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Haasch, Richard T
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Richard T. Haasch, Lane W. Martin, and Eric Breckenfeld

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Single Crystal Rare-earth Scandate Perovskites Analyzed Using X-ray Photoelectron Spectroscopy: 3. GdScO₃(110)

Richard T. Haasch^{a)}

Department of Materials Science and Engineering and Materials Research Laboratory,
University of Illinois, Urbana-Champaign

Lane W. Martin

Department of Materials Science and Engineering and Materials Research Laboratory,
University of Illinois, Urbana-Champaign; Department of Materials Science and Engineering,
University of California, Berkeley; and Materials Science Division, Lawrence Berkeley National
Laboratory

Eric Breckenfeld

Department of Materials Science and Engineering and Materials Research Laboratory,
University of Illinois, Urbana-Champaign; and Naval Research Laboratory, Washington, DC

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X-ray photoelectron spectroscopy (XPS) was used to analyze a commercially available GdScO₃ (110) bulk single crystal. XP spectra were obtained using incident monochromatic Al K_α radiation at 0.83401 nm. A survey spectrum together with Gd 3d, O 1s, Sc 2p, Gd 4p, C 1s, Gd 4d, Sc 3s, Gd 5s, Sc 3p, O 2s, Gd 5p, and Gd 4f core level spectra and the valence band are presented. The spectra indicate the principle core level photoelectron and Auger electron signals and show only minor carbon contamination. Making use of the O 1s, Sc 2p, Gd 4d lines and neglecting the components related to surface contaminants, XPS quantitative analysis reveals an altered stoichiometry of the air-exposed crystal surface of Gd_{1.07}ScO_{2.21}. © 2014 American Vacuum Society. [<http://dx.doi.org/10.1116/11.20140908>]

Keywords: gadolinium scandium oxide; rare-earth scandate; perovskite

INTRODUCTION

Transition metal oxides present an impressive variety of functionality which is not available in more traditional systems such as group IV and III-V semiconductors or elemental metals. Among the many possible functionalities are, for instance, ferroelectricity (Ref. 1) and magnetism (Ref. 2), colossal magnetoresistance (Ref. 3), and high temperature superconductivity (Ref. 4), with transport character ranging from insulating to semiconducting to metallic. Furthermore, these properties are extremely sensitive to perturbations from chemistry, structural defects, strain and many other effects and this, in turn, provides the materials engineer a number of routes by which to engineer new functionalities in this class of materials (Ref. 5). While even simple oxide systems, such as binary oxides, exhibit a broad diversity of properties, it is the ternary systems which have received the most attention in recent years. In particular, materials possessing the perovskite structure (with chemical formula ABO₃) have been observed to exhibit an incredible variety of functionality and phenomena. Advances in thin film epitaxy, particularly pulsed laser deposition, RF magnetron sputtering, and molecular beam epitaxy, have enabled researchers to carefully tune material properties using epitaxial strain. Such approaches have provided an opportunity to apply large biaxial strains (as much as several percent in some cases) to nanoscale films of various materials which would lead to cracks in bulk materials under similar values of hydrostatic strain (Ref. 6).

^{a)}Author to whom correspondence should be addressed.

SPECIMEN DESCRIPTION (ACCESSION #01317)

Host Material: Single crystal GdScO₃

CAS Registry #: unknown

Host Material Characteristics: homogeneous; solid; single crystal; dielectric; inorganic compound

Chemical Name: gadolinium scandium oxide

Source: Crystec, GmbH. Grown by the Czochralski method.

Host Composition: GdScO₃

Form: single crystal

Structure: orthorhombic distorted perovskite-like structure Pnma
Z = 4, a = 0.5745(1) nm, b = 0.7929(2) nm, c = 0.5481(1) nm,
V = 0.2497(1) nm³ (Ref. 7)

History & Significance: Various perovskite-based compounds have been widely used as substrates for a number of important applications such as epitaxial substrates for high TC oxide superconductors (Ref. 8), ferroelectric materials (Ref. 9), high-quality optoelectronic semiconductors (Ref. 10), and colossal magnetoresistive materials (Ref. 11). One particular group of perovskite-based materials, rare-earth scandates, is gaining attention as a candidate for high-k dielectrics (Refs. 12 and 13). In order to gain an increased understanding of the surfaces and hetero-interfaces of perovskite-based materials, a GdScO₃ (110) bulk single crystal was analyzed using X-ray photoelectron spectroscopy.

