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. The silicon powder of SRM 640d displays a slight preferred orientation in the [111] direction. 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

$$0.543\ 123\ \text{nm} \pm 0.000\ 008\ \text{nm}$$

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. 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.

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 laser scattering particle size data (Table 1) were collected by M. Peltz of the NIST Materials and Construction Research Division.

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Certificate Issue Date: 26 May 2010

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J. Evans of Durham University, Durham, UK developed a template for the input files used in data analysis.

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.

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 using data from a NIST-built diffractometer that includes several advanced design features. This SRM was initially certified in July, 2009 [3]. While the methods and procedures of the present certification are largely identical to those used previously, improvements in the equipment have permitted the reduced expanded uncertainly of the present certification. The optical layout of the diffractometer is that of a conventional divergent-beam instrumentation of Bragg-Brentano geometry. Rigorous analyses of data from said geometry requires knowledge of both the diffraction angle and the effective source-sample-detector distance. Two additional models must therefore be included in the data analyses to account for the factors that affect the distances critical in the use of this geometry. The inclusion of these models places additional uncertainties on the certified lattice parameters relative to those determined from a parallel beam instrument. Linkage to the International System of Units (SI) is established via the emission spectrum of Cu Kα radiation employed as the basis for constructing the diffraction profiles via the fundamental parameters approach (FPA) [4] method of data analyses. 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 [5] 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 ± 1 arc-second accuracy, and approximately 0.035 arc-second precision. The optics, X-ray generator, tube shield, and sample spinner of the machine are conventional in nature; they were originally components of a Siemens D5000 diffractometer, ca. 1992. The sample spinner, however, was modified to allow for remote mounting, and therefore thermal isolation, of its drive motor.

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

[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.

detected with a scintillation detector. Samples were spun at 0.5 Hz during data collection. The machine is located within a temperature-controlled laboratory space where the nominal short-range control of temperature is ± 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 [6] and SRM 676a Alumina Powder for Quantitative Analysis by X-Ray Diffraction [7] using procedures discussed by Cline [8].

Eleven units of SRM 640d were selected in a stratified random manner from the population of units during the bottling operation. Data for homogeneity testing were recorded from 2 samples prepared from each of 11 bottles, for a total of 22 samples. Data used to determine the certified parameters themselves were collected on one sample from each of the 11 bottles. 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 22 hours.

Data Analysis: The certification data were analyzed using the FPA method with a Rietveld [9-11] refinement as implemented in TOPAS [12]. The analysis used the Cu $K\alpha_1/K\alpha_2$ emission spectrum, including a satellite component, as characterized by G. Hölzer *et al*. [13,14]. The Lorentzian breadths of the Cu emission spectrum were refined with constraints to preserve asymmetric profile shape as modeled by Hölzer. The refined parameters included the scale factors, second-order Chebyshev polynomial terms for modeling of the background, 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" [15], a Soller slit value in the "full" axial divergence model [16], specimen displacement, an attenuation term, structural parameters, and a size-broadening term of a Lorentzian profile. An 8th order spherical harmonic was used to model the slight [111] preferred orientation displayed by the silicon powder of SRM 640d.

Examination of the fit to the individual profiles revealed a discrepancy between the model and the observations in the low-angle region. It is well known that low-angle profiles are more prone to error than high-angle lines as the optical aberprations 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 line was, therefore, not used in obtaining the certified parameters. The thermal expansion of silicon as reported by Bergamin *et al*. [17] 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 0.543 123 44 nm with a $k = 2$ Type A expanded uncertainty of 0.000 000 54 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 640d Using Cu Kα Radiation, λ = 0.154 059 29 nm [13]

h	k	l	2θ, degrees
1	1	1	28.441
2	2	0	47.300
3	1	1	56.119
4	0	0	69.126
3	3	1	76.371
4	2	2	88.024
5	1	1	94.946
4	4	0	106.700
5	3	1	114.082
6	2	0	127.532
5	3	3	136.877

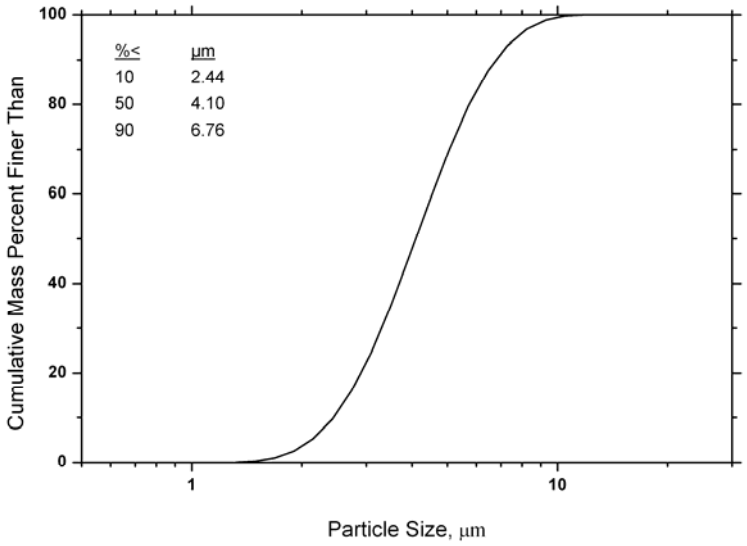

Figure 1. Typical Particle Size Distribution as Determined by Laser Scattering

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Certificate Revision History: 26 May 2010 (This revision includes a change to the certified value for lattice parameter and the information values in Table 1 and minor editorial changes); 09 July 2009 (Original certificate date).

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) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.