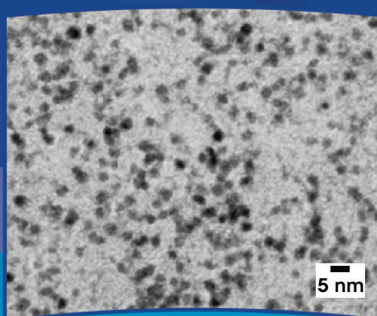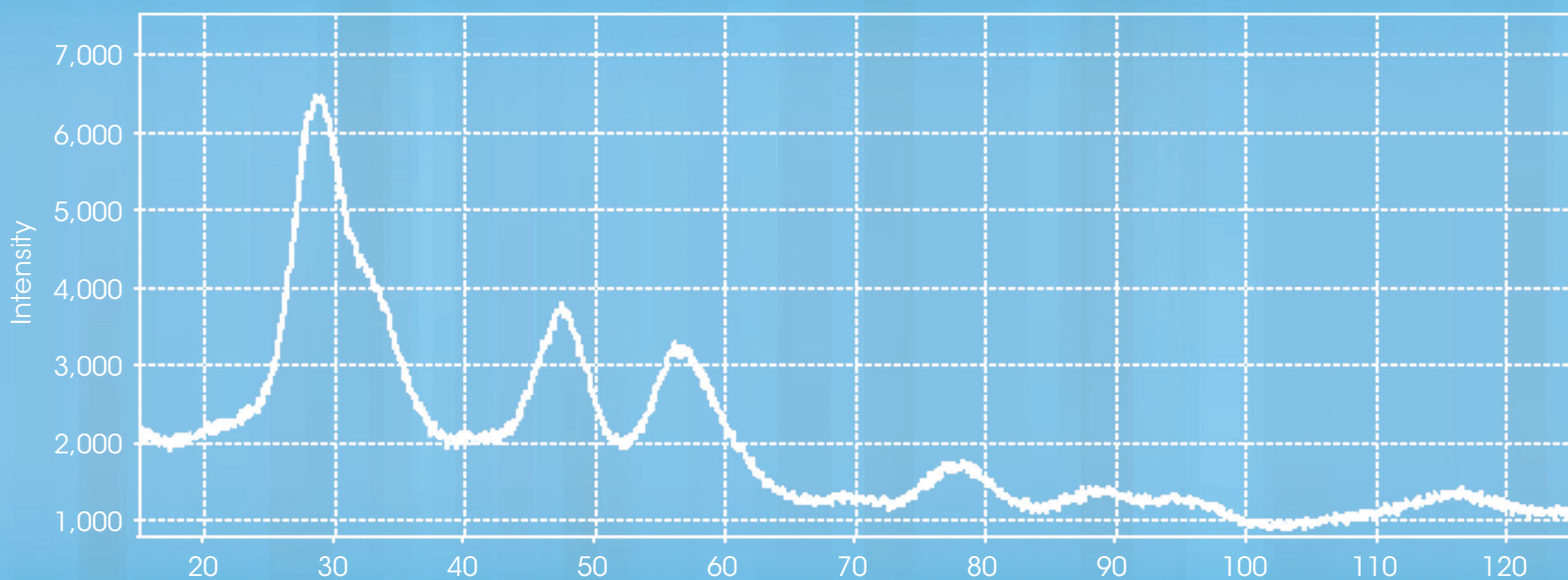# Nanomaterials

How to analyze nanomaterials using powder diffraction
and the Powder Diffraction File™

5 nm

Cerium Oxide CeO_2
PDF 00-064-0737

ICDD®
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9001:2008
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CERT. NR.
11409.1

Nanomaterials

Materials with new and incredible properties are being produced around the world by controlled design at the atomic and molecular level. These nanomaterials are typically produced in the 1-100 nm size scale, and with this small size they have tremendous surface area and corresponding relative percent levels of surface atoms. Both the size and available (reactive) surface area can contribute to unique physical properties, such as optical transparency, high dissolution rate, and enormous strength.

In this Technical Bulletin, we are primarily focused on the use of structural simulations in order to examine the approximate crystallite size and molecular orientation in nanomaterials. The emphasis will be on X-ray analysis of nanomaterials. However, electrons and neutrons can have similar wavelengths as X-rays, and all of the X-ray methods described have analogs with neutron and electron diffraction. The use of simulations allows one to study any nanomaterials that have a known atomic and molecular structure or one can use a characteristic and reproducible experimental diffraction pattern. The former are derived from single crystal structure or powder structure determinations and the latter are useful for materials with reproducible, but non-periodic structure (non-crystalline materials, dimensional, and amorphous materials). With simulations we can use the world's largest powder diffraction reference collection, the **Powder Diffraction File™ (PDF®)**, and simulate diffraction patterns for all of the database entries as representative of nanomaterials with various sizes and orientations. These tools have been verified, are easy to apply, and are useful for a wide range of applications. It is important to note that the analysts should use caution as many factors contribute to diffraction peak profiles. As several authors have noted (see references within), crystallite size methods based on line profile analysis are founded on assumptions of shape, size, and symmetry that may or may not be an accurate portrayal of the real nanomaterial. Therein lies the importance of using a multiple analytical approach, which frequently includes microscopy, dynamic light scattering, and thermal analysis. Complimentary techniques can be used to verify the model being used and validate the interpreted results.

There are many additional methods of X-ray analysis, not described in this Bulletin, that can be used for improving the accuracy of size determination of nanostructured materials. Some of these techniques are described in publications by Ungar, Scardi, Leoni and others (see references therein) and should be used if a more detailed analysis is required. In addition, a number of publications discussing line profile and nanomaterial characterization methods can be found in *Powder Diffraction* journal (http://journals.cambridge.org/action/displayJournal?jid=PDJ) and *Advances in X-ray Analysis* (http://www.icdd.com/resources/axasearch/search_based_on_vol.asp).

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About the Powder Diffraction File

The Powder Diffraction File™ (PDF®) is an analytical system of analysis. In its earliest versions established in the 1930's and 1940's, the PDF consisted of a database and series of indices used to identify unknowns. The database was organized, edited, and sorted to work intimately with the indices and a manual search and identification method (Hanawalt et. al, **1938**, Hanawalt, **1986**). The PDF analysis system evolved with time and technological advances, with more data being added and additional characterization methods developed (Jenkins and Smith, **1996**). The modern PDF can be used to analyze unknowns, quantitate a mixture, and perform a variety of microstructural analyses. It is this later set of analytical tools that will be discussed in this Technical Bulletin.