As Received Condition: as grown

Analyzed Region: same as host material

Accession #: 01317

Technique: XPS

Host Material: Single crystal GdScO₃

Instrument: Kratos Axis Ultra

Major Elements in Spectra: Gd, Sc, O

Minor Elements in Spectra: C

Published Spectra: 7

Spectra in Electronic Record: 7

Spectral Category: comparison

Ex Situ Preparation/Mounting: Samples were cleaned ultrasonically for 5 min each in Formula 409[®], methyl alcohol, and deionized water. Samples were mounted onto the sample holder using double-sided carbon tape (Pella product number 16074).

In Situ Preparation: none

Pre-Analysis Beam Exposure: less than 2 min; no x-ray degradation effects observed

Charge Control: low energy flood gun/magnetic immersion lens combination, filament current = 1.8 A, charge balance = 3.25 V, filament bias = 1 V

Temp. During Analysis: 300 K

Pressure During Analysis: $<3 \times 10^{-7}$ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Kratos Axis Ultra

Analyzer Type: spherical sector

Detector: channeltron electron multiplier

Number of Detector Elements: 8

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ Spectrometer

Analyzer Mode: constant pass energy

Throughput ($T = E^M$): $N = 0$

Excitation Source Window: not specified

Excitation Source: Al K_{α} , monochromatic

Source Energy: 1486.6 eV

Source Strength: 180 W

Source Beam Size: 2000 $\mu\text{m} \times 2000 \mu\text{m}$

Signal Mode: multichannel direct

■ Geometry

Incident Angle: 54°

Source to Analyzer Angle: 54°

Emission Angle: 0°

Specimen Azimuthal Angle: 45°

Acceptance Angle from Analyzer Axis: 0°

Analyzer Angular Acceptance Width: 40° \times 40°

DATA ANALYSIS METHOD

Energy Scale Correction: The binding energy scale was referenced to C 1s = 285.0 eV.

Recommended Energy Scale Shift: +2.233 eV for high-resolution spectra

Peak Shape and Background Method: Background: Custom three parameter Tougaard background (Ref. 14), U 4 Tougaard

(B, C, D, T0=0) (Ref. 15), was used. O 1s: B = 299 eV², C = 600 eV², D = 275 eV², Sc 2p: B = 299 eV², C = 375 eV², D = 275 eV², C 1s: B = 299 eV², C = 225 eV², D = 275 eV², Gd 4d: B = 299 eV², C = 325 eV², D = 275 eV².

Quantitation Method: Quantification was done using region and component definitions with CasaXPS version 2.3.15. Sensitivity factors supplied by Kratos Analytical. Errors are given as ± 1 standard deviation. Standard deviations are calculated by CasaXPS using a Monte Carlo method for determining the error distribution for the computed areas.

