National Institute of Standards & Technology

Certificate

Standard Reference Material® 660b

Line Position and Line Shape Standard for Powder Diffraction

This Standard Reference Material (SRM) is intended for use in calibration of diffraction line positions and line shapes determined through powder diffractometry. A unit of SRM 660b consists of approximately 6 g of lanthanum hexaboride, LaB_6, powder bottled under argon.

Material Description: The SRM was prepared in a dedicated processing run using the [11]B isotope enriched to a nominal 99 % concentration. This isotopic enrichment renders this SRM relevant to the neutron diffraction community. The resulting powder was then annealed 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

$$0.415\ 689 \text{ nm} \ \pm \ 0.000\ 008 \text{ nm}$$

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 its distribution [1]. 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. 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 0.7 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.

Expiration of Certification: The certification of **SRM 660b** 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, 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.

Contributions towards the optimization of the annealing schedule, and therefore, the microstructure were provided by B. Toby, Argonne National Laboratory, Argonne, IL USA, A. Fitch, European Synchrotron Research Facility, Grenoble, France, and W.I.F. David, Rutherford Appleton Laboratory, Didcot, UK. J. Evans of Durham University, Durham, UK developed a template for the input files used in data analysis.

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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 660b 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 [11]boron-enriched boron carbide precursor was obtained from Ceradyne Boron Products LLC, Quapaw, OK, USA. The lanthanum hexaboride was synthesized by H.C Starck GmbH, Goslar, Germany. The annealing was performed by Cerac Inc., Milwaukee, WI, USA.

Certification Method: Certification was performed using data from a NIST-built diffractometer that includes several advanced design features. The optical layout is that of a conventional divergent-beam diffractometer 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) [2] 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 aforementioned NIST-built diffractometer is of θ-2θ geometry and is of a conventional optical layout, though it is built with several features atypical of 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.

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 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 detected 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 instrument was 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 [3] and SRM 676a Alumina Powder for Quantitative Analysis by X-Ray Diffraction [4] using procedures discussed by Cline [5].

Ten units of SRM 660b 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 24 selected regions of the diffraction pattern, each region including one of the

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[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.

reflections accessible within the 2θ range of 20° to 150°. 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 24 hours.

Data Analysis: The certification data were analyzed using the FPA method with a Rietveld [6-8] refinement as implemented in TOPAS [9]. The analysis used the Cu $K\alpha_1/K\alpha_2$ emission spectrum, including a satellite component, as characterized by G. Hölzer et al. [10,11]. 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 $K\alpha$ emission spectrum, terms indicating the position and intensity of the "tube tails" [12], a Soller slit value in the "full" axial divergence model [13], specimen displacement, an attenuation term, structural parameters, and a size-broadening term of a Lorentzian profile.

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 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 100 and 110 lines were, therefore, not used in obtaining the certified parameters. The thermal expansion of lanthanum hexaboride as reported by Sirota et al. [14] 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 0.415 688 46 nm with a $k = 2$ Type A expanded uncertainty of 0.000 000 25 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 660b Using Cu Kα Radiation,
$\lambda = 0.154\ 059\ 29$ nm

h	k	l	2θ, degrees
1	0	0	21.358
1	1	0	30.385
1	1	1	37.442
2	0	0	43.507
2	1	0	48.958
2	1	1	53.989
2	2	0	63.219
3	0	0	67.548
3	1	0	71.746
3	1	1	75.844
2	2	2	79.870
3	2	0	83.846
3	2	1	87.792
4	0	0	95.672
4	1	0	99.643
3	3	0	103.661
3	3	1	107.749
4	2	0	111.934
4	2	1	116.245
3	3	2	120.723
4	2	2	130.409
5	0	0	135.800
5	1	0	141.775
5	1	1	148.679