About Powder Diffraction

Powder diffraction is one of the essential analytical tools used to characterize nanomaterials. With powder diffraction methods, wavelengths of the same size of an atom are used to interrogate the atomic and molecular structure of a material. X-rays, electrons, and neutrons are most frequently employed since sources can produce monochromatic radiation with wavelengths between 0.1 and 2.0 Angstroms.
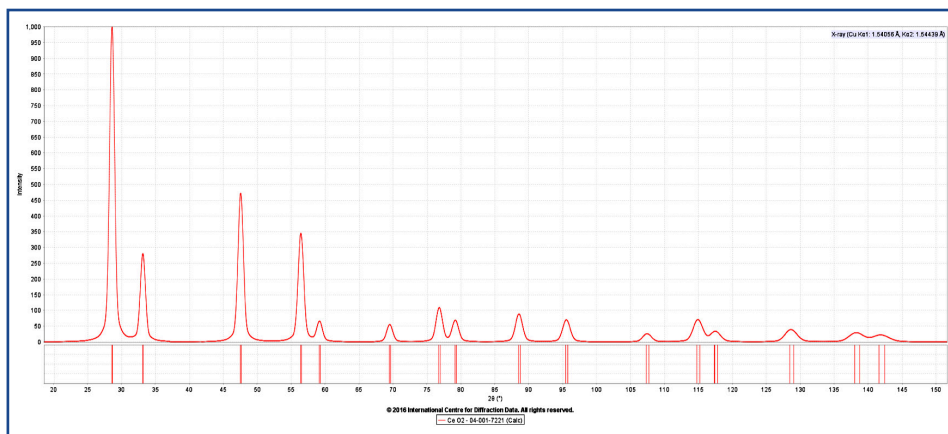
When we measure a diffraction pattern there are three critical pieces of information that we collect: peak positions, peak intensities, and peak profiles. Peak profiles are the intensity distribution over a range of positions.

Peak Positions – Interplanar d-spacings determined by the size and dimensions of the unit cell

Peak Intensity – Determined by the type and location of the atoms in the unit cell, located in specific planes, and the phase concentration

Peak Breadth – Determined by the microstructure of the material (stress, strain, crystallite size, vancancies, defects)

Analysis Tools for Nanomaterials

There are many complimentary tools that are useful for the analysis of nanomaterials. Microscopy can be used to determine grain, crystal, and agglomerate sizes. Thermal analysis, especially differential scanning calorimetry, can be used to look at reactivity, melting, and glass transition points.
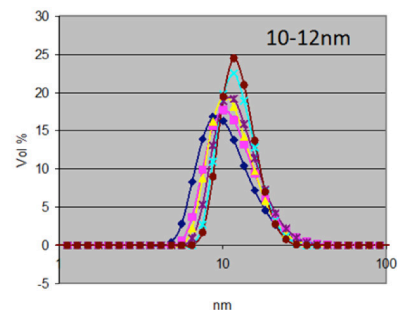
Dynamic light scattering (above) provides information on agglomeration sizes and dispersability of the nanomaterials in a variety of matrices.
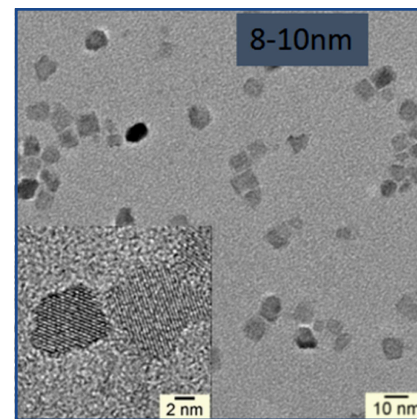
The example above is a transmission electron microscopy (TEM) photograph of a nanoanatase (TiO_2). In this photograph, one can see nominally monodispersed nanoparticles.

Crystallite Size and Particle Size

In the early years of X-ray analysis, there was considerable debate about what exactly were the X-rays measuring in a peak profile analysis. Early literature can often be confusing (as well as inaccurate) in describing grain sizes, crystal sizes, crystallite sizes, and particle sizes. Today several analytical techniques can be applied to the same material and results can be compared providing some clarity.

2 nm
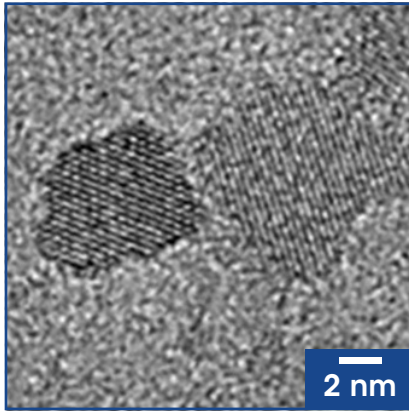
Diffraction measures the perfect crystallite domains within a grain or crystal. In the atomic resolution TEM image above, this would be the center portion of each of the two grains shown. Grain boundaries, dislocations, amorphous or atomically unsaturated surfaces all disrupt the perfect crystalline domain. In most comparative measurements of size, the crystallite size is usually the smallest size since laser scattering and microscopy often measure some degree of agglomeration not measured by XRD.

These data fundamentally relate to the arrangement of atoms in the molecular structure, the atom types and locations, and their variation about these locations caused by microstructural effects such as vacancies, modulations, stress, strain, and crystallite size.

XRPD Pattern for NaCl – An Example
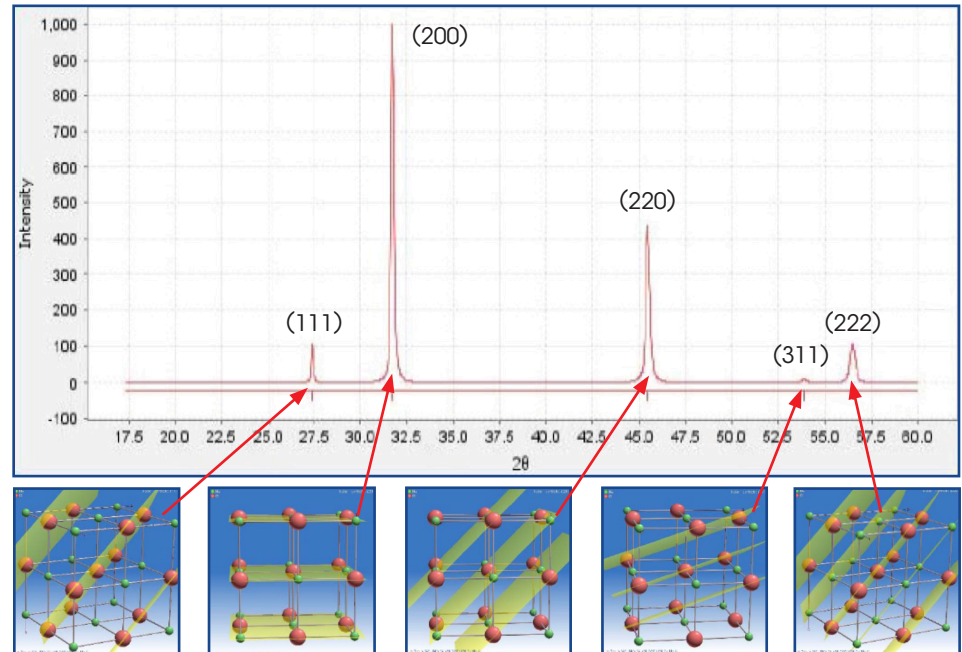
An example is given above for sodium chloride where the locations for various diffraction peaks are attributed to atom planes, described in three dimensional space by Miller Indices.

X-ray diffraction was discovered by Friedrich, Knipping and Laue in April, 1912 in a famous experiment in Munich, Germany (Friedrich et. al., **1912**). The events both before and after this amazing discovery are described in the *"Early Years of X-ray Crystallography"* by Andre Authier (Authier, **2013**). The relationships between the observed diffraction peaks, atom planes and diffraction angles was further explained by William and Lawrence Bragg (Bragg, **1912**). Von Laue received the Nobel Prize in 1914 and the Braggs received the Nobel Prize in 1915.

$$n\lambda = 2d\ \sin\Theta$$

The Bragg equation describes the relationships between the incident wavelength λ, the distance between atomic planes d, and the angle of diffraction θ.

