SRM 1979: A NIST SRM FOR NANO-CRYSTALLITE SIZE BROADENING

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The NIST Nano-Crystallite Size Standard Reference Material (SRM) 1979 will provide a standard for both scientific and commercial laboratories to quantify the size distribution and shape of nano-crystallites using X-ray line profile and electron microscopy techniques. We demonstrate the use of Bayesian/Maximum entropy (MaxEnt) method developed specifically for the SRM certification to quantify the plausibility of models used to describe certified size distributions. It is expected that SRM 1979 will play a pivotal role in the rapidly developing nano-technology industry by providing a reference for the measurement of crystallite size and shape data, while clarifying the underlying assumptions of many existing line profile analysis techniques.

In this paper, we discuss the preparation and analysis of the two proposed SRM 1979 candidate materials. An outline of the MaxEnt/Bayesian procedure is given, together with a discussion of the results from “conventional” methods X-ray line profile analysis used to determine both the particle size and shape information.

SRM 1979 will consist of two materials that are to be prepared via co-precipitation methods in 1kg batches. This will be accomplished using a NIST development fixed-element flow reactor that insures all volume elements of the reactants receive an identical exposure to one another. The chemical processes and annealing schedules have been optimized to minimize the presence of structural defects that may result in strain broadening in the line profiles. The first material sample is ceria (cerium (IV) oxide, CeO₂) with an (approximate) average spherical crystallite size of 20 nm over a size range of 5–35 nm. This material is produced from a precipitation reaction between cerium (IV) sulfate solution and an ammonium hydroxide solution, conducted in a. Ceria has a cubic symmetry resulting in well-spaced diffraction lines. This allows rapid and simplified analysis techniques to be used to determine the shape and dimensions of the crystallites, while minimizing systematic error arising from overlapping peaks. Moreover, the spherical morphology ensures that the size broadening will be isotropic in hkl. This enables models for simple shapes to be applied.

The second SRM 1979 specimen is zinc oxide (ZnO) which is also prepared by a precipitation reaction between zinc acetate and an ammonium hydroxide solution. This material has cylindrical crystallite morphology with an approximate length of 80 nm and a size range of 60–100 nm. ZnO has a hexagonal symmetry, producing a large number of (overlapped) lines. Consequently, this specimen requires more complex size and shape models to be applied in order to extract the necessary information from the X-ray diffraction data. Specifically, the anisotropic broadening for various hkl provides a direct indication of the crystallite morphology, while the size distribution reveals the spread in the cylinder heights and diameters.

Line profile data used for the certification were collected on a diffractometer that utilized a Johansson incident beam monochromator; this eliminates the satellite lines, “tube tails”, and Kα₂ contributions to the IPF. Data from conventional equipment are to be included for purposes of comparison. The IPF was characterized with SRM 660a. Additional synchrotron may be presented.

The Bayesian/MaxEnt analysis technique involves two steps: The first applies Fuzzy pixel/MaxEnt deconvolution methods simply to remove the instrumental broadening to yield the specimen profile. Using this data, simple microstructural models for the crystallite size/shape (and if necessary defect content) are developed. This data serves as the a priori information for the full Bayesian/MaxEnt analysis constituting the second step. This approach provides a basis for developing a series of models from which the most probable model can be determined using Bayesian model selection theory. This analysis takes full account of the form of the instrumental, background and statistical noise contributions embedded in the diffraction data. In addition to providing the most probable solution, the second step also produces a full error analysis of the size distribution – a critical element in certifying SRM 1979.

Results from analyses of these line profile data using integral breadth and Fourier techniques will be contrasted with the certified values of the SRM. The X-ray analyses presented here will also be compared with the results of direct observations of SRM 1979 using TEM imaging, and a discussion based on this comparison will be presented.