STANDARD REFERENCE MATERIAL 640d FOR X-RAY METROLOGY

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Abstract

The National Institute of Standards and Technology (NIST) certify a variety of Standard Reference Materials (SRMs) to address specific aspects of instrument performance for divergent beam diffractometers. This report describes SRM 640d, the fifth generation of this powder diffraction SRM which is certified with respect to lattice parameter. It consists of approximately 7.5 g silicon powder specifically prepared to produce strain-free particles in the size range between 1 μm and 10 μm to eliminate size broadening effects. It is commonly used for calibrating powder diffractometers for line position and line shape. A NIST built diffractometer, incorporating many advanced design features, was used to certify the lattice parameter of the silicon powder. Both Type A, statistical, and Type B, systematic, errors have been assigned to yield a certified value for the lattice parameter of a = 0.543159 nm ± 0.000020 nm.

Introduction

The laboratory based divergent beam x-ray diffractometer can provide a wealth of structural and microstructural information about a wide variety of materials. However, to successfully interpret the data, the operator must have both a properly aligned instrument and take into consideration the aberrations inherent to the para-focusing optics. One method to accomplish this is to use standards to evaluate instrument performance. The National Institute of Standards and Technology (NIST) certify a variety of standard reference materials (SRMs) to address specific aspects of instrument performance. This report describes SRM 640d, the fifth generation of this powder diffraction standard which is certified with respect to lattice parameter. It consists of approximately 7.5 g of silicon powder specifically prepared to have minimal line broadening and is commonly used for calibrating powder diffractometers for line position and line shape.

Material

The silicon feedstock for SRM 640d was prepared from ultra-high purity, float-zone intrinsic silicon obtained from Siltronic AG, Munich, Germany 1. Lattice parameter measurements of the single-crystal silicon boules were performed on the NIST lattice comparison apparatus (Kessler et al., 1994). This provided a test of the material uniformity as well as a le Système International d'unités (SI) traceable measurement of lattice parameter from the as-supplied material. A total of 11 crystal samples were taken from the boules and a total of 32 lattice comparison measurements were performed covering the longitudinal and radial boule directions. The relative lattice

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.
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variation, $\Delta d/d$, of the input material inferred from these measurements was $\pm 4.8 \times 10^{-8}$ (95% confidence level) indicating the material was sufficiently uniform for use as a powder line position SRM to be certified for lattice parameter. The boules were then crushed and jet milled to produce a narrow particle size distribution, in the 1 $\mu$m to 10 $\mu$m range. Typical particle size data from laser scattering measurements are shown in figure 1. The low end of the distribution is above 1 $\mu$m ensuring that diffraction data from SRM 640d would not display the effects of size broadening. The resulting powder was annealed in 31 lots of approximately 200 g each to "remove" crystallographic defects that would otherwise lead to strain broadening. Annealing was performed in quartz boats in gettered argon at a temperature of 1000 °C for two hours (van Berkum et al., 1995). The furnace was evacuated and backfilled three times before the start of each annealing run. Bottling was performed under argon to protect against humidity.

![Figure 1. Particle size distribution of silicon feed stock.](image)

**Instrumentation**

The certification of SRM 640d was performed utilizing the NIST-built, Ceramics Division Divergent Beam Diffractometer (CDDBD). This is a divergent beam diffractometer of Bragg-Brentano geometry that incorporates several advanced design features, as discussed below. A rigorous analysis of data from this instrument requires knowledge of both the diffraction angle and the effective source-to-sample-to-detector distance. Determination of this distance is generally not possible as it is dependent on both the depth to which the X-rays penetrate the sample, which is in turn dependent on the packing density of the powder sample, and the $z$ height. Models for both of these effects can be incorporated into the data analysis procedures. However, results are then dependent on the efficacy of these models, which cannot be tested until suitable parallel beam data are realized. Therefore, while the strict SI traceability of the results may be debated, an analysis using the fundamental parameters approach (Cheary and
Coelho, 1992) does link the refined lattice parameter to the emission spectrum of Cu Kα, thereby establishing plausible linkage to the SI.