A few years later, physicist Paul Scherrer (Scherrer, **1918**) discovered the relationship between the peak breadth β and the domain size L of the material being measured.

$$\beta = \frac{\int I(2\Theta)d2\Theta}{I(2\Theta_B)} = \frac{\lambda}{L\cos\Theta}$$

The implications of these two discoveries meant that materials scientists could use the peak profiles in a diffraction pattern to measure the domain size in specific directions (interatomic spacings) within a polycrystalline material. Using powder diffraction we can measure the size of a nanomaterial.

In the decades following the discoveries of the Bragg's and Scherrer, many scientists explored the fundamental physics of diffraction intensities and intensity profiles. Programs were developed to not only examine the crystallite size, but also to extract

other information present in peak profiles, such as stress, strain, vacancies, and dislocation populations (Unger et al, **1999**, Scardi et. al., **2005** and **2015**). Many of the critical discoveries and their publication are found in the *Powder Diffraction* journal and *Advances in X-ray Analysis*.

In total, these collective works can be used to outline two important practical considerations. First, the study of nanomaterials, crystallite sizes, and microstructure by X-ray powder diffraction is an analysis of the intensity distribution of a peak. Second, since peaks are related to specific crystallographic directions within a nanomaterial, an analysis of several peaks provides a more comprehensive picture of the microstructural characteristics of the material being analyzed. Combining these two considerations is often referred to as "total pattern analysis" where we extract as much microstructural information as we can from the entire diffraction pattern.

Total Pattern Analysis and the Powder Diffraction File

The transition of the Powder Diffraction File to a total pattern analysis database began in 2001 with the developments of relational database data storage formats and increases in storage and memory capacities for modern computers (Faber and Fawcett, **2002**, Kabekkodu et. al. **2002**). The process is still evolving today as we incorporate neutron, synchrotron, and multidimensional data. Total pattern analysis requires full pattern profiles that can be experimental powder data or calculated from structure elucidation (single crystal or powder) experiments. In both cases, it requires processing of thousands to millions of data points. The former may involve the processing of a single pattern of laboratory data, the latter could involve an analysis of thousands of patterns simultaneously with multidimensional data. It can also involve the combined use of experimental and reference data and clustering techniques (Barr et. al., **2004, 2004a**).

The first step in providing a reference database for microstructure analysis is to convert all data into a digital pattern where all peaks have profiles. (Faber, **2004, 2004a**). This is currently accomplished in the 2016 release of PDF-4+ by using 6 different algorithms. Three of the algorithms are used based on the type of source data being converted. These algorithms correspond to data sources with atomic coordinates; without atomic coordinates but with structure factors; and, older historic sources where there are no experimental data, atomic coordinates or structure factors (Fawcett et. al., **2015**). It is encouraged at ICDD to have either atomic coordinates or full experimental data patterns with new submissions so this latter algorithm is only used for older data. We also have 3 algorithms for special cases. These algorithms are only used with entries containing atomic coordinates and are applied for modulated structures (Petricek et. al. **2014**), constant wavelength neutron data, and time of flight neutron data. In each of these cases, specific scattering tables, geometric considerations, and absorption corrections are applied as appropriate (Faber et al., **2015**). The development of these algorithms and their verification has taken many years and has been the subject of several publications by a variety of authors.

Pair Distribution Function Analysis

Pair distribution function analysis is another diffraction method that is useful for studying nanomaterials (Petkov et. al., **2013**, Egami and Billinge, **2012**). The pair distribution analysis uses a Fourier transform of the diffraction pattern to calculate nearest atom distances (the peaks) in a material as a function of interatomic separation.
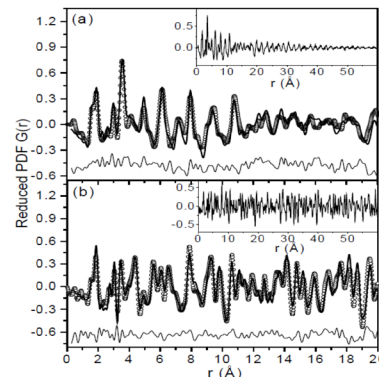
For a crystalline material the pair distribution function analysis might look like the patterns above.
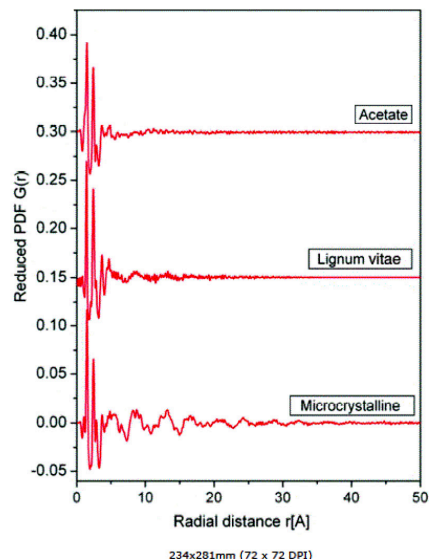
For nano and amorphous materials the pattern dampens at extended distances since there is no long term order in the particle. In the examples above, the top data set is from an amorphous material and the bottom data set from a nanomaterial.

Amorphous Materials

By definition, nanomaterials are materials of nanometer size. Materials of this size have very large surface areas and a characteristic of these groups of materials is that the surface atoms can be a significant weight and volume percentage of the entire specimen. Oftentimes, these unusual surface characteristics contribute significantly to the unusual properties exhibited by nanomaterials.

The crystalline lattice is no longer perfect at the surface. Surface atoms can be disordered, reacted*, or easily chemically altered. Therefore, it is very common, almost expected, to see contributions from amorphous scatter in the pattern of a nanomaterial.

The study of nanomaterials by total pattern methods often involves both an analysis of the nanocrystalline component and an analysis of amorphous components.

Amorphous scatter can also be characteristic due to nearest neighbor atomic scattering. The PDF also has references of stable amorphous materials.

*Nanoceramic oxides frequently react with moisture and have surface hydroxyl groups. Nanoceramic nonoxides typically have a surface layer of oxides from reaction with the air. The hydroxyl groups can be detected by infrared spectroscopy and the oxide can be measured by techniques, such as X-ray photoelectron spectroscopy.
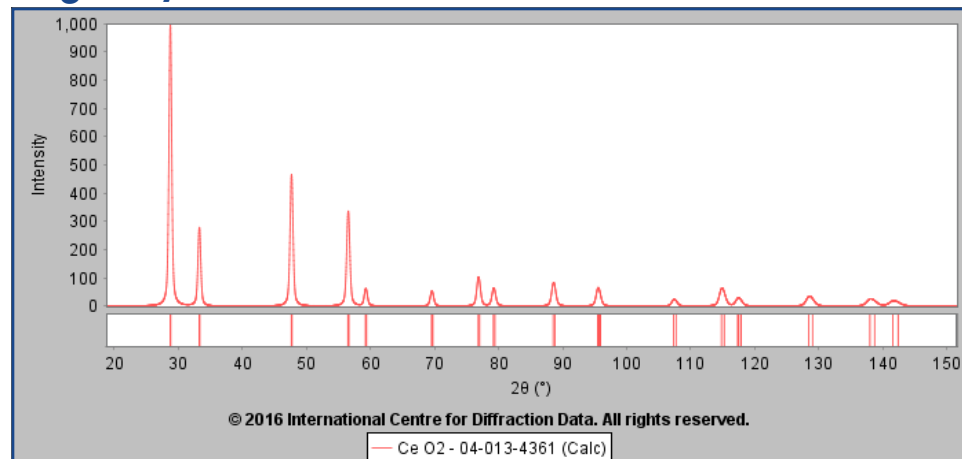
Experimental Powder Data (d, I) – Option to Apply Instrument Function

Ce O2 - 00-034-0394 (Experimental)
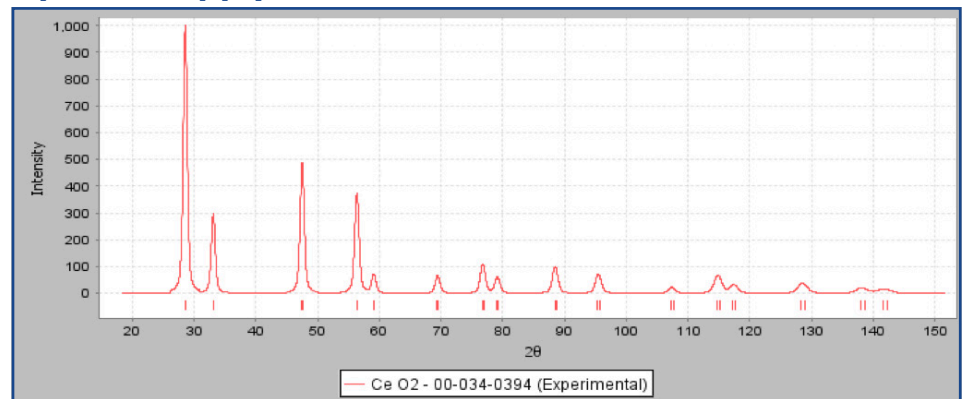
Single Crystal Data Scattering Factors

Ce O2 - 01-071-4807 (Calculated)
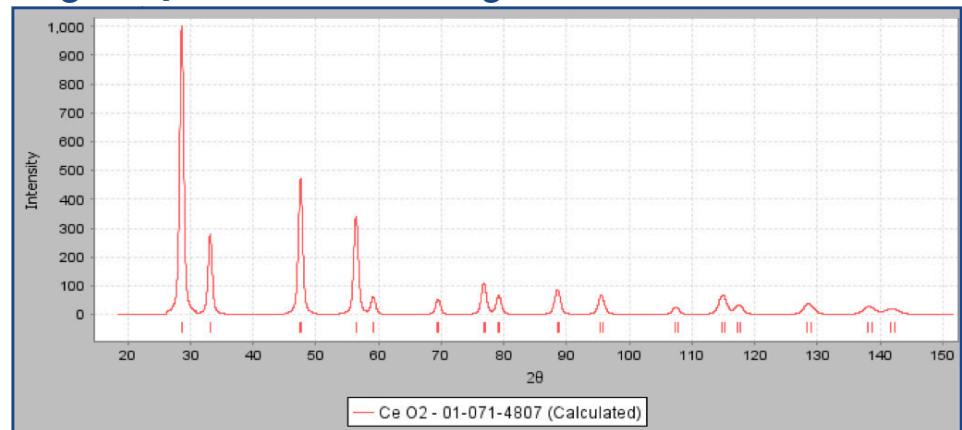
Single Crystal or Powder Data with Atomic Coordinates

Ce O2 - 04-013-4361 (Calc)

When the algorithms are applied appropriately one should see the exact same digital diffraction pattern independent of the source data. This is shown in the figure above for cerium oxide (CeO_2) from three literature sources that contained different types of information. All three data entries have been converted to the same simulated pattern.

Once the reference data are converted to a digital pattern, the pattern can be modified for known instrumental and specimen factors, including adjustments for crystallite size and preferred orientation. Then the "adjusted" references are compared as full patterns to the experimental data. While this process is complicated, it can be performed very quickly with modern computers and large groups of data can be compared in seconds.

Technical Bulletin – Nanomaterials

Crystallite Size and Variance

While there are many methods for the analysis of microstructure, the ICDD has adopted the methodology described by Professors Paolo Scardi and Matteo Leoni at the University of Trento in Italy (Scardi et. al., **2005**). Their method deconvolutes a diffraction peak profile into a series of various contributions that include a measurement of crystallite size. This method varies from some others in that not only is a mean crystallite size σ calculated, but also a variance μ that describes a gamma distribution of crystallites.

$$P_r(D) = \frac{\sigma}{\mu\Gamma(\sigma)} \left(\frac{\sigma D}{\mu}\right)^{\sigma-1} e^{\left(\frac{-\sigma D}{\mu}\right)}$$

They have worked out the mathematics for several crystal shapes and then worked with Dr. John Faber (ICDD) to incorporate this system into the crystallite size module of the Powder Diffraction File (Scardi et. al., **2006**).
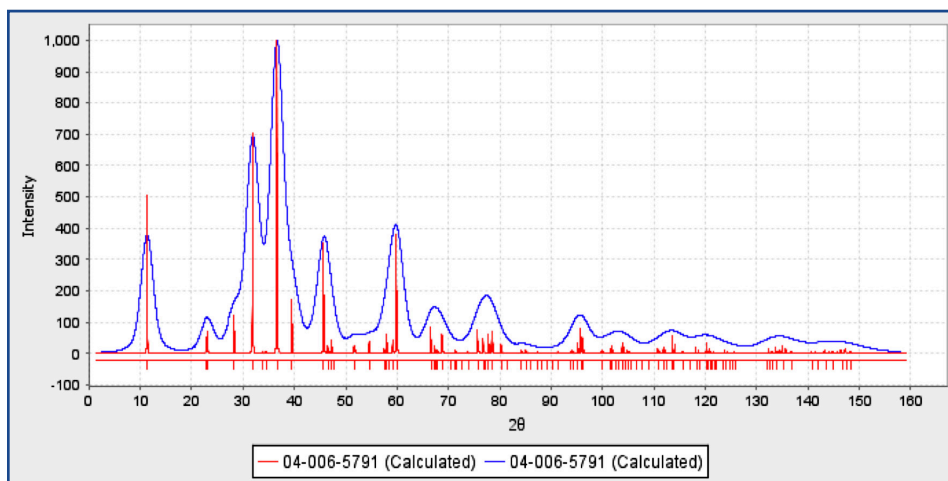
One can now take any digital diffraction pattern and apply a specific crystallite size, as in the example above for $Sr_2CuCl_2O_2$. In this example, the diffraction pattern (blue) was calculated from the single crystal atomic coordinates and a 25 Å crystallite size with a variance of 10 Å.

Since every data set in the Powder Diffraction File can be expressed as a digital pattern, every constant wavelength data set can also be displayed as a nanomaterial.

This system can be used in practice to simulate various sizes and distributions that can be matched to experimental data (Fawcett et. al. **2015**).

In the following example, we use a specimen of nanoanatase produced at the Eastman Kodak Company. The X-ray diffraction data were collected experimentally and found in the PDF as entry PDF 00-064-0863. The two TEM photographs shown previously in this Technical Bulletin correspond to this material (page 1). As shown by the TEM photos, the particles are generally monodispersed with a small amount of particle necking and agglomeration. Multiple light scattering measurements show a particle distribution centered between 10 and 12 nm.

SAXS – Small Angle X-ray Scattering

Shortly after the discovery of powder diffraction, Professor Peter Debye studied the scattering from non-crystalline systems (Debye, **1915**). Debye considered the case of diffraction to be coherent scattering and focused on the physics of incoherent scattering. Klug and Alexander (1974) describe a generalized scattering function to describe the observed broad profiles.

$$s = \frac{2\sin\Theta}{\lambda}$$

Debye related the intensities of scattered profiles to a radial distribution function of nearest neighbor atoms. Use of a Fourier transform as a practical means of obtaining the radial distribution functions directly was first proposed by Zernicke and Prins (**1927**). The textbook, *"X-ray Diffraction Procedures"* by Klug and Alexander, describes the relationship between these two works and the general theory of radial distribution function analysis in their chapter on the study of noncrystalline materials (Klug and Alexander, **1974**). The general theory applies to both small angle scattering and pair distribution analysis described on page 3.

It was later discovered that particles and various microstructural arrays could also act as scattering centers and that this scattering occurred at low angles due to the particle or structure size (tens to hundreds of Angstroms).
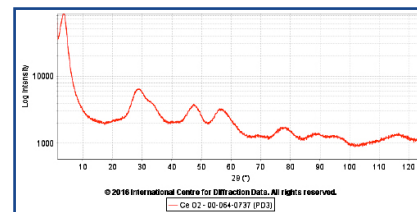
This is the full reference pattern for PDF 00-064-0737, nano CeO_2 plotted on a log intensity scale. This is an unusual case where the particle size is so uniform the SAXS peak is significantly more intense than any diffraction from the lattice planes. The rescaled data without the SAXS peak is shown on the cover of this Technical Bulletin. The scattering maximum at 25.9 Å is from the uniform particle (not crystallite) size. From the conventional wide angle data analysis the crystallite size was estimated at 12Å. If the particle size is uniform, a nanomaterial should exhibit both wide angle and small angle peaks.

Tools in the Powder Diffraction File for Nanomaterial Analysis

Digital Nano Patterns
All references can be expressed as digital patterns and all references can be calculated as user specified nanomaterials.

Amorphous and Nano References
The PDF contains experimental, amorphous, and nanomaterial references. Some nanomaterial references also contain SAXS reference data.

Nearest Neighbor Atom Distances
PDF-4+ contains nearest neighbor atomic distances for all materials with atomic structures (>250,000). This can be used to interpret and assign pair distribution function peaks.

Electron Diffraction
PDF-4+ contains simulated electron diffraction spot, ring, and EBSD patterns for nanomaterial analysis by electron diffraction.

Search Nanomaterials
The PDF includes normalized R-index integral index pattern search capabilities. This is a whole pattern search that excels at searching nanomaterials and amorphous materials.

Molecular Orientation
Most simulations can be adjusted for preferred orientation using a March-Dollase function.

PDF 00-064-0863
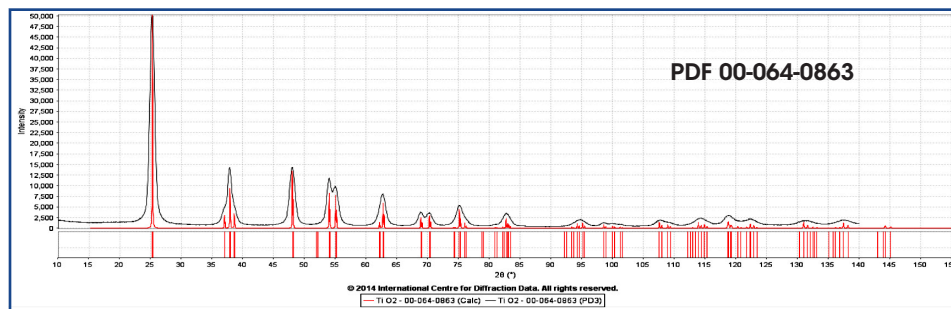
The figure above shows the experimental pattern in black and the red peaks are the diffraction peak positions described by the atomic structure.

70 Å crystallite size
μ = 7 Å

PDF 00-064-0863
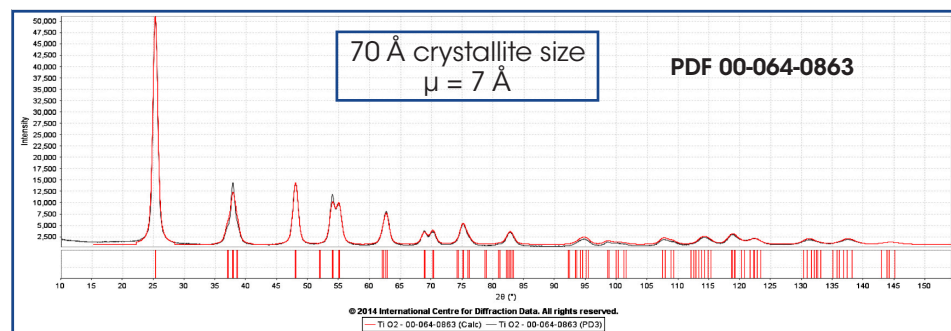
In the simulation above, the red pattern was calculated using a 70Å crystallite size with a narrow variance of 7 Å. The fit to the experimental data (black) is excellent. The variance is exhibited by the fitting of the profile tails. Amorphous contributions were not needed to describe the pattern and the crystallite size applied was isotropic as approximate for a cube or sphere. This size is very consistent with TEM photos and the light scattering measurements, since the latter also measures contributions from agglomerates. The three techniques together gives the experimentalist an idea of the crystallinity, crystallite size, grain size, particle size, and disperseability. In this particular material, the particles were close to single grain and single crystallite. In most materials they are not and the differences in these measurements often provide insight to performance and properties. For nanomaterial analyses we recommend the use of multiple analytical techniques for a more complete characterization.

PDF 00-064-0863
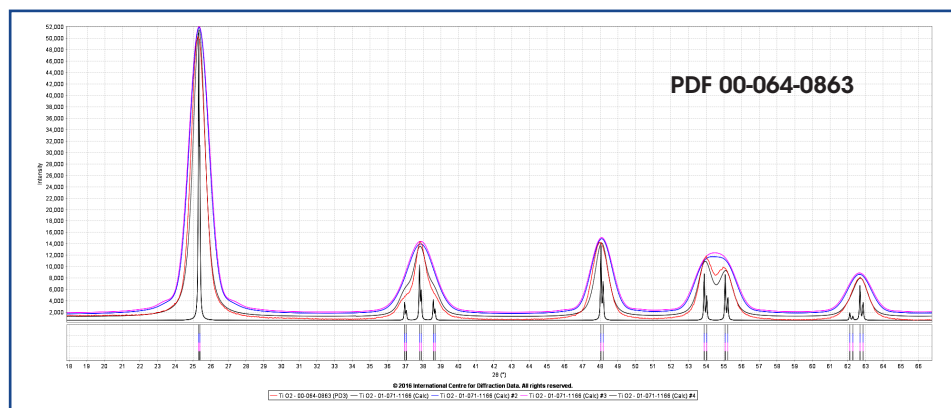
The influence of variance on the diffraction peak profiles can be seen in the above pattern containing the 18-70 degree window for nanoanatase. The experimental data are in red. For comparison we have a simulation at infinitely large crystallite size (black) and three simulations with 70 Å mean crystallite diameter (grey, blue, purple). In the 70 Å simulations the variance was set to 5 Å (grey), 35 Å (blue) and 70 Å (purple). As the variance become smaller, distributions narrow and the peak become sharper, with less pronounced tailing. (Scardi et. al., **2006**). The simulations suggest a narrow distribution for nanoanatase (grey simulation versus red experimental data).

Combining Tools

Many tools in the PDF were applied in the analysis of a series of nanozirconias produced by varying temperature and pressure in a Paar reactor. These materials have become a series of references, PDF 00-065-0686; 00-065-0687; 00-065-0727; and, 00-065-0728. The reference data in the PDF also includes a TEM photo and reference synthesis conditions. The complete analysis has been reported in a recent publication (Fawcett et. al., **2015**).
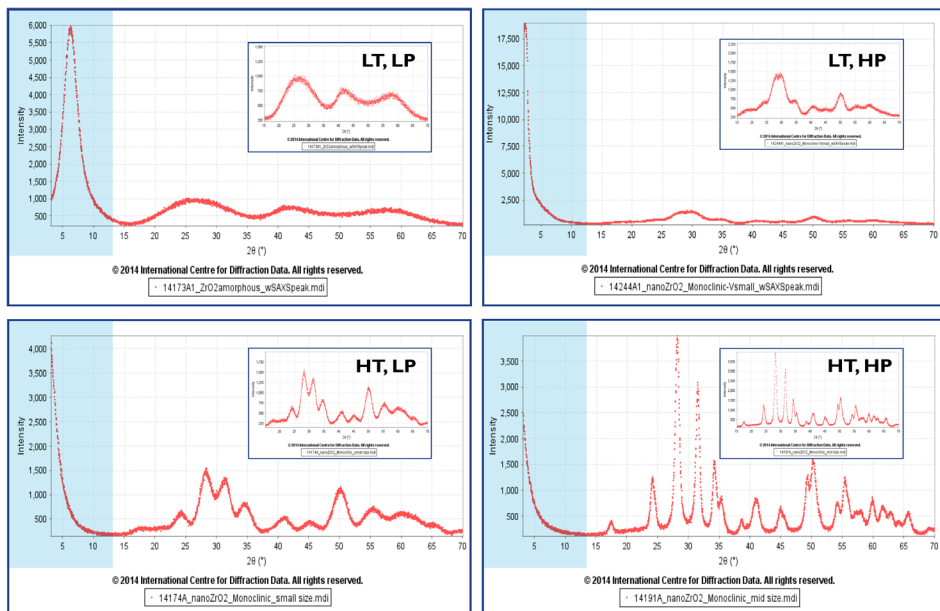
The experimental data are shown above, including small angle data in the highlighted box. In the top 2 data sets, the SAXS data maxima are visible at 14 and 36 Å. TEM data corresponding to the same sample as the bottom right diffraction pattern, measured particle sizes between 60 and 80 Å.

Through the use of the crystallite size and variance simulator we could monitor the decrease in size as a function of reaction temperature and pressure. For the top right data set, the pattern was simulated and matched to the experimental data by using an orientation function, crystallite size of 35Å, variance of 25Å, plus addition of amorphous content.
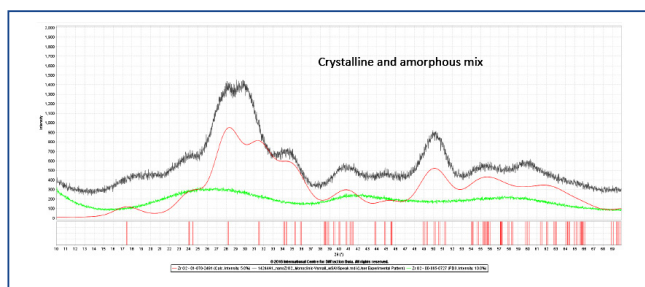

In this specific case, we used pattern PDF 00-065-0727 as the amorphous reference (top left pattern) as the particle size is known to be very small from the SAXS data and the diffraction pattern does not fit any crystalline model. The graph above shows the individual contributions for this pattern simulation.

This is another case, like the titania example, where the particle size measured by TEM and SAXS is very close to the crystallite size as determined in our simulations. This indicates that the particles were isolated and that there is very little agglomeration so that particle size $\cong$ grain size $\cong$ crystallite size.

Electron Diffraction

Electron diffraction is another powerful tool in the analysis of nanomaterials. Electron diffraction is usually associated with a physical device attached to an electron microscope. An advantage of using electron diffraction is that the spot size for the analytical electron beam can be controlled to nanometer sizes. This can allow the analyst to measure a single particle or grain and in special cases even focus on the particle surface or raster across a particle. In this way one can explore crystalline, nano-crystalline, disordered, and amorphous domains that contribute to the nanomaterial properties.
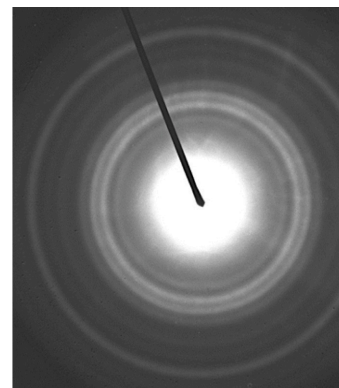
Nano ZrO₂ electron diffraction pattern
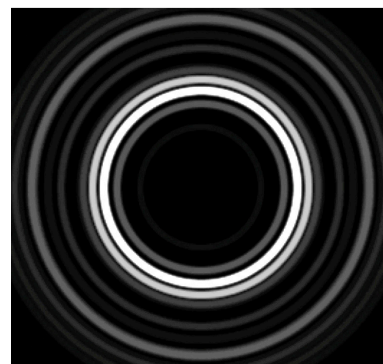
PDF 04-004-4339 simulation of 80 Å ZrO₂

To help electron diffractionists, the PDF-4 has a series of electron diffraction simulations for ring, spot, and EBSD patterns (Reid et. al. **2011**).

The above micrograph is an electron diffraction pattern of a powdered sample of nanozirconia. Electron microscopy image analysis estimated the particle size between 60 and 80 Å. The bottom photograph is an 80 Å electron diffraction pattern simulation. The top data were collected on a specimen related to the bottom right XRD pattern on the four panel set of zirconias on this page. The XRD data estimated the crystallite size to be 80 Å by profile simulation.

Limitations

All methods described in this Technical Bulletin have advantages, as well as limitations.

The crystallite size calculation in the PDF is optimum for nanomaterials between 1 and 100 Angstroms in size. This is due to two principal factors. First, the size is inversely proportional to the peak breadth. The smaller the size, the more accurately it can be measured. Second, the method does not account for other known line broadening effects and assumes that they are negligible. This is a fair assumption since most of these effects are minor contributors to the peak breadth. However, as peaks narrow these contributions become more significant, hence the upper limit on the optimum size. Between 100 and 1000Å the method continues to work, but should be used for trend analysis not accurate determination.

