National Institute of Standards & Technology

Certificate

Standard Reference Material® 640e

Line Position and Line Shape Standard for Powder Diffraction
(Silicon Powder)

This Standard Reference Material (SRM) is intended for use as a standard for calibration of diffraction line positions and line shapes, determined through powder diffractometry. A unit of SRM 640e consists of approximately 7.5 g of silicon powder bottled under argon.

Material Description: The SRM was prepared from ultra-high purity, intrinsic silicon boules that were crushed and jet milled to a median particle size of 4.1 μm. The resulting powder was then annealed under gettered argon at 1000 °C for two hours [1] and bottled under argon. Analysis of X-ray powder diffraction data indicated that the SRM material is homogeneous with respect to diffraction properties.

Certified Value: The certified lattice parameter for a temperature of 22.5 °C is

0.543 117 9 nm ± 0.000 008 nm

The interval defined by this value and its expanded uncertainty ($k = 2$) is dominated by a Type B uncertainty estimated from a technical understanding of the measurement data and its distribution. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account. The certified values and uncertainties were calculated according to the method described in the ISO/JCGM Guide [2]. The measurand is the lattice parameter. Metrological traceability is to the SI unit for length (expressed as nanometers).

Information Values: The analyses of the certification data included refinement of the full-width half-maximum (FWHM) of a Lorentzian profile to account for sample-induced broadening. The angular dependence of the FWHM term varying as $1/\cos\theta$ is interpreted as size-induced broadening. The value obtained was consistent with a mean volume-weighted domain size of approximately 0.4 μm. The term varying as $\tan\theta$, interpreted as microstrain, refined to zero. The information values for computed peak positions are given in Table 1. The typical particle size distribution as determined by laser scattering is given in Figure 1. An information value is considered to be a value that will be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 640e** is valid indefinitely, within the uncertainty specified, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Storage"). Periodic recertification of this SRM is not required. The certification is nullified if the SRM is damaged, contaminated or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Overall coordination and technical direction of the certification were performed by J.P. Cline of the NIST Materials Measurement Science Division.

The preparation, measurements and data analyses were performed by J.P. Cline, M.H. Mendenhall, D. Black and E.G. Kessler of the NIST Materials Measurement Science Division and A. Henins of the NIST Quantum Measurement Division.

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Robert L Watters, Jr., Director
Office of Reference Materials

Collection of the laser scattering particle size data for informational value was performed by M. Peltz of the NIST Materials and Structural Systems Division.

Statistical analysis was by provided J.J. Filliben of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

INSTRUCTIONS FOR STORAGE

SRM 640e was bottled under argon to protect against humidity. When not in use, store the unused portion of this powder tightly capped in the original bottle or in a manner with similar or greater protection against humidity.

SOURCE, PREPARATION, AND ANALYSIS[1]

Source of Material: The silicon was obtained from Siltronic AG, Munich, Germany. The comminution was performed by Hosokawa Micron Powder Systems, Summit, NJ.

Certification Method: Certification was performed using data from a NIST built diffractometer [3], with analyses via the fundamental parameters approach (FPA) [4] using the Rietveld method [5]. These analyses were used to verify homogeneity and certify the lattice parameters. The linkage of the certified lattice parameter values to the fundamental unit for length, as defined by the International System of Units (SI) [6], was established with use of the emission spectrum of Cu Kα radiation as the basis for constructing the diffraction profiles. With the use of the FPA, diffraction profiles are modeled as a convolution of functions that describe the wavelength spectrum, the contributions from the diffraction optics, and the sample contributions resulting from microstructural features. Analysis of data from a divergent-beam instrument requires knowledge of both the diffraction angle and the effective source-sample-detector distance. Two additional models are therefore included in the FPA analyses to account for the effect of the sample height and attenuation. Certification data were analyzed in the context of both Type A uncertainties, assigned by statistical analysis, and Type B uncertainties, based on knowledge of the nature of errors in the measurements, to result in the establishment of robust uncertainties for the certified values.

The uniformity of the single-crystal silicon material was verified prior to comminution. These measurements were performed on the NIST lattice comparison apparatus [7] using 11 crystal samples taken from the supplied material. A total of 32 lattice comparison measurements covering the longitudinal and radial boule directions were made. The relative lattice variation indicated by these measurements was $\pm 4.8 \times 10^{-8}$ (95 % confidence level). This level of uniformity is consistent with the use of this silicon feedstock for this powder diffraction SRM.

Certification Procedure: The data were collected with a 2.2 kW sealed copper tube of long fine-focus geometry which was operated at a power of 1.8 kW, 45 kV and 40 mA. The source size was approximately 12 mm × 0.04 mm and the variable divergence slit was set nominally to 0.8°. Axial divergence of the incident beam was limited by a 2.2° Soller slit. The goniometer radius was 217.5 mm. A 2 mm anti-scatter slit was placed approximately 113 mm in front of the 0.2 mm (0.05°) receiving slit. Scattered X-rays were filtered with a graphite post-sample monochromator, and counted with a scintillation detector. Samples were spun at 0.5 Hz during data collection. The machine was located within a temperature-controlled laboratory space where the nominal short-range control of temperature was ± 0.1 K. The temperature and humidity were recorded during data collection using Veriteq SP 2000 monitors stated to be accurate to ± 0.15 K. The source was allowed to equilibrate at operating conditions for at least an hour prior to recording any certification data. The performance of the machine was qualified with the use of SRM 660b Line Position and Line Shape Standard for Powder Diffraction [8] and SRM 676a Alumina Powder for Quantitative Analysis by X-Ray Diffraction [9] using procedures discussed by Cline *et al*. [3].