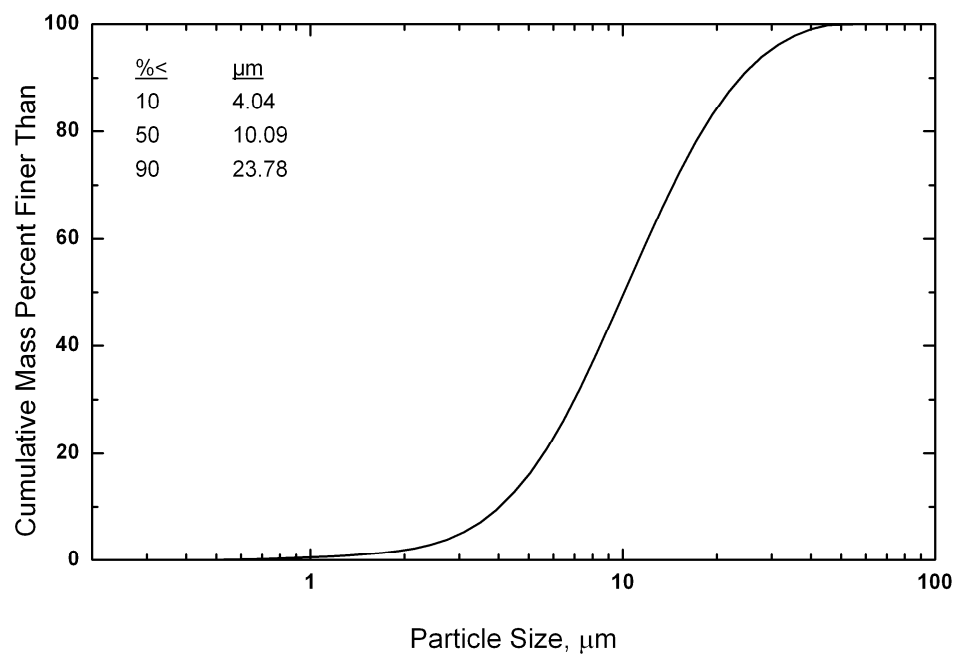|	
%<	µm
10	4.04
50	10.09
90	23.78

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

REFERENCES

[1]   JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (ISO GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Apr 2010); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at http://www.nist.gov/physlab/pubs/index.cfm (accessed Apr 2010).

[2]   Cheary, R.W.; Coelho, A.A.; *A Fundamental Parameters Approach to X-ray Line-Profile Fitting*; J. Appl. Cryst., Vol. 25, pp. 109-121 (1992).

[3]   SRM 660a; *Lanthanum Hexaboride Powder Line Position and Line Shape Standard for Powder Diffraction*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (13 September 2000).

[4]   SRM 676a; *Alumina Internal Standard for Quantitative Analysis by X-ray Powder Diffraction*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (28 January 2008).

[5]   Cline, J.P.; *Use of NIST Standard Reference Materials for Characterization of Instrument Performance*; Chapter in Industrial Applications of X-ray Diffraction, ed. by F.H. Chung and D.K. Smith, pub. by Marcel Dekker, Inc, pp 903-917 (2000).

[6]   Rietveld, H.M.; *Line Profiles of Neutron Powder Diffraction Peaks for Structure Refinement*, Acta Crysallogr., Vol. 22, pp. 151-152 (1967); Rietveld, H.M., *A Profile Refinement Method for Nuclear and Magnetic Structures*; J. Appl. Cryst., Vol. 2, pp. 65-71 (1969)

[7]   Young, R.A.; *The Rietveld Method*; Oxford University Press: New York (1993).

[8]   Bish, D.L.; Post, J.E., Eds.; *Modern Powder Diffraction*; Rev. Mineral., Vol. 20, p. 369 (1989).

[9]   TOPAS, *General Profile and Structure Analysis Software for Powder Diffraction Data*; V4.2, Bruker AXS GmbH, Karlsruhe, Germany.

[10]   Hölzer, G.; Fritsch, M.; Deutsch, M.; Härtwig, J.; Förster, E.; $K\alpha_{1,2}$ and $K\beta_{1,3}$ X-Ray Emission Lines of the 3d Transition Metals; Phys. Rev. A, Vol. 56, Issue (6), pp. 4554-4568 (1997).

[11]   Maskil, M.; Deutsch, M.; *X-Ray $K\alpha$ Satellites of Copper*; Phys. Rev. A, Vol. 38, pp. 3467-3472 (1988).

[12]   Bergmann, J.; Kleeberg, R.; Haase, A.; Breidenstein, B.; *Advanced Fundamental Parameters Model for Improved Profile Analysis*; In Proceedings of the 5th European Conference on Residual Stresses, Delft-Noordwijkerhout, The Netherlands, September 29-30, 1999, Editors: A.J. Böttger, R. Delhez, and E.J. Mittemeijer, Trans Tech Publications, 347-349, pp. 303-308 (2000).

[13]   Cheary, R.W.; Coelho, A.A.; *Axial Divergence in a Conventional X-Ray Powder Diffractometer I. Theoretical Foundations*, J. Appl. Cryst., Vol. 31, pp. 851-861 (1998), and Cheary, R.W.; Coelho, A.A.; *Axial Divergence in a Conventional X-Ray Powder Diffractometer II, Implementation and Comparison with Experiment*; J. Appl. Cryst., Vol. 31, pp. 862-868 (1998).

[14]   Sirota, N.N.; Novikov, V.V.; Vinokrov, V.A.; Paderno, B.Yu.; *Temperature Dependence of Heat Capacity and Lattice Constant of Lanthanum and Samarium Hexaborides*; Phys. Sold State, Vol. 40 (11), pp. 1856-1858 (1998).