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Single Crystal Perovskites Analyzed Using X-ray Photoelectron Spectroscopy: 3. LaAlO₃(001)

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X-ray photoelectron spectroscopy (XPS) was used to analyze a commercially available LaAlO₃(001) bulk single crystal. XP spectra were obtained using incident monochromatic Al K_α radiation at 0.83401 nm. A survey spectrum together with La 3d, O 1s, C 1s, La 4p, Al 2s, La 4d, Al 2p, La 5s, O 2s and La 5p 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, La 4d, Al 2p lines and neglecting the components related to surface contaminants, XPS quantitative analysis reveals an altered stoichiometry of the air-exposed crystal surface of LaAl_{1.03}O_{2.23}. © 2014 American Vacuum Society. [<http://dx.doi.org/10.1116/11.20140903>]

Keywords: lanthanum aluminum oxide; 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).

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SPECIMEN DESCRIPTION (ACCESSION #01312)

Host Material: Single crystal LaAlO₃

CAS Registry #: 120003-65-5

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

Chemical Name: Lanthanum aluminum oxide

Source: Crystec, GmbH

Host Composition: LaAlO₃

Form: single crystal

Structure: rhombohedral, perovskite-like structure, a = 0.5357 nm, c = 1.322 nm (Ref. 7)

History & Significance: Although originally intended as a substrate for high TC superconducting oxides, LaAlO₃ has become attractive for a number of additional applications. LaAlO₃ has been considered as a possible candidate for “high-κ” gate dielectrics in complementary metal oxide semiconductor gate stacks (CMOS) as a result of a larger band offset with Si, low atomic diffusion rates in LaAlO₃, and a lower likelihood of SiO₂ formation during processing as compared to other candidate dielectrics (Ref. 6). More recently, much research has focused on the heterointerface between LaAlO₃ and SrTiO₃ where a conducting state was discovered in 2004 (Ref. 8). This conducting state has been studied in numerous experiments, and there have been a number of interesting findings related to these interfaces including the observation of magnetic ground states (Ref. 9), superconductivity (Ref. 10), built-in polarizations (Ref. 11), and other interesting effects (Ref. 12). The conductivity is hypothesized to arise from

electronic reconstruction that occurs to avoid the so-called polar catastrophe. This model predicts a critical thickness for the emergence of conductivity of just 4 unit cells and can be considered an intrinsic response of the system to the build-up of electrostatic energy (Ref. 13). In order to gain an increased understanding of the surfaces and hetero-interfaces of perovskite-based materials, a $\text{LaAlO}_3(001)$ bulk single crystal was analyzed using X-ray photoelectron spectroscopy.

As Received Condition: as grown

Analyzed Region: same as host material

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 V, filament bias = 1 V

Temp. During Analysis: 300 K

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

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: +2.103 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, C 1s, La 4d, Al 2p: B = 299 eV², C = 542 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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REFERENCES

1. M. Dawber, K. M. Rabe, and J. F. Scott, *Rev. Mod. Phys.* **77**, 1083 (2005).
2. S. A. Chambers, T. C. Droubay, C. M. Wang, K. M. Rosso, S. M. Heald, D. A. Schwartz, K. R. Kittilstved, and D. R. Gamelin, *Mater. Today* **9**, 28 (2006).
3. A. P. Ramirez, *J. Phys.: Condens. Matter* **9**, 8171 (1997).
4. J.-M. G. Chen Langlois, Y. Guo, and W. A. Goddard III, *Proc. Natl. Acad. Sci. U.S.A.* **86**, 3447 (1989).
5. D. G. Schlom, L.-Q. Chen, C.-B. Eom, K. M. Rabe, S. K. Streiffner, and J.-M. Triscone, *Annu. Rev. Mater. Res.* **37**, 589 (2007).
6. L. W. Martin and D. G. Schlom, *Curr. Opin. Solid State Mater. Sci.* **16**, 199 (2012).
7. See <http://www.sigmaldrich.com/catalog/product/aldrich/634735?lang=en®ion=US>.
8. A. Ohtomo and H. Y. Hwang, *Nature* **427**, 423 (2004).
9. A. Brinkman, M. Huijben, M. van Zalk, J. Juijben, U. Zeitler, J. C. Maan, W. G. van der Wiel, G. Rijnders, D. H. A. Blank, and H. Hilgenkamp, *Nat. Mater.* **6**, 493 (2007).
10. N. Reyren, S. Thiel, A. D. Caviglia, L. Fitting-Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Ruetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone, and J. Mannhart, *Science* **317**, 1196 (2007).
11. G. Singh-Bhalla, C. Bell, J. Ravichandran, W. Siemons, Y. Hikita, S. Salahuddin, A. F. Hebard, H. Y. Hwang, and R. Ramesh, *Nat. Phys.* **7**, 80 (2011).
12. J. W. Park, D. F. Bogorin, C. Cen, D. A. Felker, Y. Zhang, C. T. Nelson, C. W. Bark, C. M. Folkman, X. Q. Pan, M. S. Rzchowski, J. Levy, and C.-B. Eom, *Nat. Commun.* **1**, 94 (2010).
13. S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider, and J. Mannhart, *Science* **313**, 1942 (2006).
14. S. Tougaard, *Surf. Interface Anal.* **25**, 137 (1997).
15. N. Fairley and A. Carrick, *The Casa Cookbook Part 1: Recipes for XPS Data Processing* (Acolyte Science, Cheshire, UK, 2005), pp. 147–671.
16. L. Guan, L. Jin, W. Zhang, Q. Li, J. Guo, and B. Geng, *Adv. Mater. Res.* **79–82**, 385 (2009).