Ten units of SRM 640e were selected in a stratified random manner from the population of units during the bottling operation. Certification data were recorded from 2 samples prepared from each of 10 bottles, for a total of 20 samples. Data were collected from 11 selected regions of the diffraction pattern, each region including one of the reflections accessible within the 2θ range of 25° to 140°. The angular widths of the scan ranges were 20 to 30 times the observed FWHM values of the profiles and were chosen to provide at least 0.3° 2θ of apparent background straddling each peak. The step width was chosen to include at least eight data points above the FWHM. The count time spent on each profile was inversely proportional to the observed diffraction intensity so as to realize constant counting statistics amongst the profiles. The total collection time for each sample was about 15 hours.

[1]Certain commercial equipment, instruments, or materials are identified in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Data Analysis: The certification data were analyzed using the FPA method as implemented in TOPAS [10] as well as a NIST Python-based code that replicates the FPA models [11]. While TOPAS allows for a Rietveld analysis using a structural model, within the Python code, peak positions are constrained by space group symmetry to permit refinement of lattice parameters. The Python-based code allowed for the simultaneous refinement of a large number of data sets in a single, global analysis; this allowed for the determination of parameters specific to the instrument profile function (IPF) in the context of highly favorable Poisson counting statistics. The twenty data sets used for the certification of SRM 660c [12], collected in a manner analogous to that described for SRM 640e, were analyzed in a global refinement to determine IPF parameters. The analysis used the Cu $K\alpha_1/K\alpha_2$ emission spectrum, including a satellite component, as characterized by G. Hölzer *et al.* and Maskil & Deutsch [13,14]. The breadths of the four Lorentzian profiles used to describe the Cu Kα emission spectrum were refined in order to assess the impact of the post-monochromator [3]. The FWHM ratios of the two pairs of profiles, the $K\alpha_{11}$ vs. the $K\alpha_{12}$ and the $K\alpha_{21}$ vs. the $K\alpha_{22}$, were constrained to those reported by Hölzer. The intensities and positions of the Cu $K\alpha_2$ line, the satellite line and the "tube tails" [15] were refined. Again, constraints were applied to positions and intensities of the $K\alpha_{21}$ and $K\alpha_{22}$ lines to preserve the overall shape as per Hölzer. A Soller slit value, constrained to be identical for both the incident and diffracted beam, using the "full" axial divergence model [16], was refined. Lastly, the analysis included a term for Lorentzian size broadening. With the exception of the size broadening term, the parameter values obtained from this analysis were specific to the IPF, and were fixed in subsequent analyses.

TOPAS was used to refine the data sets individually with an FPA Rietveld analysis. The refined parameters included the scale factors, Chebyshev polynomial terms for modeling of the background, the lattice parameters, specimen displacement and attenuation terms, a Lorentzian size broadening term and structural parameters. With the NIST Python-based code, two global refinements were set up using the twenty data sets. The first was set up as per that of the aforementioned refinement of SRM 660c and was used to obtain the informational value for crystallite size reported on page 1. The second was set up to obtain a single lattice parameter; the profile positions were constrained by space group symmetry and the specimen displacement and transparency terms were allowed to refine independently. The lattice parameter obtained with the NIST Python-based code and the average of the twenty values obtained from the analyses with TOPAS agreed to within ± 2 fm.

The results from the analyses using TOPAS were used to obtain the certified lattice parameters. The thermal expansion of silicon as reported by Bergamin *et al*. [17] was used to adjust the lattice parameter values to 22.5 °C. A statistical analysis of the data indicated that the mean of the measurements was 0.543 117 88 nm with a $k = 2$ Type A expanded uncertainty of 0.000 000 31 nm. However, a Type B uncertainty due to systematic error must be incorporated into the uncertainty bounds of the certified lattice parameter. Consideration of trends in the data used in the certification leads to an assignment of a Type B uncertainty and value as stated on page 1.

Table 1. Information Values for Peak Positions Computed for SRM 640e Using Cu Kα Radiation, λ = 0.15405929 nm

h	*k*	*l*	2θ (degrees)
1	1	1	28.441
2	2	0	47.300
3	1	1	56.120
4	0	0	69.126
3	3	1	76.372
4	2	2	88.025
5	1	1	94.947
4	4	0	106.701
5	3	1	114.084
6	2	0	127.534
5	3	3	136.880

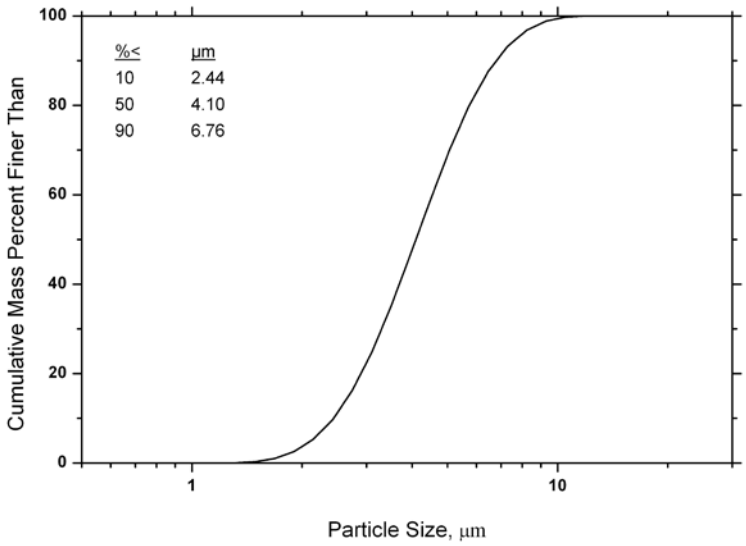

Figure 1. Typical Particle Size Distribution as Determined by Laser Scattering

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Users of this SRM should ensure that the Certificate in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.