ACKNOWLEDGMENTS

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SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV × cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
01317-02	Gd 3d _{5/2}	1186.9	5.34	GdScO ₃
01317-02 ^a	Gd 3d _{5/2}	1196.6	3.67	GdScO ₃
01317-02	Gd 3d _{3/2}	1219.0	5.76	GdScO ₃
01317-03	O 1s	529.4	0.99	24512.2	0.780	30.18	GdScO ₃
01317-03 ^b	O 1s	531.4	1.90	6810.3	0.780	8.39	hydroxide
01317-03 ^a	O 1s	533.0	1.54	3003.5	0.780	3.70	carbonate
01317-04	Sc 2p	26660.2	1.875	13.65	...
01317-04	Sc 2p _{3/2}	401.1	1.04	GdScO ₃
01317-04 ^c	Sc 2p _{3/2}	412.6	2.23	GdScO ₃
01317-04	Sc 2p _{1/2}	405.5	1.30	GdScO ₃
01317-04 ^c	Sc 2p _{1/2}	417.1	2.23	GdScO ₃
01317-05	Gd 4p _{3/2}	271.0	5.67	GdScO ₃
01317-05	Gd 4p _{1/2}	306.5	5.67	GdScO ₃
01317-05	Gd 4p _{1/2}	312.6	6.00	GdScO ₃
01317-05	Gd 4p _{1/2}	318.0	3.49	GdScO ₃
01317-05 ^d	C 1s	285.0	1.13	5508.8	0.278	19.03	hydrocarbon
01317-05 ^b	C 1s	286.7	1.70	1903.0	0.278	6.57	C-hydroxide
01317-05 ^b	C 1s	288.7	1.38	1112.4	0.278	3.84	carbonate
01317-06	Gd 4d	37844.5	2.484	14.63	...
01317-06	Gd 4d	142.0	3.99	GdScO ₃
01317-06	Gd 4d	147.2	3.99	GdScO ₃
01317-07	Sc 3s	52.7	2.60	GdScO ₃
01317-07	Gd 5s	43.6	2.35	GdScO ₃
01317-07	Sc 3p	31.0	1.74	GdScO ₃
01317-07	Gd 5p _{3/2}	20.2	3.00	GdScO ₃
01317-07	Gd 5p _{1/2}	27.1	3.10	GdScO ₃
01317-07	O 2s	22.9	3.10	GdScO ₃
01317-07	Gd 4f _{7/2}	7.8	1.24	GdScO ₃
01317-07	Gd 4f _{5/2}	8.9	1.24	GdScO ₃
01317-07 ^e	valence band	5.6	2.01	GdScO ₃
01317-07 ^f	valence band maximum (VBM)	3.4	1.15	GdScO ₃

^a Satellite

^b Result of exposure to air

^c Bulk plasmon

^d Region overlaps with Gd 4p_{1/2}

^e O 2p and Sc 3d (Ref. 16)

^f The position of VBM was estimated by subtracting 1/2 of the full width at half maximum (FWHM) from the position of the maximum intensity at the VBM.

