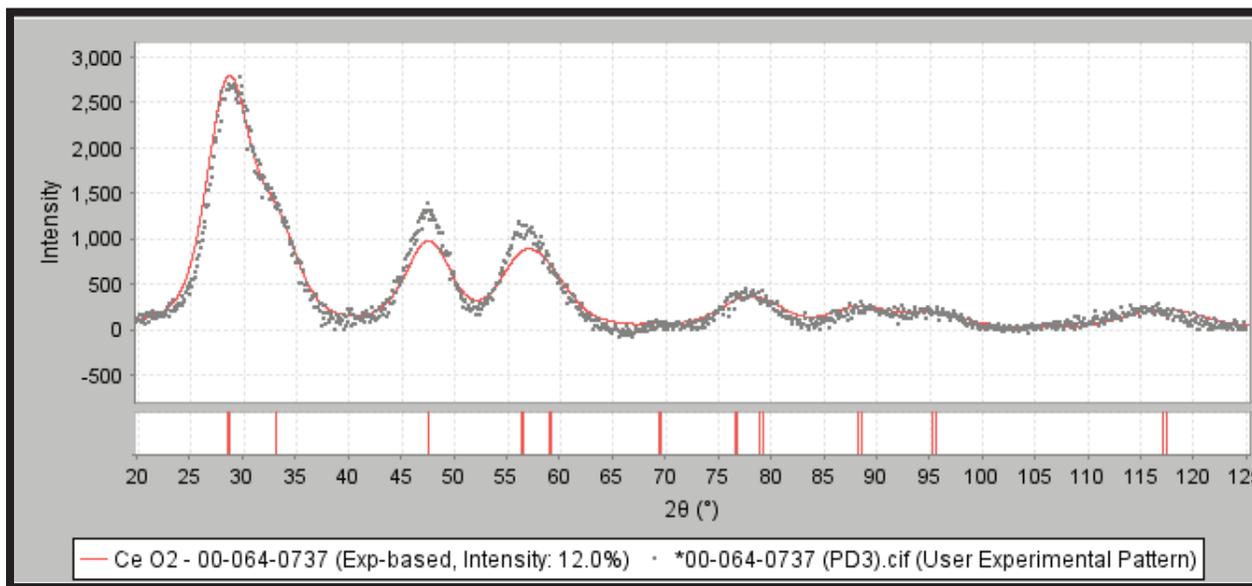


Figure 5. Comparison of experimental data for nano ceria (black dots) compared to a digital pattern simulation using a 14 Å mean crystallite size with a 10 Å variance (red line).

While the ICDD software offers the user a selection of five different profile functions and an option to provide a user defined instrumental profile function, for nanomaterial references we recommend the use of the crystallite size function. This utilizes a crystallite size and mean variation for the distribution. Figures 3 through 6 show the diffraction patterns of well characterized nanomaterials; anatase, indium tin oxide, cerium oxide and zirconium oxide. These materials are commercial products that were synthesized under conditions where the crystallite size approximates the particle size allowing crystallite size measurements to be compared to particle size determinations.

We have used the simulation tools to calculate crystallinity and crystallite size in a series of nano zirconia as a function of synthesis conditions. As crystallite size become progressively smaller, eventually the short range order in small crystallites is disrupted and we have an amorphous material. We can follow the crystallite size, molecular orientation and crystallinity in the synthetic series. The interpretation is shown in Figure 6. The amorphous pattern in the top left of Figure 6 was used in combination with the nanocrystalline simulation to interpret the amorphous, crystalline content by full pattern addition.

