National Institute of Standards & Technology

Certificate

Standard Reference Material® 640d

Silicon Powder
Line Position and Line Shape Standard for Powder Diffraction

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 640d 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. An 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

0.543 159 nm ± 0.000 020 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 the distribution in said data. 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 [2]. A certified value is the present best estimate of the "true" value based on the results of analyses performed at NIST.

Information Values: The fundamental parameters analyses 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 domain size of approximately 0.6 μm. The term varying as $\tan\theta$, interpreted as microstrain, is 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.

Expiration of Certification: The certification of **SRM 640d** 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 Use"). 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) will facilitate notification.

The overall coordination of the preparation and technical direction of the certification were performed by J.P. Cline, D. Black, D. Windover, E.G. Kessler, and A. Henins of the NIST Ceramics Division.

The collection of the laser scattering particle size data for informational value was performed by M. Peltz of the NIST Materials and Construction Research 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 Measurement Services Division.

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Certificate Issue Date: 09 July 2009

Robert L. Watters, Jr., Chief
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INSTRUCTIONS FOR USE

Storage: SRM 640d 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 with the analysis of data from a NIST-built diffractometer that includes several advanced design features. It is, however, a divergent-beam diffractometer of Bragg-Brentano geometry. Rigorous analyses of data from said geometry require knowledge of both the diffraction angle and the effective source-sample-detector distance. Determination of the latter parameter is largely intractable as it is dependent on the depth to which the X-rays penetrate the sample; this, in turn, is dependent on the packing density of the powder sample. Data from this instrument cannot be analyzed to yield a result that is strictly SI traceable. However, analysis using the fundamental parameters approach [3] uses the emission spectrum of Cu Kα as a basis for constructing the diffraction profiles, establishing plausible linkage to the SI. 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 [4] 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.

The aforementioned NIST-built diffractometer is of θ-2θ geometry and is of a conventional optical layout, though it is built with several features atypical for conventional equipment of this nature. The θ and 2θ motions of the goniometer assembly are provided by Huber 420 rotation stages that are actuated via a worm gear driving a ring gear. These are mounted concentrically with the rotation axes horizontal, allowing for utilization of an automatic sample changer/spinner. The alignment specifications realized for the goniometer assembly matched those cited by the manufacturer for the individual stages: an eccentricity (concentricity) of less than 3 μm, and a wobble (parallelism) of less than 0.0008° (3 arc-seconds). Both stages incorporate Heidenhain optical encoders mounted so as to measure the angle of the ring gear. The encoders with the associated Heidenhain IK220 interpolation electronics provide $\pm$ 1 arc-second accuracy, and approximately 0.035 arc-second precision. The optics, X-ray generator, tube shield, and 40-position sample changer/spinner of the machine are conventional in nature; they were originally components of a Siemens D5000 diffractometer, ca. 1992.

Certification Procedure: The 2.2 kW sealed copper tube of long fine-focus geometry was operated at a power of 1.8 kW during certification measurements. 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 is 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 detected with a scintillation detector. Samples were spun at 2 Hz during data collection. The machine is located within a temperature-controlled laboratory space where the nominal short-range control of temperature is $\pm$ 0.1 K. The instrument is controlled via LabVIEW software. Data were recorded in true x-y format. 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 NIST SRM 660a Lanthanum Hexaboride Powder Line Position and Line Shape Standard for Powder Diffraction [5] and SRM 676a Alumina Powder for Quantitative Analysis by X-Ray Diffraction [6] using procedures discussed by Cline [7].

[1]Certain commercial equipment, instruments, or materials are identified in this 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.

Eleven units of SRM 640d were selected at random from the population of units during the bottling operation. Certification data were recorded from 2 samples prepared from each of 11 bottles, for a total of 22 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 approximately 15 times the observed FWHM values of the profiles. 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 12 hours.

Data Analysis: The certification data were analyzed using the fundamental parameters approach for Rietveld [8-10] refinement as implemented in TOPAS [11]. The analysis used the Cu $K\alpha_1/K\alpha_2$ emission spectrum, including a satellite component, as characterized by G. Hölzer et al. [12,13]. The refined parameters included the scale factors, first-order Chebyshev polynomial terms, the lattice parameters, the intensities and position of the $K\alpha_2$ and satellite components of the Cu Kα emission spectrum, terms indicating the position and intensity of the "tube tails" [14], a Soller slit value in the "full" axial divergence model [15], specimen displacement, an absorption term, and a size-broadening term of a Lorentzian profile. However, examination of the individual profiles revealed a discrepancy between the model and the observations of the low-angle profiles. It is well known that low-angle profiles are more prone to error than high-angle lines as the optical aberrations affecting their position are more complex. Also, the reported lattice parameter is more strongly affected by angular errors in the low-angle region. The 111 and 220 lines were, therefore, not used in obtaining the certified parameters. The thermal expansion of silicon as reported by Bergamin et al. [16] was used to adjust the lattice parameter to 22.5 °C. A statistical analysis of the data indicated that the mean of the measurements was 0.543 158 93 nm with a $k = 2$ Type A expanded uncertainty of 0.000 000 64 nm. However, a Type B uncertainty due to systematic error must be incorporated into the uncertainty bounds of the certified lattice parameter owing to the fact that the measurements themselves are not metrological in nature and the aforementioned low-angle discrepancy. Consideration of the data used in the certification leads to an assignment of a Type B uncertainty and value as stated on page 1.

Table 1. Informational Values for Peak Positions Computed for SRM 640d Using Cu Kα Radiation, $\lambda = 0.15405929$ nm

h	k	l	2θ, degrees
1	1	1	28.439
2	2	0	47.297
3	1	1	56.115
4	0	0	69.120
3	3	1	76.365
4	2	2	88.017
5	1	1	94.937
4	4	0	106.690
5	3	1	114.071
6	2	0	127.516
5	3	3	136.858

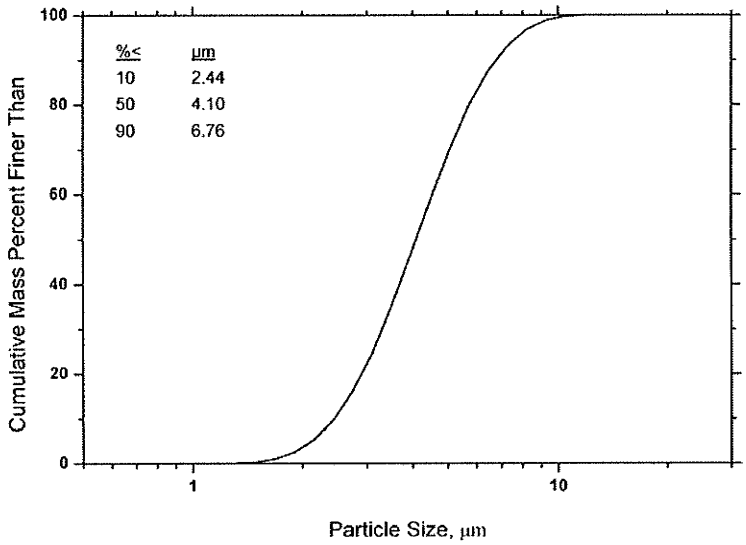

Figure 1. Typical Particle Size Distribution as Determined by Laser Scattering

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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 at: telephone (301) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.