The CDDBD, shown in figure 2, is a 0-2θ diffractometer of essentially conventional layout, although it is built with several features not typically found in commercial equipment of this nature. The goniometer assembly consists of a pair of Huber 420 rotary stages each utilizing a worm gear driving a ring gear to produce a 360:1 gear ratio. These stages are mounted concentrically with the rotation axes horizontal, allowing an automatic sample changer/spinner to be mounted. The goniometer was assembled using a specialized jig that aligned the two rotation axes to within the manufacturer’s specifications for both concentricity (3 μm) and parallelism.
(14 μrad). The optics, X-ray generator, tube shield, and sample changer were originally components of a Siemens D5000 diffractometer, ca. 1992. The detector arm also carries an adjustable counter weight to counteract the torque applied by the weight of the various detector configurations. Both stages incorporate Heidenhain optical encoders to measure the angle of the ring gear, to which the sample and detector stages are mounted. These encoders provide 36000 features per rotation with ±4.8 μrad (±1 arc second) accuracy. The output from both encoders was further subdivided to ≈1024 points per feature using the Heidenhain IK220 interpolation electronics resulting in ≈102400 features per degree, or ≈0.17 μrad (0.035 arcsec) precision. The use of optical encoders on both axes circumvents the inherent limit on angular accuracy, 121 μrad (25 arcsec), of the Huber 420 stage.

The CDDBD uses a sealed copper tube with a long fine focus, operated at a power of 1.8 kW. The instrument is equipped with a variable divergence incident beam slit, 40 position sample changer/spinner, a graphite post-sample monochromator, and a scintillation detector. The source size was approximately 12 mm x 0.04 mm, the goniometer radius is fixed at 217.5 mm; the variable divergence slit was set nominally to 14 mrad (0.8˚) for the collection of certification data. A 2 mm anti-scatter slit was placed approximately 113 mm in front of the receiving slit of 0.2 mm, corresponding to a divergence of 0.87 mrad (0.05˚). Operation of the CDDBD was provided through control software written in LabVIEW. This software provides for a number of scan configurations, including full range scans and individual peak scans with up to 25 separate peaks. It also provides for separate control of the 0 and 20 axes which is required to perform a variety of alignment procedures. The x-ray tube is mounted so as to provide adjustment of the source position vertically, the x-ray take off angle, and alignment of the line source with respect to the goniometer rotation axis. The entire apparatus is mounted on an optical table within a temperature controlled laboratory space where the nominal short-range control of temperature is ±0.1 K. The performance of the CDDBD was validated by the procedure described in Cline (2000). Individual profile fitting of SRM 660a (2000), LaB₆, is used to evaluate the performance of the goniometer while a Rietveld analysis of SRM 676a (2008), alumina, is used to evaluate the optics.

Data Collection and Analysis

Certification data were recorded for 2 samples prepared from material extracted from each of 11 randomly selected bottles, for a total of 22 samples. Data were collected from selected regions of the diffraction pattern, each region including only one of the 11 allowed reflections accessible within the 2θ range of 25° to 140°. The scan parameters are given in table 1. 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 and calculated so that the total collection time for each sample was about 12 hours. Certification data were recorded with the x-ray tube operating at an accelerating voltage of 45 kV and a current of 40 mA. The source slit was set so that at the lowest 0 angle, the projected size of the source was just less than the sample size. This geometric consideration gives a value of 0.8˚ for the setting of the equatorial divergence slit. A Soller slit with a divergence of 2.2˚ further defined the incident beam in the axial direction. The source was allowed to equilibrate at operating conditions for at least an hour prior to recording any calibration data. Samples were selected in
an arbitrary order and typically 4 samples were run as a group. The temperature within the radiation enclosure was monitored and the variation in temperature over the course of any scan was typically less than 0.1 K.

Table 1. The scan parameters for each peak.

<table>
<thead>
<tr>
<th>hkl</th>
<th>low angle (˚)</th>
<th>high angle (˚)</th>
<th>step size (˚)</th>
<th>time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>26.8</td>
<td>30</td>
<td>0.01</td>
<td>1.5</td>
</tr>
<tr>
<td>220</td>
<td>45.2</td>
<td>48.9</td>
<td>0.01</td>
<td>2</td>
</tr>
<tr>
<td>311</td>
<td>54</td>
<td>57.7</td>
<td>0.01</td>
<td>3</td>
</tr>
<tr>
<td>400</td>
<td>67.6</td>
<td>70.5</td>
<td>0.01</td>
<td>15</td>
</tr>
<tr>
<td>331</td>
<td>74.7</td>
<td>77.8</td>
<td>0.01</td>
<td>5</td>
</tr>
<tr>
<td>422</td>
<td>86</td>
<td>89.6</td>
<td>0.01</td>
<td>6</td>
</tr>
<tr>
<td>333</td>
<td>93.4</td>
<td>96.4</td>
<td>0.01</td>
<td>12</td>
</tr>
<tr>
<td>440</td>
<td>105.1</td>
<td>108.3</td>
<td>0.01</td>
<td>20</td>
</tr>
<tr>
<td>531</td>
<td>112.5</td>
<td>116</td>
<td>0.012</td>
<td>15</td>
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<tr>
<td>620</td>
<td>125.8</td>
<td>129.5</td>
<td>0.014</td>
<td>18</td>
</tr>
<tr>
<td>533</td>
<td>134.9</td>
<td>139</td>
<td>0.015</td>
<td>30</td>
</tr>
</tbody>
</table>