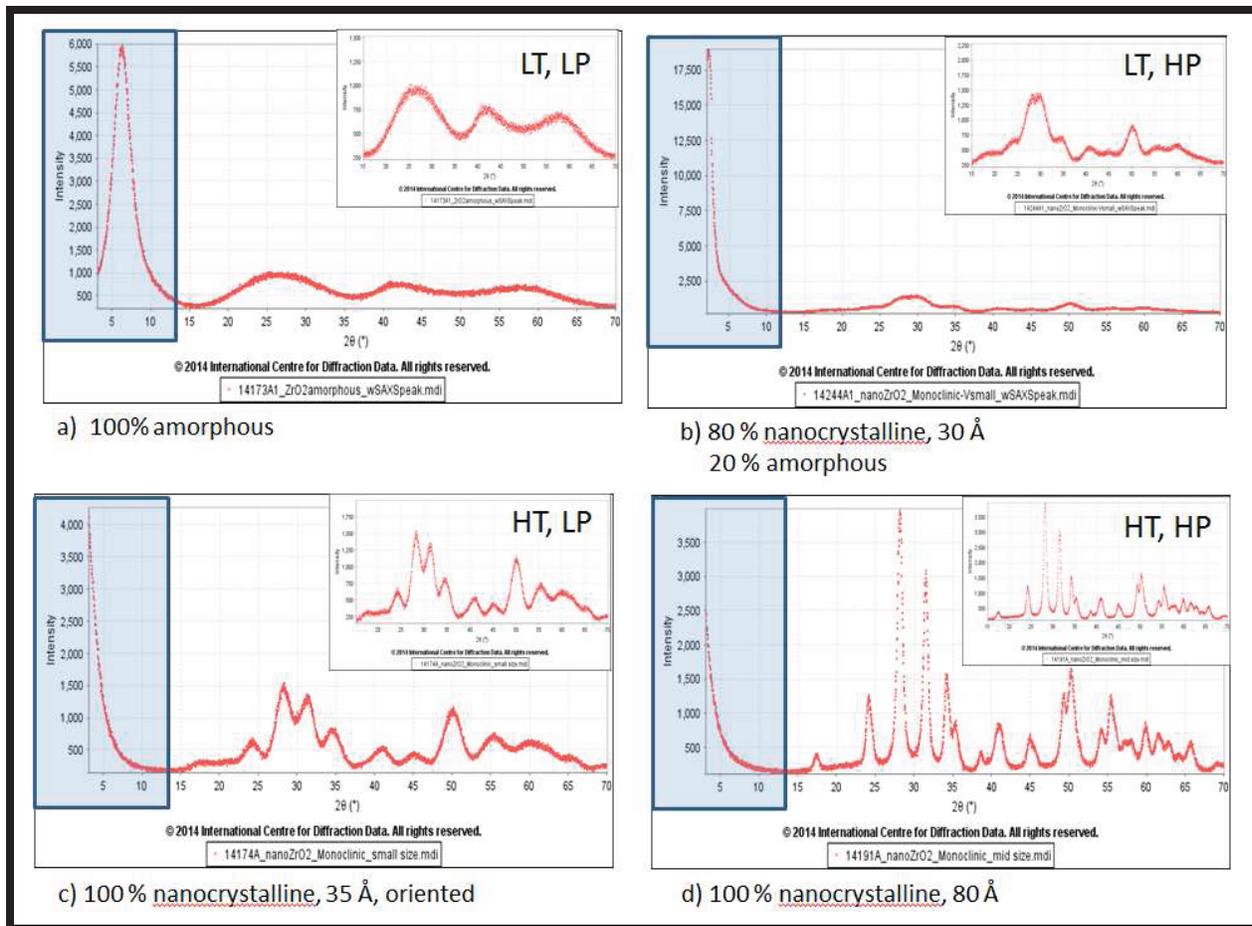


Figure 6. X-ray diffraction patterns for a series of ZrO_2 nanomaterials synthesized in a Parr reactor with varying temperature and pressure. (a) low temperature, low pressure, (b) low temperature, high pressure, (c) high temperature, low pressure, (d) high temperature, high pressure.

We can now compare crystallite and particle sizes for the materials shown.

| Material | Reference | Crystallite Size | Particle Size (Method) |
|------------------------------|-----------------|------------------|------------------------|
| CeO_2 | PDF 00-064-0737 | 14 Å | 26 Å (SAXS) |
| TiO_2 | PDF 00-064-0863 | 70 | 80-100 (TEM) |
| ZrO_2 -a | | NA | 19 (SAXS) |
| ZrO_2 -b | | 30 | 36 (SAXS) |
| ZrO_2 -c | | 35 | |
| ZrO_2 -d | PDF 01-070-2491 | 80 | 60-80 (TEM) |
| $Cu_2(OH)_2CO_3$ | PDF 00-064-0864 | 90 | |
| $In_{1.91}Sn_{0.09}O_{3.05}$ | | 70 | |

Qualitatively these results are self consistent. The SAXS and light scattering data measure average particle size, and while these samples have very small sizes, they are lightly agglomerated as shown in various TEM photos so one would expect the SAXS average to be slightly higher than the crystallite size in every case. As mentioned by the authors (Scardi et al, 2006), the crystallite size measurement does not account for instrument, strain and stress broadening. In the crystallite size algorithm employed in this study all broadening is assumed to be due to crystallite size. In the 1-10 nm region this is a reasonable assumption, where crystallite broadening is measured in degrees and most of these other contributions would be measured in centidegrees, but this assumption would not be reasonable in the measurement of larger crystallite sizes. For typical laboratory instruments the instrumental broadening as measured using an instrument standard (i.e. NIST SRM LaB₆) would be of the order of 0.08-0.12 degrees full width at half maximum height (Fawcett et. al, 1986) and substantially less for high resolution instruments and synchrotrons (Toby, 2008). This means that the algorithm would systematically calculate smaller crystallite sizes at larger crystallite size values, without an instrument correction.