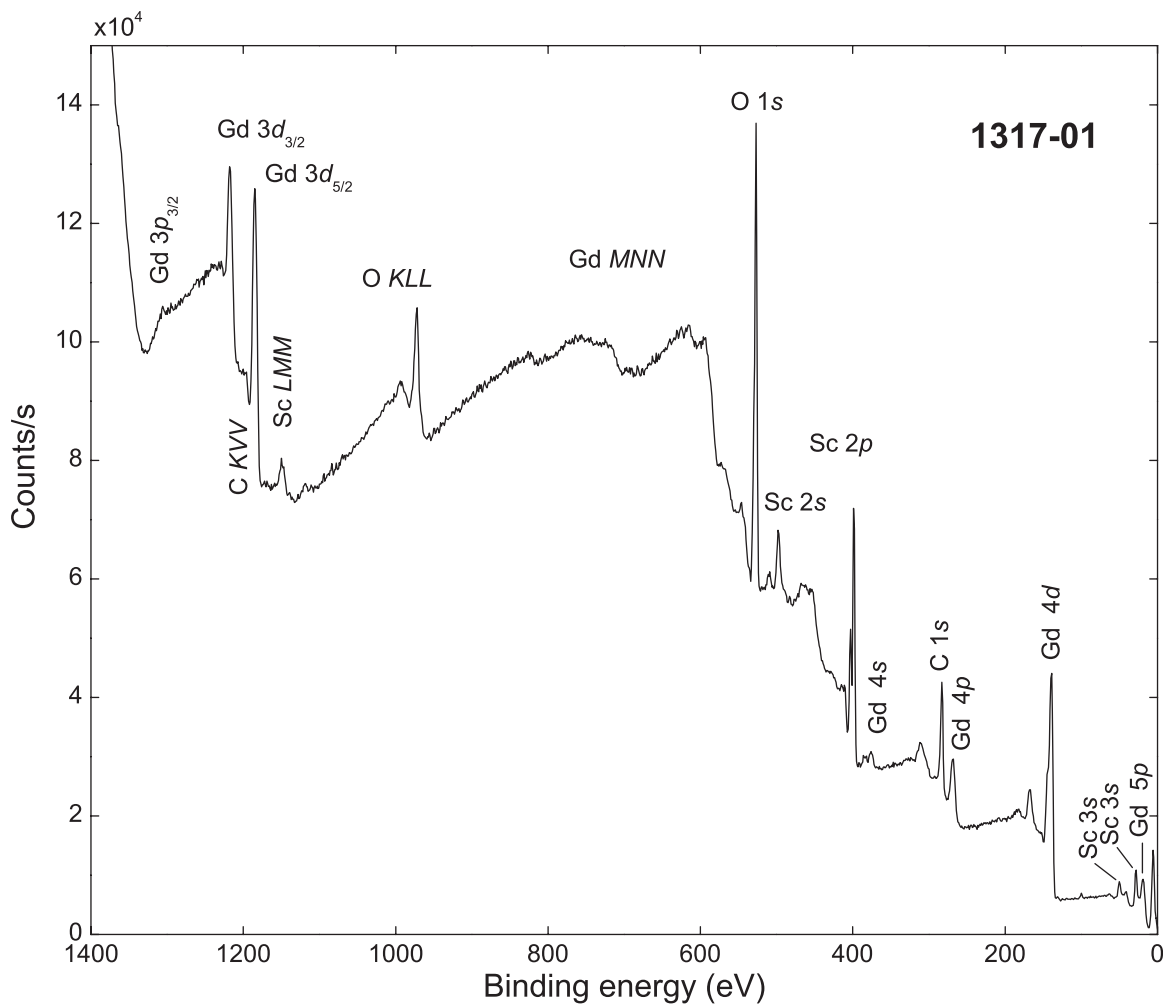
ANALYZER CALIBRATION TABLE

Spectrum ID #	Element/Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV × cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
	Au 4f _{7/2}	84.0	0.72	151917.9
	Ag 3d _{5/2}	368.2	0.58	230506.2
	Cu 2p _{3/2}	932.6	0.88	410979.8

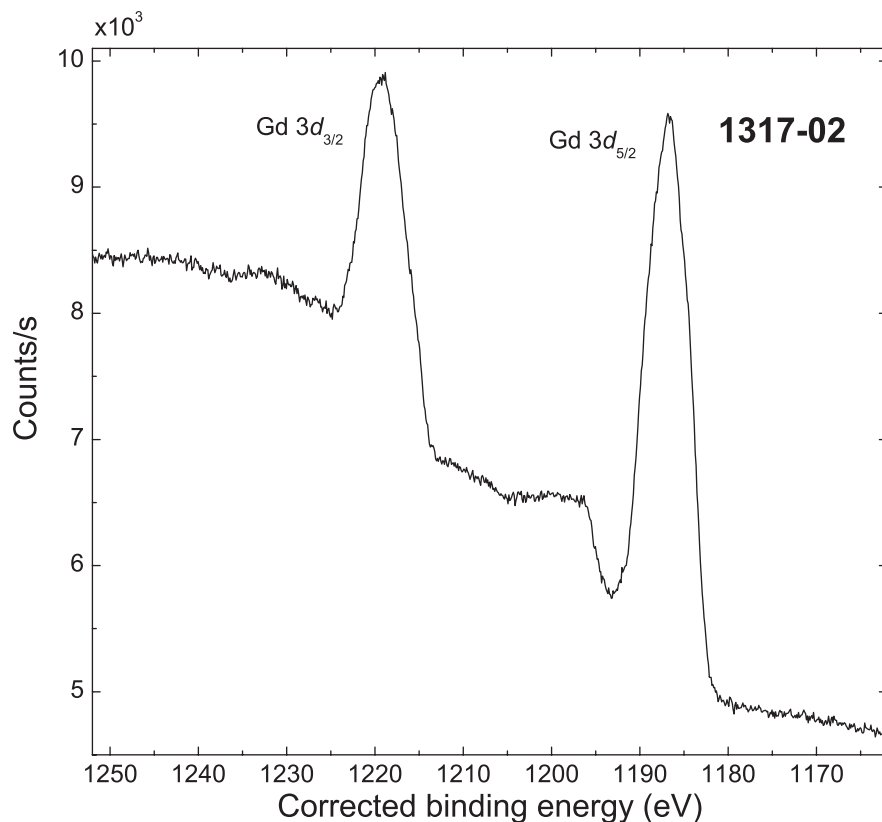
GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
1317-01	survey	0	1	0	
1317-02	Gd 3d	-2.233	1	0	
1317-03	O 1s	-2.233	1	0	
1317-04	Sc 2p	-2.233	1	0	
1317-05	Gd 4p, C 1s	-2.233	1	0	
1317-06	Gd 4d	-2.233	1	0	
1317-07	Sc 3s, Gd 5s, Sc 3p, Gd 5p, O 2s, Gd 4f	-2.233	1	0	