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
01312-02	La 3d _{5/2}	833.9	1.41	LaAlO ₃
01312-02	La 3d _{5/2}	838.4	1.89	LaAlO ₃
01312-02	La 3d _{3/2}	850.7	1.24	LaAlO ₃
01312-02	La 3d _{3/2}	855.1	2.00	LaAlO ₃
01312-03	O 1s	529.6	1.06	35304.4	0.780	37.79	LaAlO ₃
01312-03 ^a	O 1s	531.6	2.80	9963.5	0.780	10.67	hydroxide, carbonate
01312-04 ^a	C 1s	285.0	1.25	3994.4	0.278	12.00	hydrocarbon
01312-04 ^a	C 1s	286.6	1.79	1058.5	0.278	3.18	C-hydroxide
01312-04 ^a	C 1s	288.9	1.78	641.2	0.278	1.93	carbonate
01312-05	La 4p _{3/2}	195.3	1.71	LaAlO ₃
01312-05	La 4p _{3/2}	198.6	3.48	LaAlO ₃
01312-06	Al 2s	118.4	1.68	LaAlO ₃
01312-07	La 4d	50295.6	2.475	16.97	...
01312-07	La 4d _{5/2}	101.9	1.28	LaAlO ₃
01312-07	La 4d _{5/2}	105.1	3.04	LaAlO ₃
01312-07	La 4d _{3/2}	105.1	1.28	LaAlO ₃
01312-07	La 4d _{3/2}	108.1	3.04	LaAlO ₃
01312-08	Al 2p	4037.3	0.193	17.47	...
01312-08	Al 2p	73.5	1.14	LaAlO ₃
01312-09	La 5s	34.7	1.35	LaAlO ₃
01312-09	O 2s	22.0	2.32	LaAlO ₃
01312-09 ^a	O 2s	24.3	2.10	hydroxide, carbonate
01312-09	La 5p _{3/2}	16.9	1.34	LaAlO ₃
01312-09	La 5p _{1/2}	19.3	1.34	LaAlO ₃
01312-09 ^b	valence band	9.1	2.00	LaAlO ₃
01312-09 ^c	valence band	7.2	1.43	LaAlO ₃
01312-09 ^c	valence band	5.6	1.53	LaAlO ₃
01312-09 ^d	valence band maximum	1.4	1.50	LaAlO ₃

^a Result of exposure to air

^b O 2p and Al 3s (Ref. 16)

^c O 2p and Al 3p (Ref. 16)

^d 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.

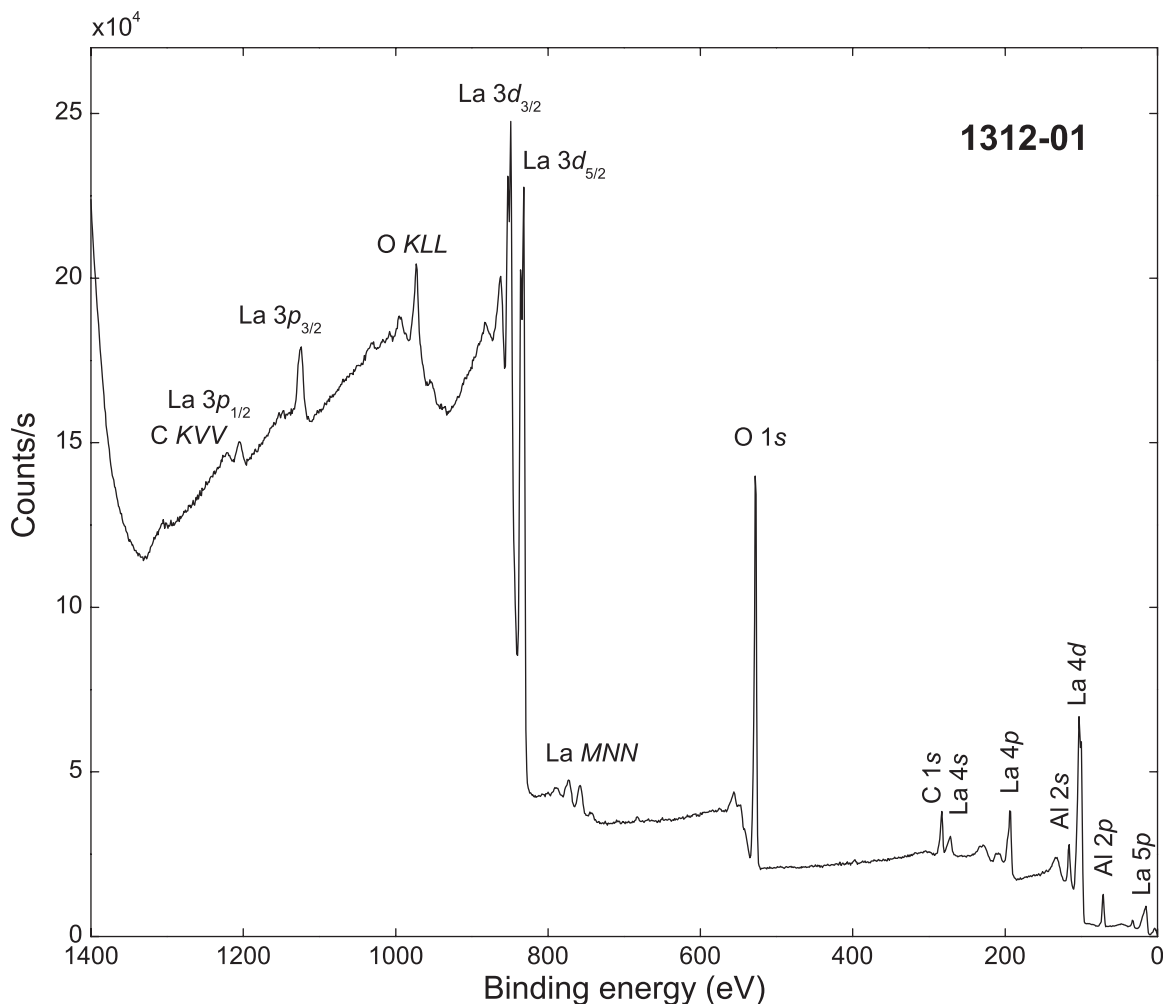
ANALYZER CALIBRATION TABLE

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

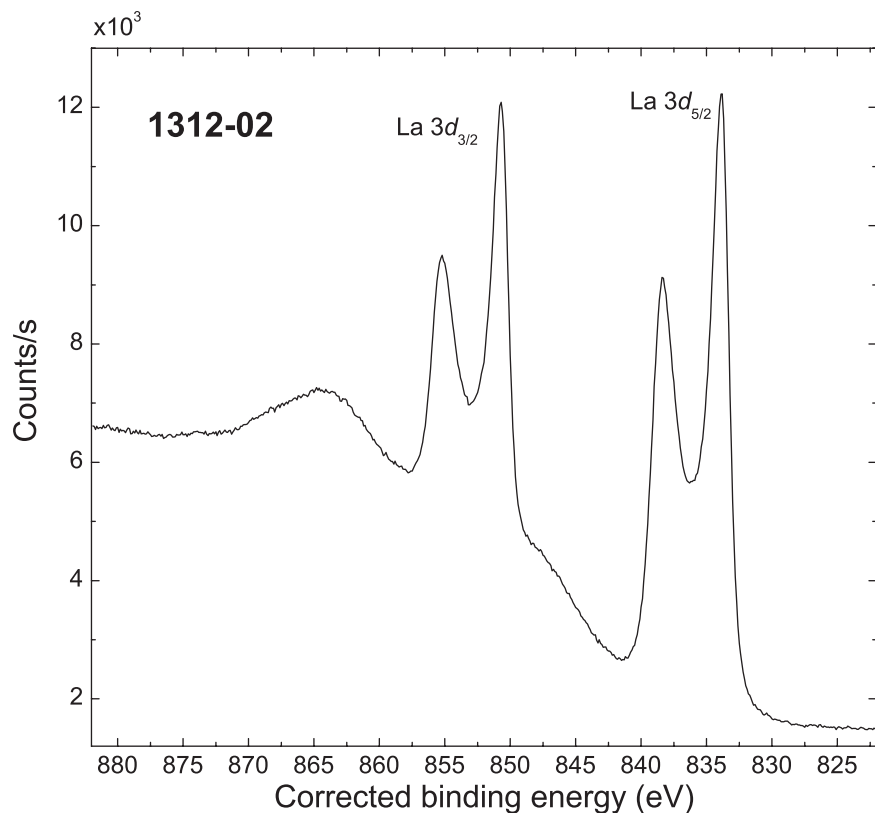
Spectrum (Accession) #	Spectral Region	Voltage Shift[*]	Multiplier	Baseline	Comment #
1312-01	survey	0	1	0	
1312-02	La 3d	-2.103	1	0	
1312-03	O 1s	-2.103	1	0	
1312-04	C 1s	-2.103	1	0	
1312-05	La 4p	-2.103	1	0	
1312-06	Al 2s	-2.103	1	0	
1312-07	La 4d	-2.103	1	0	
1312-08	Al 2p	-2.103	1	0	
1312-09	La 5s, O 2s, La 5p, valence band	-2.103	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.



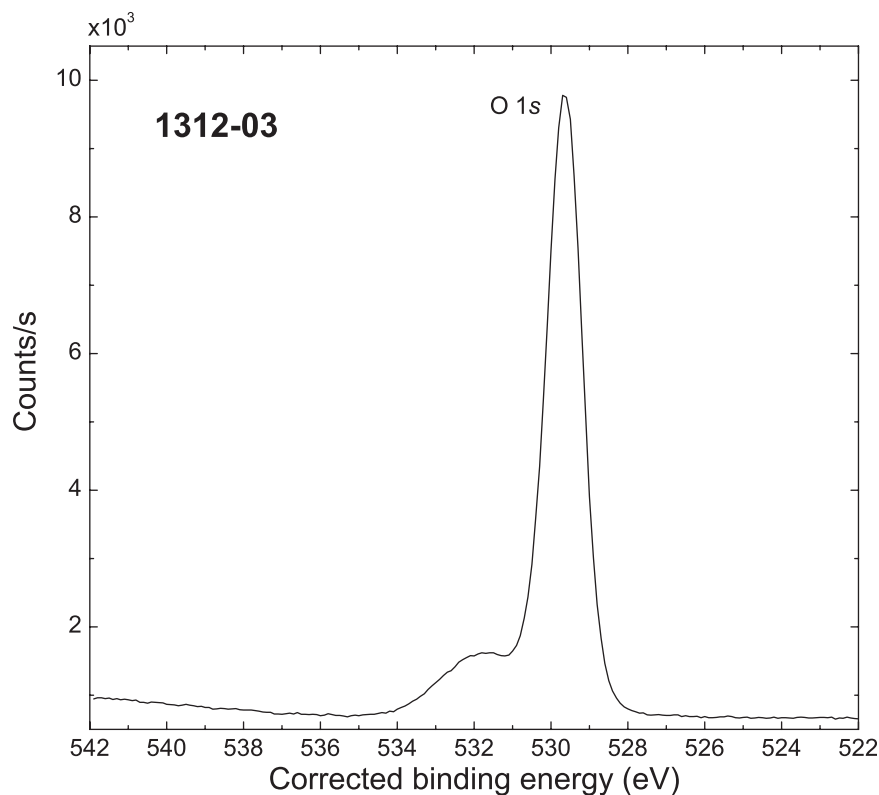
1312-01

Accession #	01312-01
Host Material	Single crystal LaAlO 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



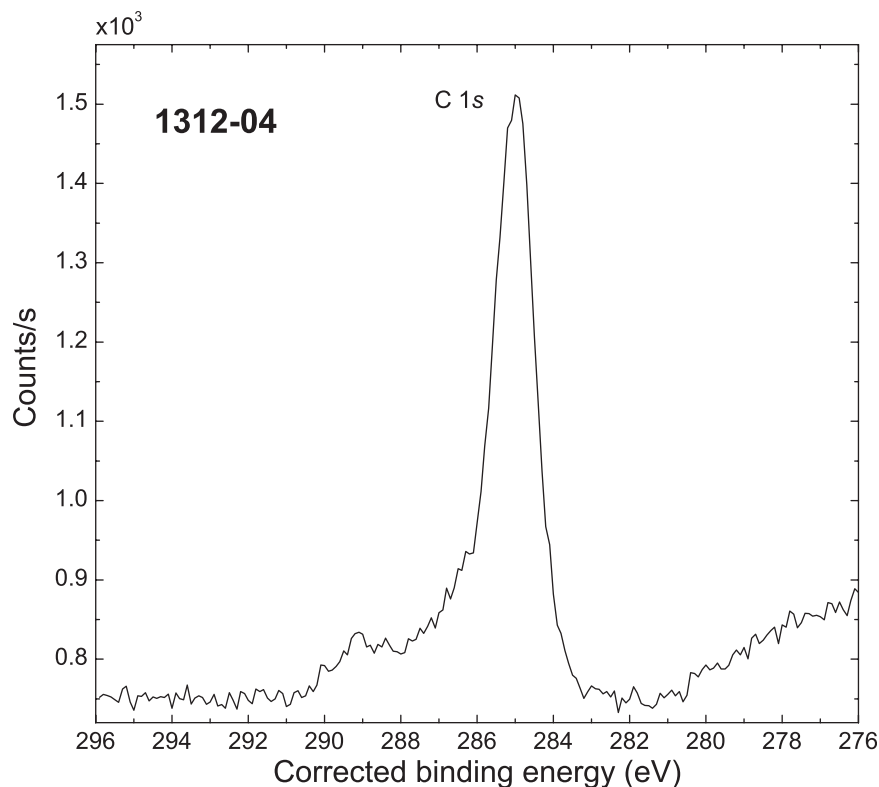
- **Accession #:** 01312-02
- **Host Material:** Single crystal LaAlO_3
- **Technique:** XPS
- **Spectral Region:** La 3d

Instrument: Kratos Axis Ultra
 Excitation Source: Al K_α monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 180 W
 Source Size: 2 mm \times 2 mm
 Analyzer Type: spherical sector
 Incident Angle: 54°
 Emission Angle: 0°
 Analyzer Pass Energy: 160 eV
 Analyzer Resolution: 0.3 eV
 Total Signal Accumulation Time: 3606 s
 Total Elapsed Time: 9916.5 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV



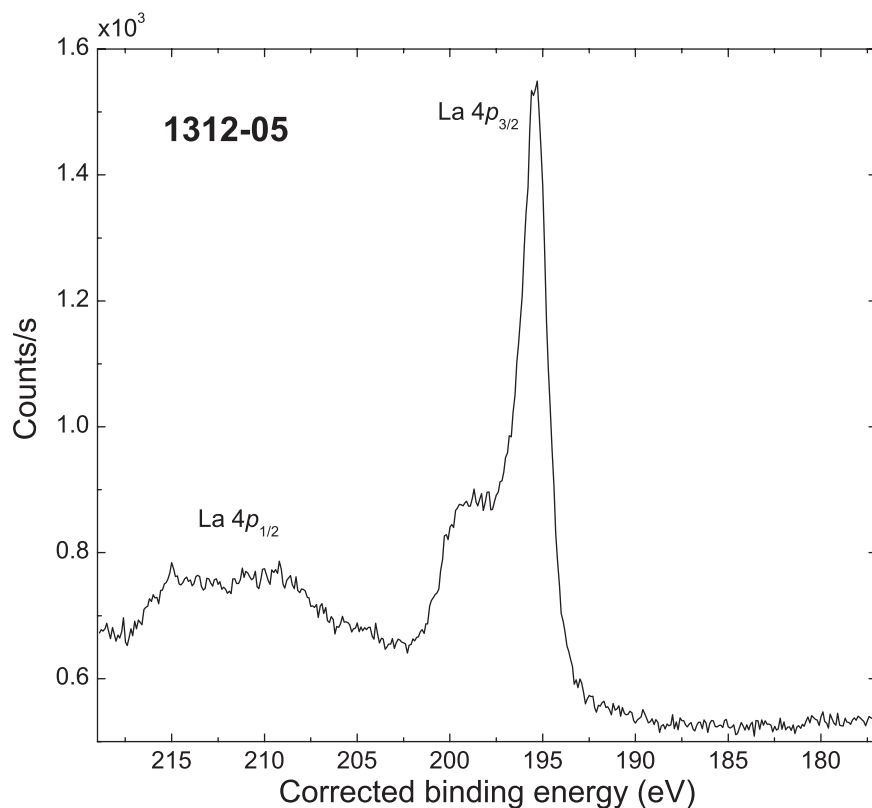
- **Accession #:** 01312-03
- **Host Material:** Single crystal LaAlO_3
- **Technique:** XPS
- **Spectral Region:** O 1s

Instrument: Kratos Axis Ultra
 Excitation Source: Al K_α monochromatic
 Source Energy: 1486.6 eV
 Source Strength: 180 W
 Source Size: 2 mm \times 2 mm
 Analyzer Type: spherical sector
 Incident Angle: 54°
 Emission Angle: 0°
 Analyzer Pass Energy: 160 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



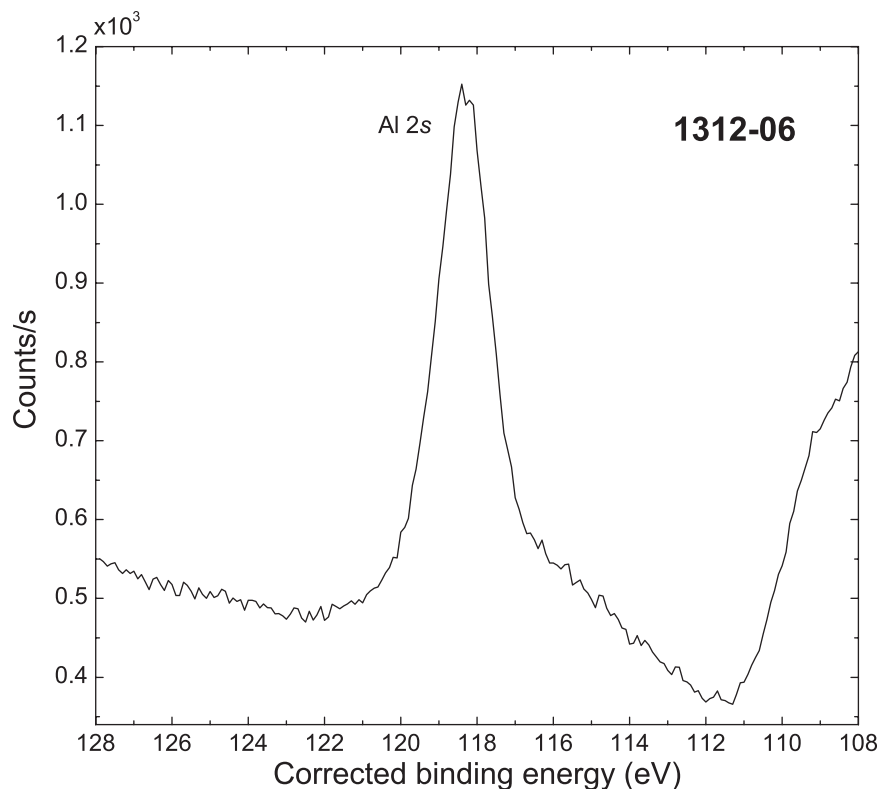
■ **Accession #:** 01312-04
 ■ **Host Material:** Single crystal LaAlO₃
 ■ **Technique:** XPS
 ■ **Spectral Region:** C 1s

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: 160 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



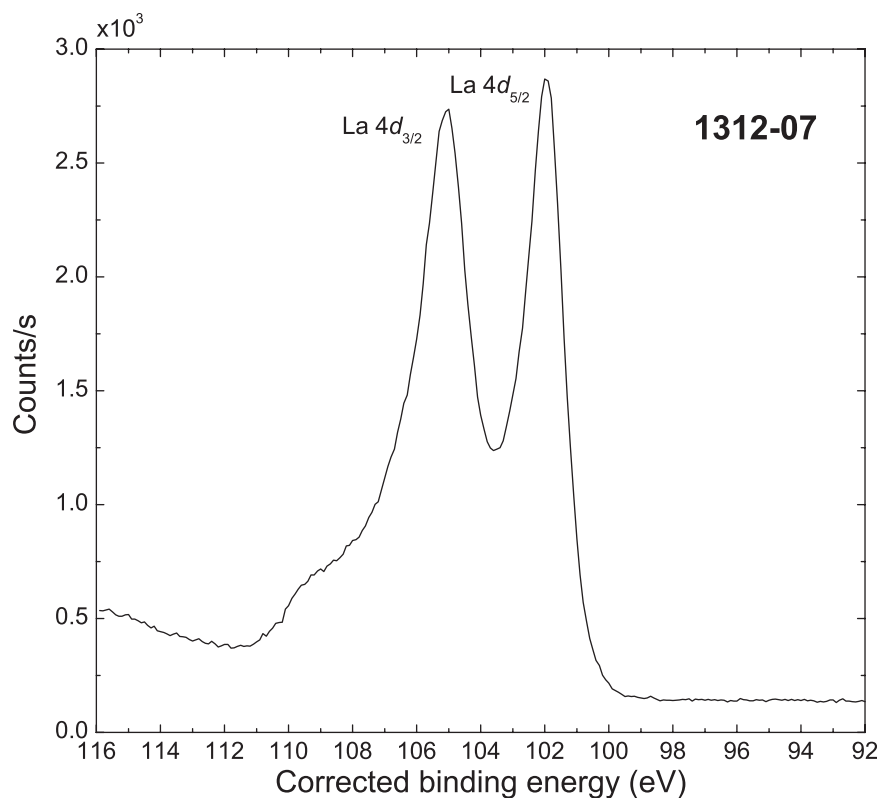
■ **Accession #:** 01312-05
 ■ **Host Material:** Single crystal LaAlO₃
 ■ **Technique:** XPS
 ■ **Spectral Region:** La 4p

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: 0.3 eV
 Total Signal Accumulation Time: 2526 s
 Total Elapsed Time: 6946.5 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV



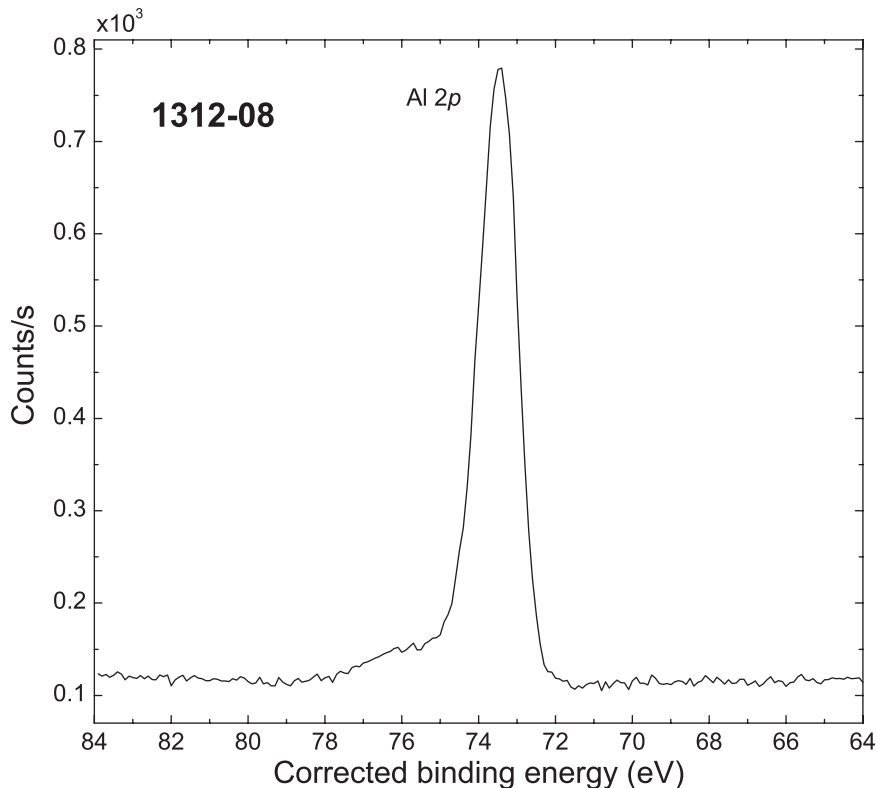
- Accession #: 01312-06
- Host Material: Single crystal LaAlO₃
- Technique: XPS
- Spectral Region: Al 2s

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: 0.3 eV
 Total Signal Accumulation Time: 1608 s
 Total Elapsed Time: 4422 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV



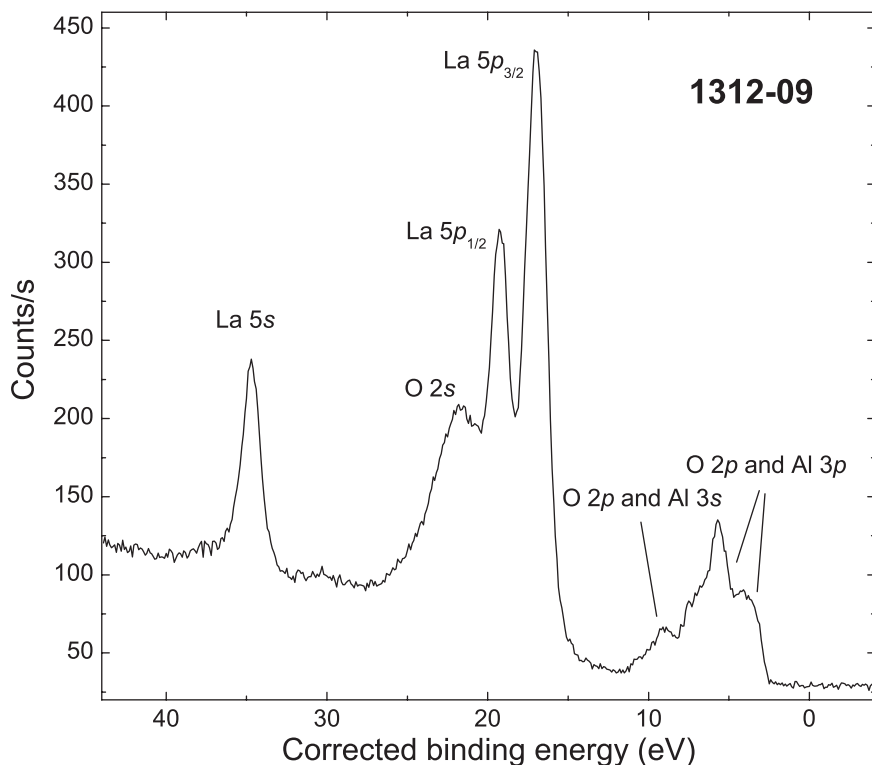
- Accession #: 01312-07
- Host Material: Single crystal LaAlO₃
- Technique: XPS
- Spectral Region: La 4d

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: 160 eV
 Analyzer Resolution: 0.3 eV
 Total Signal Accumulation Time: 1446 s
 Total Elapsed Time: 3976.5 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV



- Accession #: 01312-08
- Host Material: Single crystal LaAlO₃
- Technique: XPS
- Spectral Region: Al 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: 160 eV
 Analyzer Resolution: 0.3 eV
 Total Signal Accumulation Time: 1608 s
 Total Elapsed Time: 4422 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV



- Accession #: 01312-09
- Host Material: Single crystal LaAlO₃
- Technique: XPS
- Spectral Region: La 5s; O 2s; La 5p; 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: 160 eV
 Analyzer Resolution: 0.3 eV
 Total Signal Accumulation Time: 6734 s
 Total Elapsed Time: 18518.5 s
 Number of Scans: 20
 Effective Detector Width: 4.2 eV