Nanomaterial and Amorphous References - Nanomaterial and amorphous references are both considered because of their interrelationship. In the study of 1-10 nanometer materials, one has to consider the surface area of the particle or crystallite where large fractions of atoms are on the surface and are not part of the crystallite domain measured with a crystallite size measurement. The surface atoms may be chemically altered or different, such as a thin oxide layer on metals and non-oxide ceramics, or have various degrees of disorder, caused by a number of factors. At small sizes it is likely that the diffraction pattern exhibits both nanocrystalline coherent diffraction as well as an incoherent amorphous scatter contributed by the large number of surface atoms. One way to study this dynamic is to develop reference standards for both the nanocrystalline materials as well as the amorphous material and use a whole pattern deconvolution method to identify the composite pattern. In the zirconium oxide series shown in Figure 6, there was a distinct transition for the smallest size specimen (Figure 6a), whereby the crystalline model with crystallite size simulation could no longer account for the critical features of the observed diffraction pattern. The patterns for this series are all shown in Figure 7 on the same plot. On the bottom of Figure 7 is a highly crystalline reference pattern from PDF 01-071-2491. Both particle and crystallite sizes are progressively reduced during the experiment from top to bottom. Where observed the particle size is estimated by the SAXS peak while the crystallite size is simulated and matched to the experimental data. In Figure 7, one can see that the major peak positions align with the crystalline reference in the top 3 experimental data scans, showing that these materials are predominately nanocrystalline. The bottom experimental data set cannot be simulated using a crystalline model and it also has the smallest SAXS peak spacing at approximately 19 Å. While lack of fit to a crystalline model is a negative proof for amorphous content, the researchers were also able to thermally cycle and anneal this material back to a nanocrystalline state supporting the assignment of sample prepared at low temperature and low pressure as an amorphous material. Similar systematic synthesis series have been carried out for nano zinc oxides. These potential reference data are currently under editorial review at ICDD.

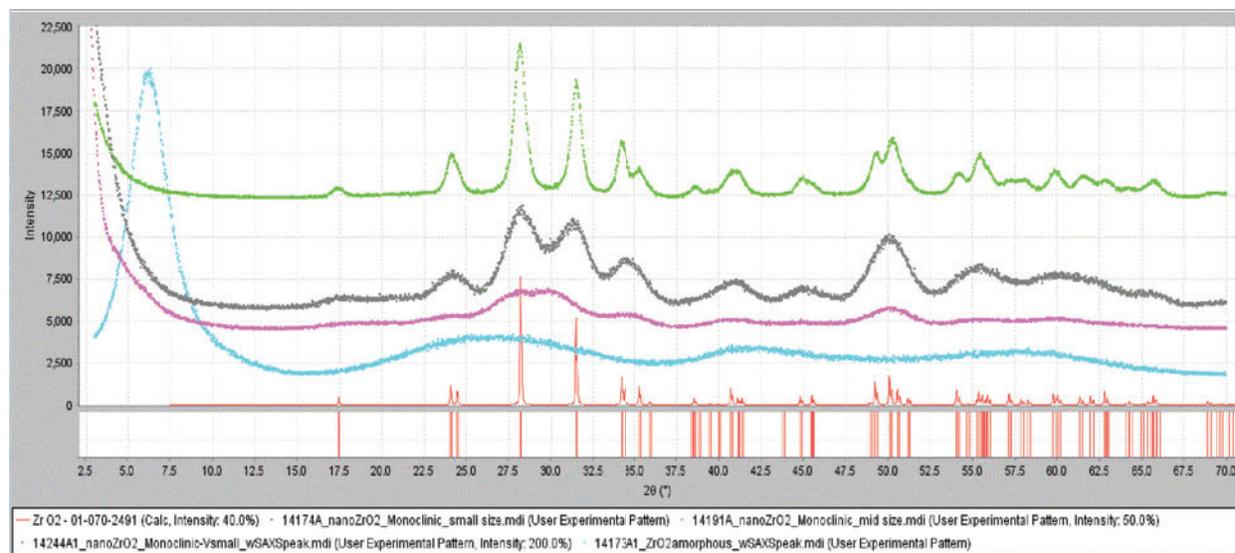


Figure 7. The X-ray diffraction patterns of a series of nano-sized zirconia's showing how the X-ray diffraction patterns change as crystallite size is reduced. The bottom pattern is the highly crystalline reference pattern PDF 01-070-2491. The experimental diffraction data are identical to Figure 6.