* Voltage shift of the archived (as-measured) spectrum relative to the printed figure. The figure reflects the recommended energy scale correction due to a calibration correction, sample charging, flood gun, or other phenomenon.

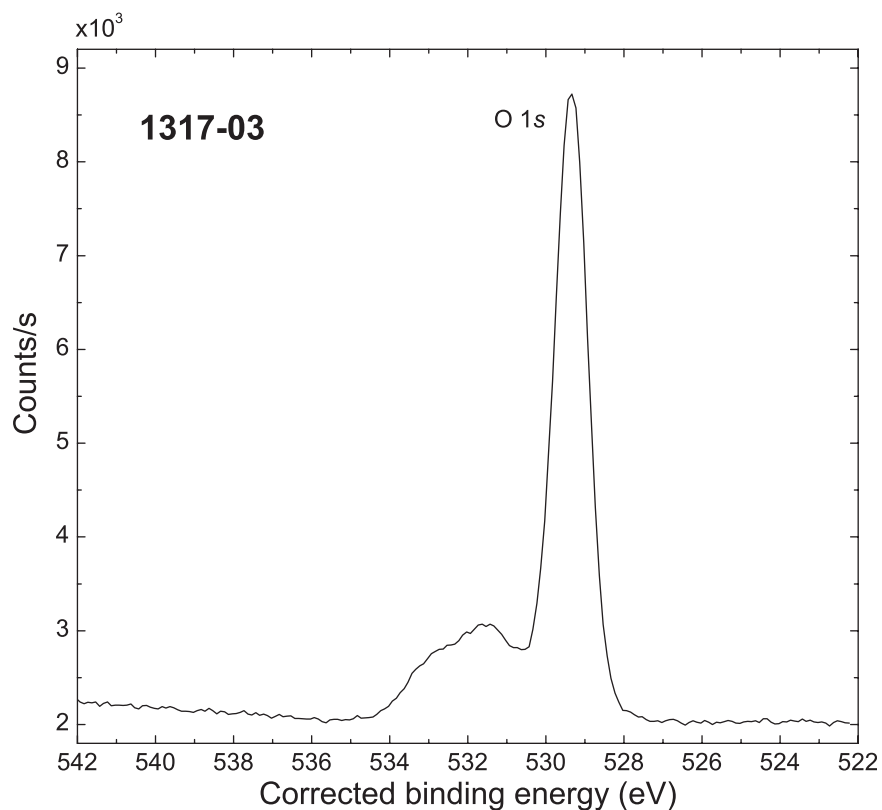


Accession #	01317-01
Host Material	Single crystal GdScO ₃
Technique	XPS
Spectral Region	survey
Instrument	Kratos Axis Ultra
Excitation Source	Al K _α monochromatic
Source Energy	1486.6 eV
Source Strength	180 W
Source Size	2 mm × 2 mm
Analyzer Type	spherical sector
Incident Angle	54°
Emission Angle	0°
Analyzer Pass Energy:	160 eV
Analyzer Resolution	2.4 eV
Total Signal Accumulation Time	560 s
Total Elapsed Time	1120 s
Number of Scans	4
Effective Detector Width	33.6 eV