If one wants a more accurate analysis at the larger sizes we would recommend the full whole pattern method by Scardi and Leoni or the published methods of Ungar and colleagues.
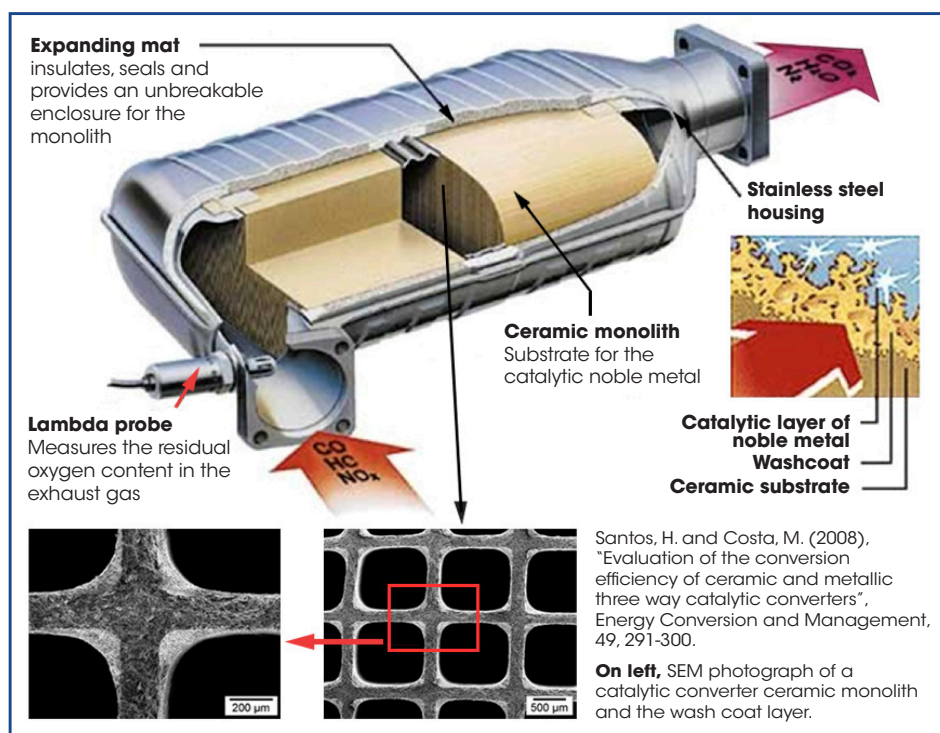
The crystallite size module can be used as an effective screening technique. Stress and strain influence peak symmetry and shape. If the PDF crystallite size model fits the data very well, particularly in the tails, then one can assume stress and strain may be minimal. An example would be the previously shown nanotitania.

In recent years, teams of ICDD member scientists have also measured and analyzed a series of cellulosic materials (Fawcett et. al. **2013**). Cellulose is formed by nature into fibers and in this case the fiber size and the measured crystallite size by diffraction are significantly different. We and others have found that pharmaceutical grade microcrystalline cellulose is really composed of nanocrystalline microfibrils (Nishiyama, **2009**). Microcrystalline refers to a mechanical sizing and purification process used by the industry. Microscopy and atomic force microscopy have found that the microcrystalline fibers are formed from microfibrils (Baker et. al. **2000**). Diffraction analyses show that the microfibrils have amorphous and nanocrystalline components. The discovery of this hierarchy of structure has directly lead to improved cellulosics through controlled chemical reaction of the fibers. Diffraction has been used to examine polymorphic form, nanocrystallite size, and molecular orientation as it relates to chemical processing and final product properties. A characteristic of many polymers is small nanocrystalline domains within an amorphous matrix. (Gates et. al., **2014**).

One of the powers of powder diffraction analysis is the ability to measure formulations and components where one part of the formulation may be nanomaterial. With powder diffraction, the analysis is not dependent upon the nanomaterial being in an isolated state.
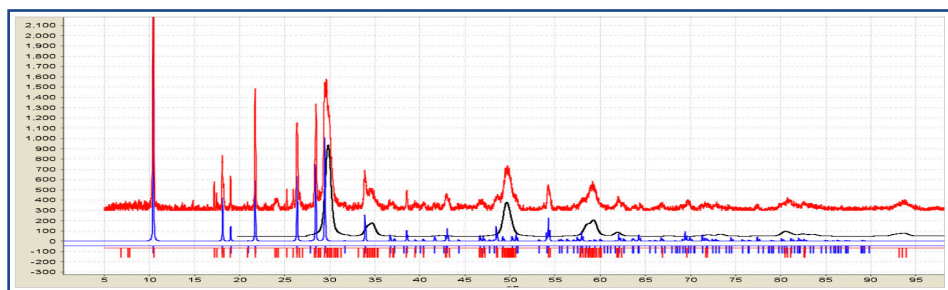
The plot above shows the diffraction pattern from a catalytic converter ceramic monolith. There are very noticeable sharp and broad diffraction maxima. A phase identification analysis shows that the sharp peaks are from the cordierite substrate, while the broad peaks are from a cerium doped zirconia. Analysis of the peak profiles show cerium doped zirconia has a 100 Å crystallite size.

Expanding mat insulates, seals and provides an unbreakable enclosure for the monolith

Stainless steel housing

Ceramic monolith Substrate for the catalytic noble metal

Catalytic layer of noble metal
Washcoat
Ceramic substrate

Lambda probe Measures the residual oxygen content in the exhaust gas

Santos, H. and Costa, M. (2008), "Evaluation of the conversion efficiency of ceramic and metallic three way catalytic converters", Energy Conversion and Management, 49, 291-300.

On left, SEM photograph of a catalytic converter ceramic monolith and the wash coat layer.

This analysis aligns perfectly with known fabrication techniques for catalytic converters, where nano size washcoats (cerium doped zirconia) are used for noble metal catalyst supports. A catalytic converter with wash coat is shown schematically in the previous figure. The figure also has inserted SEM photographs that shows the wash coat layer on top of the honeycomb cordierite.

Practical Considerations

Experimental

Nanomaterials, if present as a fine powder having isolated grains, can be a safety hazard. The extremely high surface area means that these powders are often reactive and in some cases represent a dust explosion hazard and/or inhalation hazard. Extreme care is required for handling loose powders. Commercial nanomaterials are often surface treated to reduce these hazards, but you should consult the Material Safety Data Sheet information before performing an experiment. Due to the small size of these particles, dust masks may not be effective and specimen preparation in a hood may be prudent.

Many researchers prefer to analyze nanomaterials in a dispersive medium. This will often be an oil or other non-reactive hydrocarbon. Please keep in mind that any liquid medium will also contribute scatter to your diffraction pattern and may interfere with the analysis. You may need to run a blank comprised of the dispersive medium.

The analysis of microstructure in a nanomaterial centers on the analysis of diffraction peak profiles. The Scherrer equation shows that the crystallite size is inversely proportional to the integral peak breadth. The smaller the size, the broader the peak. If you have a very small nanomaterial, 2-50 Angstroms, it is likely that you will also have amorphous contributions and small angle scattering present in your diffraction pattern. Variations in crystallite size distributions will be exhibited as differences in the peak shape and tails of the peaks. Successful deconvolution on these contributions are a key to successful analysis. This means one should start a diffraction pattern at a very low angle (2 degrees or less, Cu Kα radiation) and go to a very high angle (100 degrees) so that one will capture the profiles of amorphous and low angle scatter. For accurate total pattern analysis you need to collect the total pattern. Recent work on amorphous materials at the ICDD show that most have significant scattering intensities at high angles.

Low angle scatter and amorphous scatter often occur over several degrees for a single profile and in nanomaterials peak overlap can be severe. Using good counting statistics (high signal, low noise) is a must; very long counting times are appropriate. For the most detailed microstructural analyses you may consider using a synchrotron facility. To analyze trends, laboratory data are usually sufficient.

Similarity Indices

As peak profiles broaden with decreasing crystallite size it becomes more difficult for the material to be analyzed by automatic processes. This is because the inherent high precision in peak positions by XRD techniques are lost as peaks merge and their centroids shift.

One way to avoid this problem is not to use peaks, but to use profiles. In a profile method it does not matter whether you are analyzing coherent (crystalline) or incoherent (non-crystalline) scatter; only the shape matters (Faber and Blanton, **2008**).

Similarity indices use a point by point comparison of a pattern (does not even have to be an XRD pattern). These indices are becoming common in various types of analytical analyses. In the PDF-4, we use a normalized R-index to compare patterns within a series or compare experimental data to a reference pattern. The index can be activated by several drop down menus both in display screens (visual) and display tables (numerical).
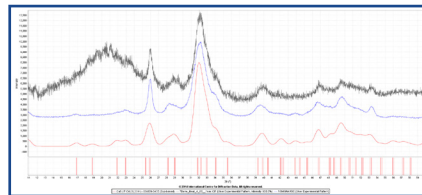
In the example above, a nano-hydroxyapatite is easily identified in a commercial fertilizer by an integral index match.

Deciding between Amorphous and Nanocrystalline

This is often a challenge even for the best scientists. This is a critical issue in many fields of science since it also applies to proof of patentability for basic composition of matter patents.

Many experts have given presentations on this subject at the ICDD Pharmaceutical Powder X-ray Diffraction (PPXRD) symposia on pharmaceutical materials. Most follow a multidimensional approach where diffraction analyses are often combined with molecular modeling, thermal analysis, and thermal modeling of kinetic and thermodynamic processes.

Does the material have a melting point (crystalline) or a glass transition (glass or amorphous)? Can the material's diffraction pattern be modeled with a crystalline structure (crystalline) or not (amorphous)? Does the pair distribution function analysis show an extensive domain structure (crystalline), a small domain (nanomaterial), or no domain (amorphous)? Can you explain the diffraction profiles through the use of an amorphous model (random walk or Monte Carlo)?

What about the glassy state or periodicity caused by intramolecular bonding along chains? What about the structure (or lack thereof in 2D clays and liquid crystals)? In general, one looks for consistency in these analyses to make a determination of crystalline, nano-crystalline, or amorphous composition.
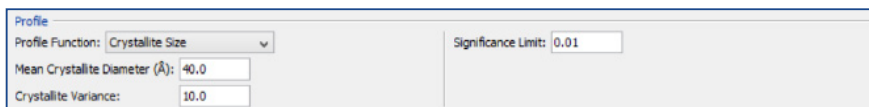
Preferences

In PDF-4 databases, the user can select their personal choices in the **Preferences Menu**. For crystallite size and profile analyses the user should select the **Diffraction Pattern** tab.
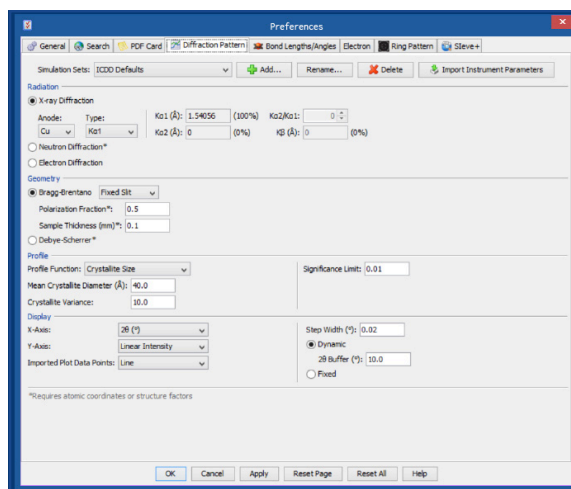

Note: ICDD updates the PDF each year. The images on this page are from the PDF-4 2016 database.

This tab allows the user to select X-ray, neutron or electron diffraction analysis. The radiation, wavelength, or energy are input. The user can choose between different instrumental optics and range and step sizes for their simulations. There is a selection for input instrument parameter files, which are particularly useful for neutron and synchrotron diffraction analyses (Kaduk and Reid, **2011**). There are also default settings that have been set by using known instrument profiles for various types of instruments.

The **Preferences – Diffraction Pattern** tab has a section for applied profiles when the user inputs a mean diameter and variance, including the Whole Pattern Fitting profile for crystallite size. This module does all of the calculations so the input is directly in Angstroms. One also has the selection of choosing Pseudo-Voight, modified TCH Pseudo-Voight, Lorentzian, or Gaussian profiles in cases where one would calculate the crystallite size manually using the Scherrer method or Williamson-Hall technique.
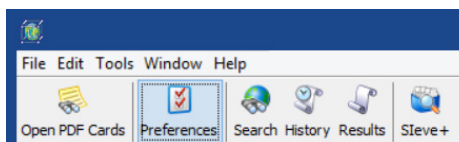
The preferences module with simulated profile selection is available through menu driven options in several areas of the PDF database. If applied with the **Start-up Menu**, shown above, then _**all**_ entries will be simulated as nanomaterials. This includes any subfile selection or the user custom PDF selection. This may be the preferred option if you have not identified the material and you want to compare data sets by the integral index method in either the display menu or in the search/identification program, **Sieve+**.

The **Preferences Menu** can also be activated in several graphic pattern display screens. In this case, you can select crystallite size and molecular orientation for specific reference materials. This is how we analyzed the catalytic converter where the wash coat was a nanomaterial and the converter substrate (cordierite) was not.

Additional Resources – Free!

ICDD tutorials describe how to use many of the tools discussed in this bulletin.

http://www.icdd.com/resources/tutorials/

- **Use PDF-4+ Database**
- **Using Similarity Indexes, Integral Index**
- **Crystallite Size Analysis – Nanomaterials**
- **Perform Pattern Simulations**

The PPXRD symposia series has several PowerPoint presentations on the topic of nanomaterials and amorphous materials. Top downloads are seen here.

http://www.icdd.com/ppxrd/ppxrd-presentations.htm

Advances in X-ray Analysis contains ~950 full on-line publications. These publications describe techniques, such as pair distribution function analysis, SAXS analysis and various peak profiles analyses used for microstructural determinations.

http://www.icdd.com/resources/axasearch/search_based_on_vol.asp

ICDD Contact Information

12 Campus Boulevard
Newtown Square, PA 19073, USA
Phone: 610-325-9814
Fax: 610-325-9823
Toll-Free: 866-378-9331 (USA & Canada only)
Email: info@icdd.com
www.icdd.com

This technical bulletin offers various descriptions of analytical methods used for analyzing nanomaterials by powder diffraction methods. For a more thorough explanation of the physics involved please see the books cited in this Reference section. This includes Klug and Alexander (**1974**), Egami and Billinge (**2012**) and Dinnebier and Billinge (**2008**).

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