The certification data were analyzed using the fundamental parameters approach for Rietveld refinement (Rietveld, 1967 and Rietveld, 1969) as implemented in TOPAS (2008). The analysis used the Cu Kα, Kα2 emission spectrum from G. Hölder, et al. (1997) including a satellite component (Maskil and Deutsch, 1998). The refined parameters included the scale factors, first order Chebyshev polynomial terms, the lattice parameters, the intensities and position of the Kα2 and satellite components of the Cu Kα emission spectrum, terms indicating the position and intensity of the “tube tails” (Bergmann et al., 2000), a Soller slit value in the “full” axial divergence model (Cheary and Coelho, 1998a and Cheary and Coelho, 1998b), specimen displacement, an absorption term, and a size-broadening term of a Lorentzian profile. Examination of the individual profiles revealed a difficulty in the analysis of the low-angle peaks. This is illustrated in figure 3. The data, illustrated by the blue line, is shown to deviate to

Figure 3. Low angle Rietveld fit of the 111 line of SRM 640d, blue = data, red = model.
low angle relative to the model, shown by the red line. This indicates either a flaw in the model or an error in the equipment. While the source of the problem is under investigation, and may well have multiple origins, 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. To investigate this difficulty, the data were analyzed using the same fundamental parameters approach as before, but with the lattice parameters allowed to refine independently for each profile. The difference between the constrained, Rietveld, lattice parameter and the individually refined parameters are plotted in figure 4. One can see that the low angle lines are most significantly different. The low angle lines were then sequentially eliminated from the Rietveld analyses and the results re-plotted. These are shown in figure 4 as the "minus 111" and "minus 111 and 220" data. It was judged that with the removal of the 111 and 220 lines that the spread of the remaining data was within acceptable limits. Therefore, the 22 data sets were analyzed with the Rietveld method, but with the 111 and 220 lines omitted.

![Figure 4. Lattice parameter difference data from the constrained (Rietveld) vs. unconstrained (profile) analyses for sample #31a (the first sample from the first bottle).](image)

The data were analyzed and assigned a statistical Type A uncertainty and a Type B uncertainty based on knowledge of the nature of errors in the measurements, to result in the establishment of robust uncertainties for the certified values (ISO, 1993 and Taylor and Kuyatt, 1994). The statistical analysis of the data indicated that the mean of the measurements was 0.54315753 nm with a $k=2$ Type A expanded uncertainty of $\pm 0.000\ 000\ 064$ nm. The intervals defined by a value and its uncertainty are approximate 95 % confidence intervals for the true value of the mean in the absence of systematic error. A Type B uncertainty due to systematic error must be incorporated into the error bounds of the certified lattice parameter due to fact that the measurements themselves are not metrological in nature. The variation in lattice parameter, as illustrated in figure 4, needs to be addressed with an assignment of a Type B uncertainty. It is
thought that this variation may be due to both faults in the model used for data analysis, and to flexing of the goniometer leading to errors in angle measurement. Considering the spread in the high angle data used in the certification, shown in figure 5, leads to an assignment of a Type B uncertainty of ±0.000 02 nm. The mean value of the lattice parameter requires a correction for the ≈1 K temperature difference between the laboratory during data collection and the reference temperature for the certified value. Using the formula in Bergamin et al. (1997) yields a value of 0.54315893 nm. Therefore, the certified lattice parameter at a temperature of 22.5 °C is:

\[ a = 0.543159 \text{ nm} \pm 0.000020 \text{ nm}. \]

Conclusion

A NIST built divergent beam diffractometer, incorporating many advanced design features, has been used to certify the lattice parameter of silicon powder for Standard Reference Material 640d. The silicon powder was specifically prepared to produce strain-free particles in the size range between 1 μm and 10 μm to eliminate size broadening effects. Both Type A, statistical, and Type B, systematic, errors have been assigned to yield a certified value for the lattice parameter of \( a = 0.543159 \text{ nm} \pm 0.000020 \text{ nm}. \)

References