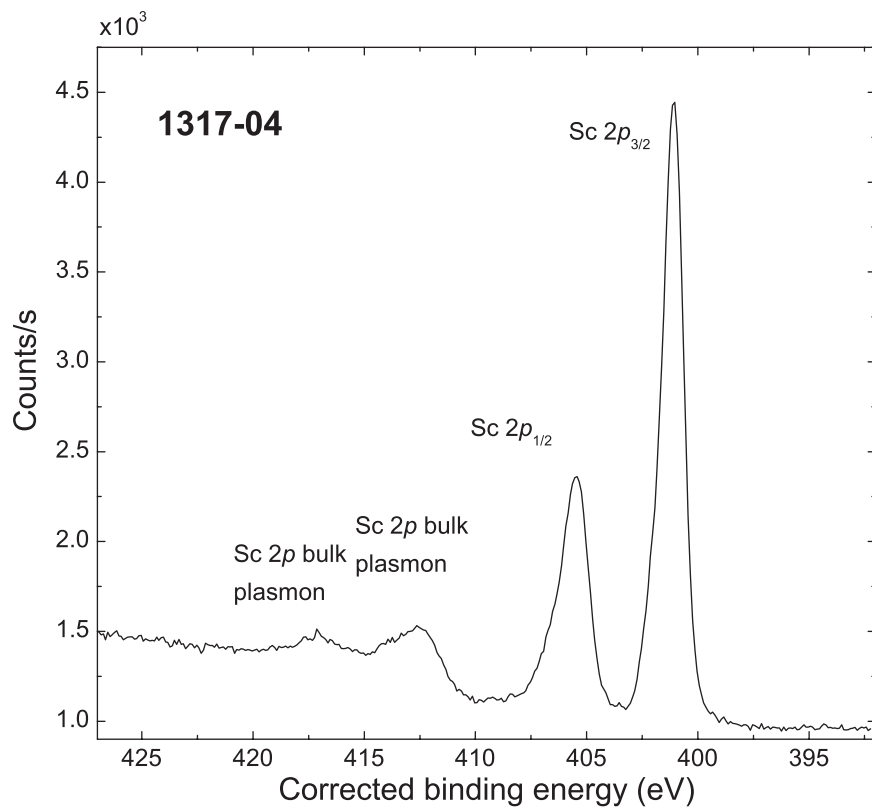
- Accession #: 01317-02
- Host Material: Single crystal GdScO₃
- Technique: XPS
- Spectral Region: Gd 3d

Instrument: Kratos Axis Ultra
 Excitation Source: Al K_α monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 180 W
 Source Size: 2 mm × 2 mm
 Analyzer Type: spherical sector
 Incident Angle: 54°
 Emission Angle: 0°
 Analyzer Pass Energy: 20 eV
 Analyzer Resolution: 0.3 eV
 Total Signal Accumulation Time: 5406 s
 Total Elapsed Time: 14866.5 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV



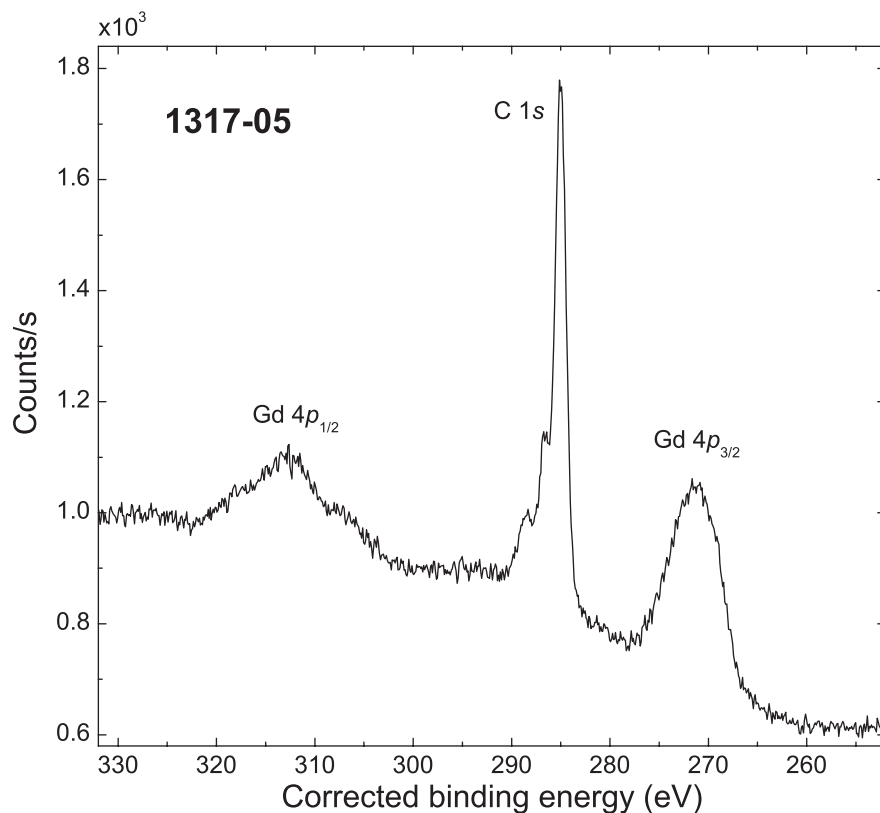
- Accession #: 01317-03
- Host Material: Single crystal GdScO₃
- Technique: XPS
- Spectral Region: O 1s