A challenge for ICDD editors as well as material scientists is whether we can cleanly determine when a material transitions from nanocrystallite domains to an amorphous state. This requires that we have additional information used in the editorial process to confirm the amorphous state. The nanocrystalline state can be identified and modeled by using a crystalline reference and applying the appropriate size model (see section on crystallite size). Additional information that can be used to identify the amorphous state include supporting microscopy or thermal analysis data, selective area electron diffraction (SAED) and/or controlled experimental procedures examining the pattern as a function of temperature and pressure. A pair distribution function can be used to look at the coherence length which can be compared to the crystallite size (Fawcett et al., 2013). The lack of an applicable crystalline model or a pattern fit to an amorphous model are both strong indicators of an amorphous state. However, these are conditions of omission versus a definitive proof.

For the ICDD database, supporting data are essential to the assignment of a proposed reference as a nanocrystalline or amorphous phase. The supporting data is incorporated into the PDF-4 data entry and referenced in the comment section.

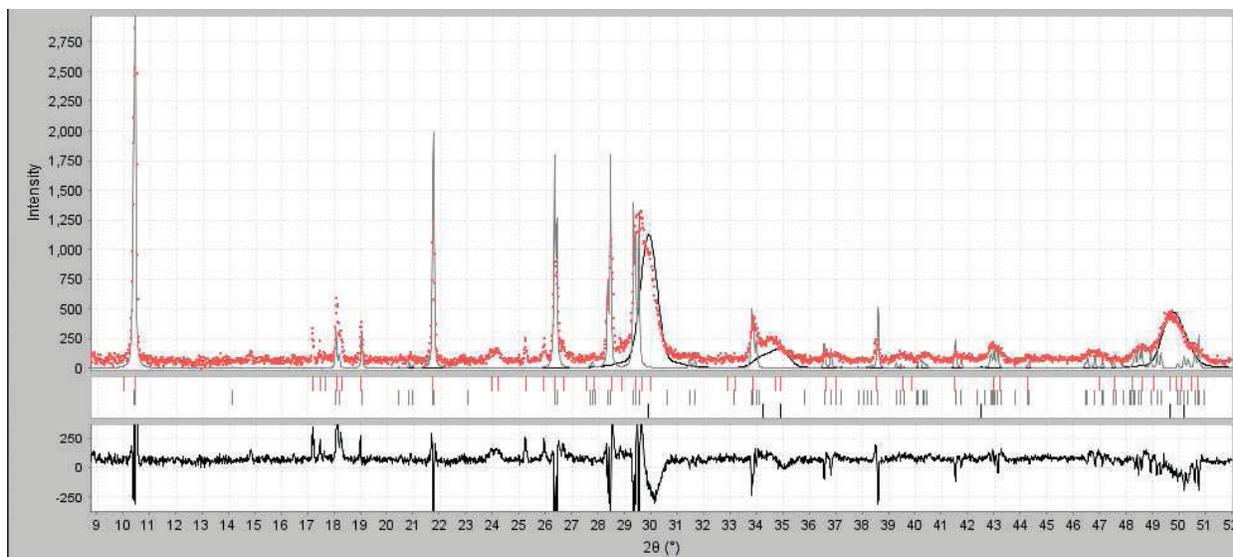


Figure 8. The diffraction pattern taken from a ground ceramic catalytic converter. The pattern exhibits the highly crystalline peaks from a cordierite honeycomb and the nanocrystalline peaks from the cerium stabilized zirconia wash coat.

Mixtures – In practice, many specimens analyzed by diffraction contain mixtures of materials having different crystallite sizes, some of which are nanomaterials. The software embedded in PDF-4 described above allows users to analyze each phase in the mixture relative to crystallite size. Figure 8 is the diffraction pattern from a catalytic converter. The pattern contains phases that are highly crystalline and others with nanocrystalline domains. Each phase can be simulated with a different crystallite size by using a drop down menu in the graphics screen that will recall the user preferences menu (Figure 1) for each phase. In the simulation, the sharp peaks arise from a highly crystalline cordierite while the broad peaks are from a 125 Å ceria doped zirconia, which is used as a wash coat carrying the precious metal catalysts. The experimental data are shown slightly above the simulations. Mixed crystallite size specimens are very common, especially in pharmaceutical formulations where celluloses are common excipients (Fawcett et. al., 2013), and in polymers (Gates et. al., 2014). Additional examples including Lipitor™ and a nano hydroxyapatite fertilizer that have been previously published (ICDD, PDF-4/Organics, 2014).

Conclusions

The ICDD and its member scientists have developed a series of analysis tools for the study of nanomaterials. All reference patterns in the PDF™ can be converted to digital patterns and then expressed as nanomaterials through a crystallite size simulation. The simulation can be adapted to various types of incident radiation and expressed in many forms of detection (i.e. diffraction patterns, ring patterns etc). Finally, experimental digital patterns are also included to provide reference data that can be used in pattern fitting methods and as validation for the simulations.

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