Instrument: Kratos Axis Ultra
 Excitation Source: Al K_α monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 180 W
 Source Size: 2 mm × 2 mm
 Analyzer Type: spherical sector
 Incident Angle: 54°
 Emission Angle: 0°
 Analyzer Pass Energy: 20 eV
 Analyzer Resolution: 0.3 eV
 Total Signal Accumulation Time: 1206 s
 Total Elapsed Time: 3316.5 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV



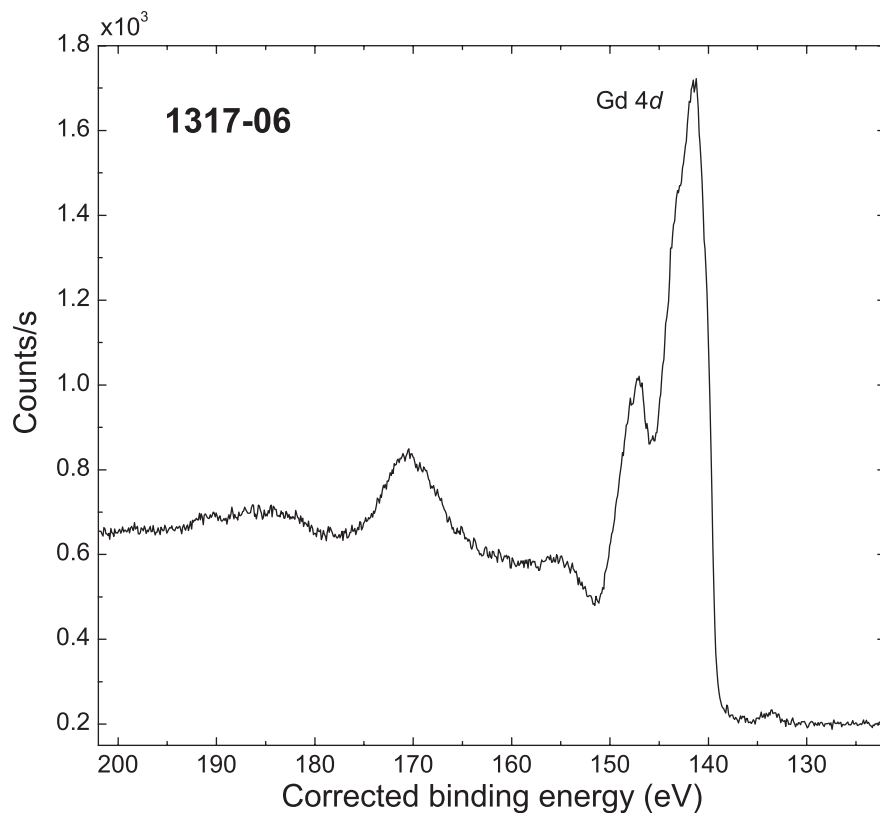
- Accession #: 01317-04
- Host Material: Single crystal GdScO₃
- Technique: XPS
- Spectral Region: Sc 2p

Instrument: Kratos Axis Ultra
 Excitation Source: Al K_α monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 180 W
 Source Size: 2 mm × 2 mm
 Analyzer Type: spherical sector
 Incident Angle: 54°
 Emission Angle: 0°
 Analyzer Pass Energy: 20 eV
 Analyzer Resolution: 0.3 eV
 Total Signal Accumulation Time: 2106 s
 Total Elapsed Time: 5791.5 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV



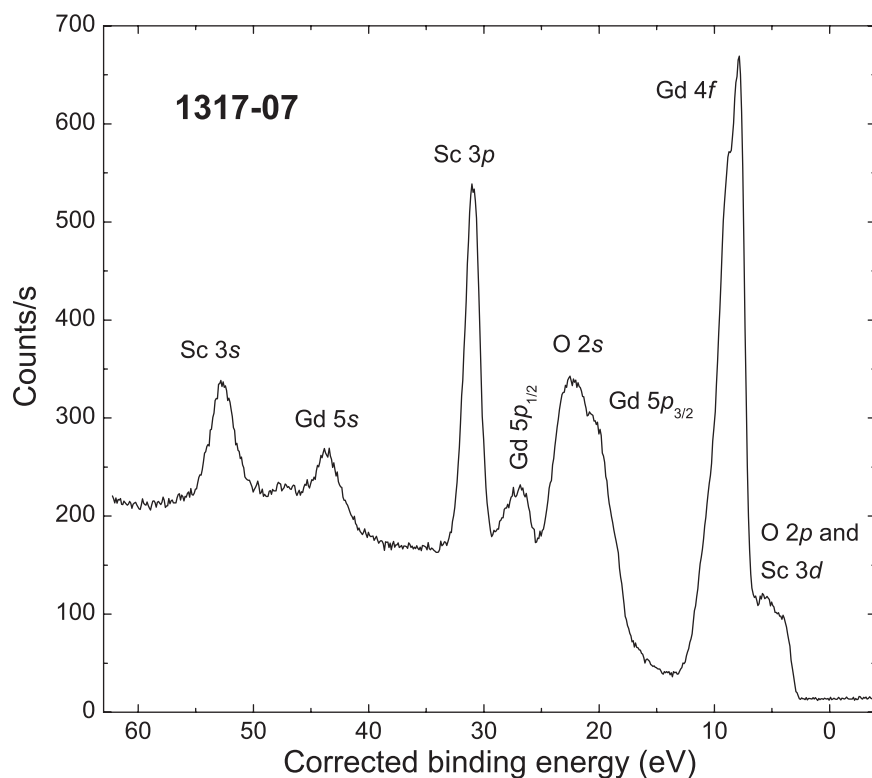
- Accession #: 01317-05
- Host Material: Single crystal GdScO₃
- Technique: XPS
- Spectral Region: Gd 4p; C 1s

Instrument: Kratos Axis Ultra
 Excitation Source: Al K_α monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 180 W
 Source Size: 2 mm × 2 mm
 Analyzer Type: spherical sector
 Incident Angle: 54°
 Emission Angle: 0°
 Analyzer Pass Energy: 20 eV
 Analyzer Resolution: 0.3 eV
 Total Signal Accumulation Time: 4806 s
 Total Elapsed Time: 13216.5 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV



- Accession #: 01317-06
- Host Material: Single crystal GdScO₃
- Technique: XPS
- Spectral Region: Gd 4d

Instrument: Kratos Axis Ultra
 Excitation Source: Al K_α monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 180 W
 Source Size: 2 mm × 2 mm
 Analyzer Type: spherical sector
 Incident Angle: 54°
 Emission Angle: 0°
 Analyzer Pass Energy: 20 eV
 Analyzer Resolution: 0.3 eV
 Total Signal Accumulation Time: 4806 s
 Total Elapsed Time: 13216.5 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV



- Accession #: 01317-07
- Host Material: Single crystal GdScO₃
- Technique: XPS
- Spectral Region: Sc 3s; Gd 5s; Sc 3p; Gd 5p; O 2s; Gd 4f; valence band

Instrument: Kratos Axis Ultra
 Excitation Source: Al K_α monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 180 W
 Source Size: 2 mm × 2 mm
 Analyzer Type: spherical sector
 Incident Angle: 54°
 Emission Angle: 0°
 Analyzer Pass Energy: 20 eV
 Analyzer Resolution: 0.3 eV
 Total Signal Accumulation Time: 9254 s
 Total Elapsed Time: 25448.5 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV