Surface Science Spectra

RESEARCH ARTICLE | JUNE 11 2024

Core-level spectra of metallic lanthanides: Lanthanum (La)

David J. Morgan

Surf. Sci. Spectra 31, 014010 (2024)
https://doi.org/10.1116/6.0003602

SSS SURFACE SCIENCE SPECTRA ARTICLE pubs.aip.org/avs/sss

Core-level spectra of metallic lanthanides: Lanthanum (La)

Cite as: Surf. Sci. Spectra 31, 014010 (2024); doi: 10.1116/6.0003602
Submitted: 8 March 2024 · Accepted: 28 May 2024 ·
Published Online: 11 June 2024

David J. Morgan[1,2]

AFFILIATIONS

[1]Cardiff Catalysis Institute, Translational Research Facility, Cardiff University, Maindy Road, Cardiff CF24 4HQ, United Kingdom
[2]HarwellXPS—The EPSRC National Research Facility for Photoelectron Spectroscopy, Research Complex at Harwell (RCaH), Didcot, Oxon OX11 0FA, United Kingdom

ABSTRACT

The core-level aluminum excited spectra for lanthanum, the eponymous parent lanthanide metal, are presented together with exemplar spectra highlighting the metals reactivity from reaction with background chamber gases. Recommendations are given for the background integrations limits and form, together with comments on sensitivity factors.

Key words: XPS, lanthanide, metal, lanthanum, rare earth

Accession #: 01918
Technique: XPS and XAES
Specimen: La
Instrument: Thermo K-Alpha$^+$
Major Elements in Spectra: La
Minor Elements in Spectra: None
Published Spectra: 9
Spectral Category: Comparison

INTRODUCTION

The rare earth metal lanthanum (La) is the eponymic element of the lanthanide series. Although typically considered the first of the *f*-block elements (Ref. 1), La does not have any *f*-electrons and exhibits a ground state electronic configuration of [Xe] $5d^1$ $6s^2$.

To date, there have been a number of papers published in *Surface Science Spectra* (*SSS*) of La based compounds, such as those in Refs. 2–5. While the spectra of La has been previously published in *SSS* as part of a series of the third-row transition metals (Ref. 6), the spectra presented herein are different for several reasons. First, these are part of a self-consistent series of spectra for the lanthanide series of elements—see, for example, Ref. 7. Second, some spectra are presented over a larger energy window than previously reported, highlighting more structure, and finally, representative spectra from the reaction of the La metal with the background chamber gases are also shown.

Much like its elemental family, La has an affinity for hydrogen, oxygen, water, and halides, hence maintaining a clean surface for analysis is difficult. Within this reference, the spectra for clean La are presented, which were obtained by light argon sputtering (30 s) between acquisitions.

To illustrate the oxidation through adsorption of background gases, Fig. 1 shows the La 3*d* and O 1*s* core-level spectra for different times during a cycle of constant analysis of the core levels. The formation of the lanthanum oxide phase in the La 3*d* spectra is quite evident following ca. 200 min, and this is concomitant with the development of a second peak in the O 1*s* spectrum which we do not ascribe to a purely hydroxyl state. Analysis of the valence band (not shown) for this data set, reveals little intensity close to that expected for the O $2p_\sigma$ bonds which would be due to OH species as discussed in Ref. 8. While the presence of small concentrations of hydroxyl groups are not discounted, this peak is assigned as in Ref. 8, to the oxygen atoms in two distinct environments, with the shift in binding energy a consequence of both initial and final state effects and discussed in Ref. 8.

SPECIMEN DESCRIPTION (ACCESSION # 01918)

Specimen: Lanthanum, La
CAS Registry #: 7439-91-0

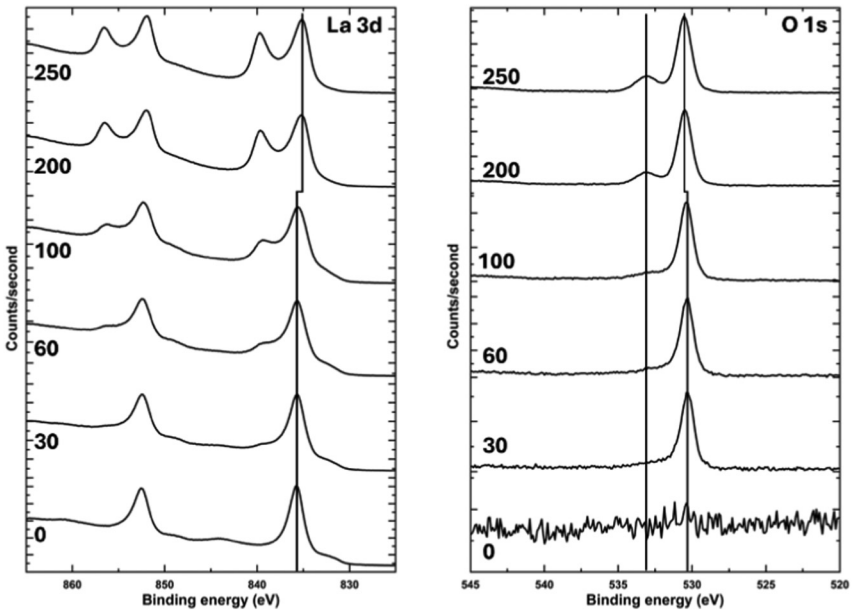


FIG. 1. La 3*d* and O 1*s* core levels spectra after approximately 0, 30, 60, 100, 200, and 250 min of data acquisition.

Specimen Characteristics: Homogeneous; solid; polycrystalline; conductor; metal; and other
Chemical Name: Lanthanum
Source: Thermo Scientific
Composition: La
Form: Solid, approximately 20×50 mm^2
Structure: La
History and Significance: Metallic pieces, 99.9% grade material obtained from Thermo Scientific in mineral oil
As Received Condition: Received as silvery-black, tarnished metallic pieces stored in a mineral oil
Analyzed Region: Elliptical region within the approximate center of the sputtered area.
***Ex Situ* Preparation/Mounting:** A suitably sized fragment was removed from the mineral oil and polished in the surface oil residue, using SiC paper (grit size 7), to form a visually flat and smooth surface. The sample was subsequently washed in iso-propyl alcohol and further polished with iso-propyl alcohol and SiC paper. The sample was rinsed, dried *via* solvent evaporation, and attached to a conducting sample plate using copper clips.
***In Situ* Preparation:** Argon ion sputtering
Charge Control: None
Temp. During Analysis: 298 K
Pressure During Analysis: 2.8×10^{-7} Pa
Preanalysis Beam Exposure: 20 s

INSTRUMENT DESCRIPTION

Manufacturer and Model: Thermo Fisher Scientific K-Alpha$^+$
Analyzer Type: Spherical sector
Detector: Multichannel resistive plate
Number of Detector Elements: 128

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

Spectrometer

Analyzer Mode: Constant pass energy
Throughput (T = EN): Calculated from a polynomial fit to a plot of log[peak area/(PE*XSF)] versus log(KE/PE), where PE is the pass energy, KE is the kinetic energy, and XSF is the relative sensitivity factor.[9]
Excitation Source Window: No window
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Beam Size: $600 \times 400\,\mu$m^2
Signal Mode: Multichannel direct

Geometry

Incident Angle: 60°
Source-to-Analyzer Angle: 60°
Emission Angle: 0°
Specimen Azimuthal Angle: 0°
Acceptance Angle from Analyzer Axis: 0°
Analyzer Angular Acceptance Width: 30° × 30°

Ion Gun

Manufacturer and Model: Thermo Scientific MAGCIS
Energy: 4000 eV
Current: 6 mA
Current Measurement Method: Faraday cup
Sputtering Species and Charge: Ar^+
Spot Size (unrastered): 50 μm
Raster Size: $2000 \times 1000\,\mu$m^2

Incident Angle: 58°
Polar Angle: 58°
Azimuthal Angle: 90°
Comment: The ion gun was used to clean the as-introduced sample for 300 s and then for 30 s between each region to minimize any adsorption of background gases which readily oxidize the material during analysis. No annealing was performed.

DATA ANALYSIS METHOD

Energy Scale Correction: The sample is conductive and mounted in direct contact with the metallic sample holder, hence no calibration is required.
Recommended Energy Scale Shift: 0
Peak Shape and Background Method: Due to the complexity of some of the photoemission peaks and background intensity (e.g., La 3*d*, primarily due to the overlap with La *MNN* Auger features), the use of a two parameter Tougaard background (U2 Tougaard background in CasaXPS) has been employed. Recommended background start and end points (±0.5 eV) are given below, together with a suggested "C" parameter for the U2 background in CasaXPS given in parentheses:
La 4*p*: 185–220 eV (−650)
La 4*d*: 94–122 eV (−150, else use Shirley)
La $3d_{5/2}$: 827–847 eV (−650)
La 3*d*—complete doublet: 827–863 eV (−350)
Quantitation Method: Data analysis was performed using CasaXPS performed in CasaXPS V2.3.26 rev1.2Y, using a U2 Tougaard background unless otherwise specified. Electron escape depth correction was performed using the TPP-2M equation within CasaXPS and peak areas corrected using Scofield sensitivity factors. A modified sensitivity factor is used for the La 4*p* level as noted in the comments on the spectral features table.

ACKNOWLEDGMENTS

This work was performed through the support of the EPSRC National Facility for x-ray photoelectron spectroscopy ('HarwellXPS', Nos. EP/Y023587/1, EP/Y023609/1, EP/Y023536/1, EP/Y023552/1, and EP/Y023544/1).

AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

David J. Morgan: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES

[1]W. B. Jensen, Found. Chem. **17**, 23 (2015).
[2]C. L. Perkins, R. Ding, M. Trenary, T. Tanaka, and S. Otani, Surf. Sci. Spectra **7**, 75 (2000).
[3]M. M. Natile, A. Galenda, and A. Gilsenti, Surf. Sci. Spectra **15**, 1 (2008).
[4]D. Barreca, A. Gasparotto, C. Margano, and E. Tondello, Surf. Sci. Spectra **11**, 52 (2004).
[5]R. P. Vasquez, Surf. Sci. Spectra **1**, 361 (1992).
[6]M. Engelhard and D. Baer, Surf. Sci. Spectra **7**, 1 (2000).
[7]D. J. Morgan, Surf. Sci. Spectra **30**, 024017 (2023).
[8]M. F. Sunding, K. Hadidi, S. Diplas, O. M. Løvvik, T. E. Norby, and A. E. Gunnæs, J. Electron Spectrosc. Relat. Phenom. **184**, 399 (2011).
[9]Thermo Scientific, Avantage Version 6 Data Analysis Reference Manual (2023).

SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV × counts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
01918-01	La 3*d*	836.0	…	44 504 074	47.62	100	La 3*d*—Energy for 5/2 peak
01918-02	Valence	…	…	…	…	…	Fermi level, La 5*p*, La 5*s*
01918-02	La $5p_{3/2}$	16.7	…	…	…	…	…
01918-02	La $5p_{1/2}$	19.2	…	…	…	…	…
01918-02	La 5*s*	34.3	…	…	…	…	…
01918-03[a]	La $4d_{5/2}$	102.6	…	937 860	6.52	…	La 4*d* doublet
01918-03[a]	La $4d_{3/2}$	105.6	…	…	…	…	…
01918-04[b]	La $4p_{3/2}$	196.2	…	393 065	2.8	…	La $4p_{3/2}$
01918-04[b]	La $4p_{1/2}$	…	…	…	…	…	See comments
01918-05	La 4*s*	274.8	…	…	…	…	…
01918-06[c]	La *MNN*	758.3	…	…	…	…	La *MNN* Auger structure
01918-07	La $3d_{5/2}$	835.8	1.8	3 991 907	28.12	…	La $3d_{5/2}$
01918-07	La $3d_{3/2}$	852.6	1.8	…	19.50	…	La $3d_{3/2}$
01918-08[d]	La $3p_{3/2}$	1126.7	5.7	1 246 836	12.11	…	La $3p_{3/2}$
01918-09[d]	La $3p_{1/2}$	1027.5	5.3	563 951	5.55	…	La $3p_{1/2}$

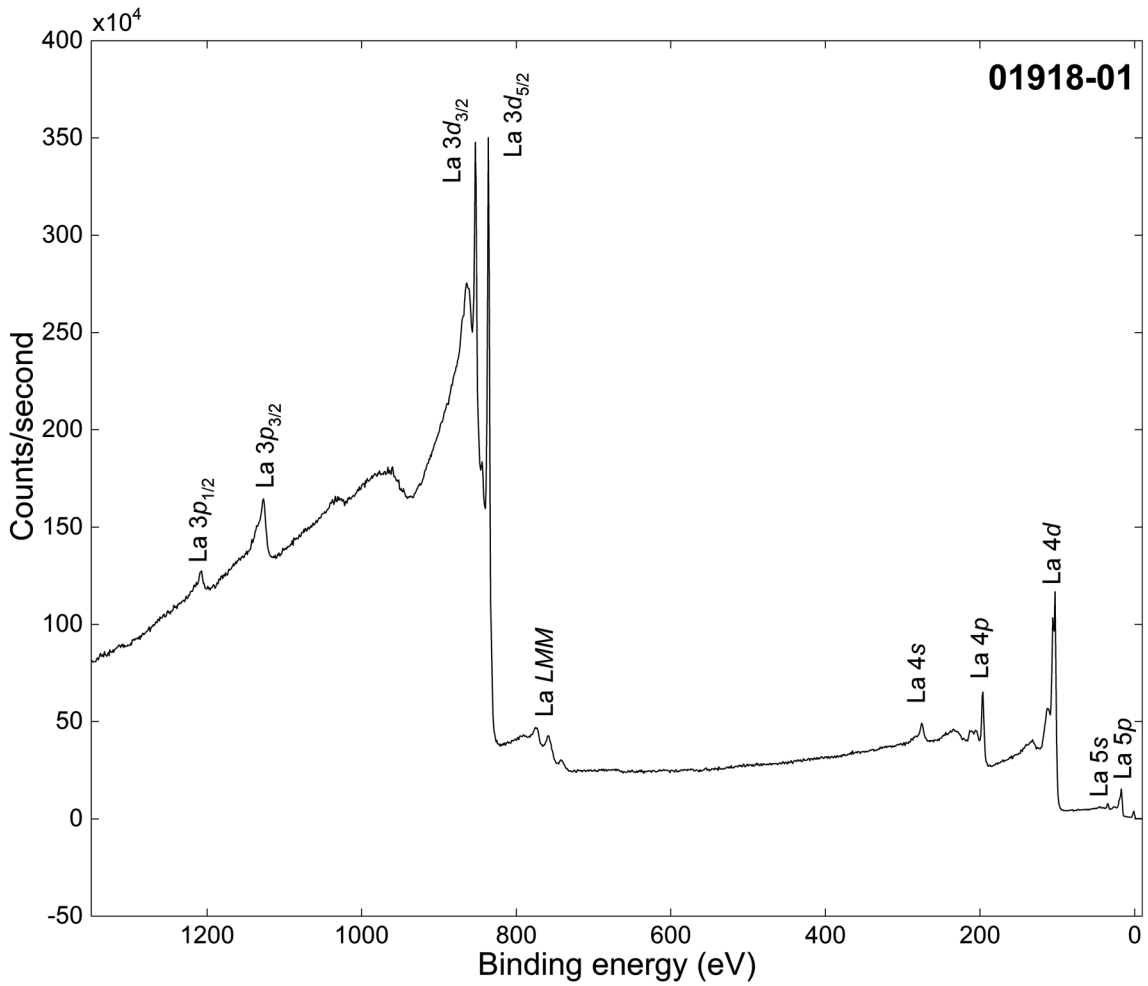
[a]Sensitivity factor is for the whole spin–orbit split peak and associated structure over the limits defined earlier.
[b]Sensitivity factor is modified from that of Scofield (4.33) to 2.8. Note this is almost equal to the sensitivity factor value for the $4p_{3/2}$ peak, which may indicate errors in assignment due to the multiplet splitting of the La 4*p* peak. Use of the full Scofield value necessitates the inclusion of structure up to ca. 250 eV.
Note the value for the $4p_{1/2}$ peak taken from the Lawrence Berkeley National Laboratory X-Ray Data Handbook (https://xdb.lbl.gov/) is 206.0 eV and given the identical reported $4p_{3/2}$ binding energies in this paper and the handbook the value is presented here for completeness. It is noted the value is different from that reported in Ref. 6, however, given complex structure in this spectral region and broadening of the $4p_{1/2}$ state in lanthanides by super Coster–Kroning effects, a distinct peak is not visible.
[c]Energy given as binding energy as plotted. Equivalent kinetic energy is 728.3 eV. This is the value for the sharpest Auger peak.
[d]Position and FWHM obtained by peak fit using an asymmetric function, LA(0.7,1.2,243) in CasaXPS, with a LA(50) peak for the remaining structure. It is not recommended to use these peaks for quantification, at least not over the presented ranges, as they do not afford a similar elemental ratio to the other orbitals.

ANALYZER CALIBRATION TABLE

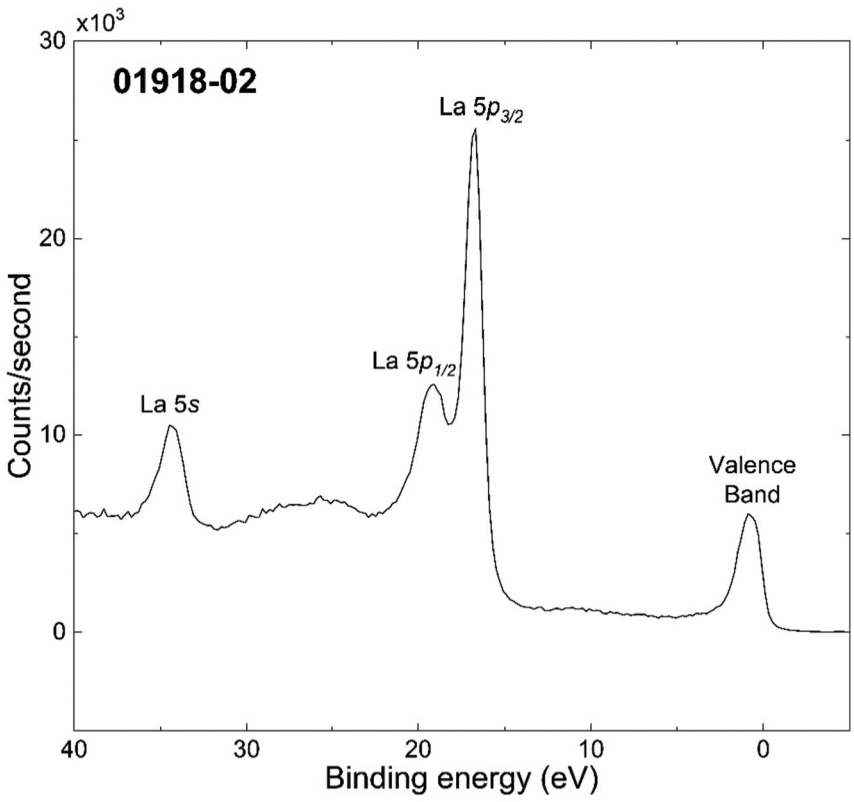
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV × counts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
…	Au $4f_{7/2}$	83.99	0.78	1 252 439	9.58	100	Gold metal
…	Ag $3d_{5/2}$	368.28	0.61	1 676 008	7.38	100	Silver metal
…	Cu $2p_{3/2}$	932.67	0.86	2 867 973	16.73	100	Copper metal

GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift	Multiplier	Baseline	Comment #
01918-01	Survey	0	1	0	…
01918-02	La 5*s*, La 5*p*, Valence	0	1	0	0.2 eV step size
01918-03	La 4*d*	0	1	0	…
01918-04	La 4*p*	0	1	0	…
01918-05	La 4*s*	0	1	0	…
01918-06	La *MNN*	0	1	0	…
01918-07	La 3*d*	0	1	0	…
01918-08	La $3p_{3/2}$	0	1	0	…
01918-09	La $3p_{1/2}$	0	1	0	…

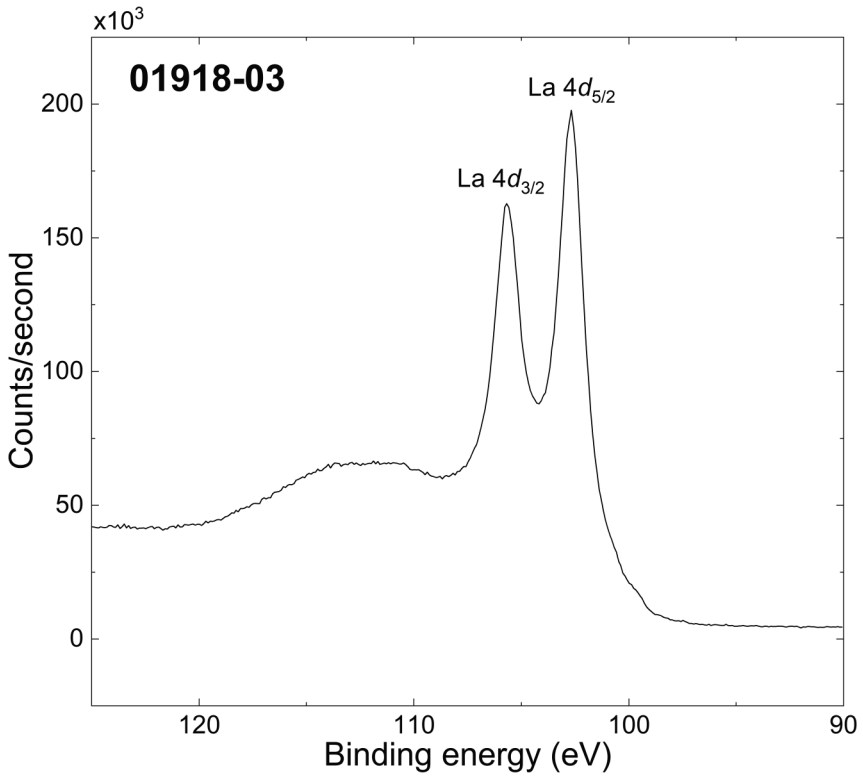


Accession #:	01918-01
■ Specimen:	La
■ Technique:	XPS
■ Spectral Region:	Survey
Instrument:	Thermo Fisher Scientific K-Alpha$^+$
Excitation Source:	Al K_α monochromatic
Source Energy:	1486.6 eV
Source Strength:	72 W
Source Size:	0.6 × 0.4 mm^2
Analyzer Type:	Spherical sector analyzer
Incident Angle:	60°
Emission Angle:	0°
Analyzer Pass Energy:	200 eV
Analyzer Resolution:	1.5 eV
Total Signal Accumulation Time:	29 s
Total Elapsed Time:	29 s
Number of Scans:	2
Effective Detector Width:	27.1 eV



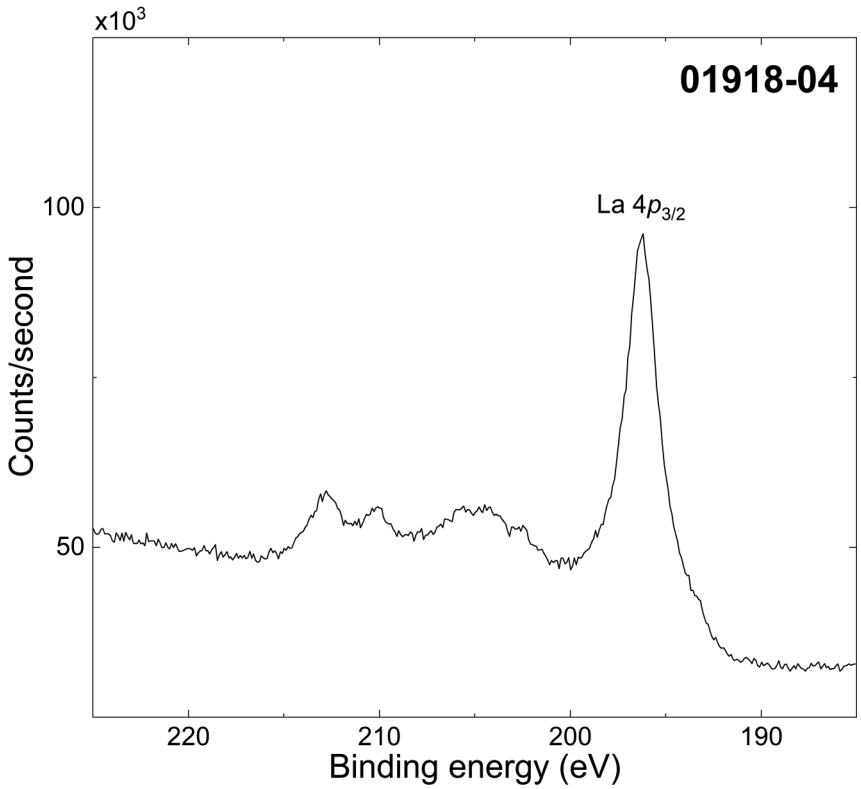
■ **Accession #:** 01918-02
■ **Specimen:** La
■ **Technique:** XPS
■ **Spectral Region:** La 5*s*, La 5*p*, Valence

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size:0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy 50 eV
Analyzer Resolution: 0.2 eV
Total Signal Accumulation Time: 111 s
Total Elapsed Time: 170 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 30 s sputter after collection of the prior spectrum to minimize any oxidation. Total elapsed time includes previous scans and sputtering time.



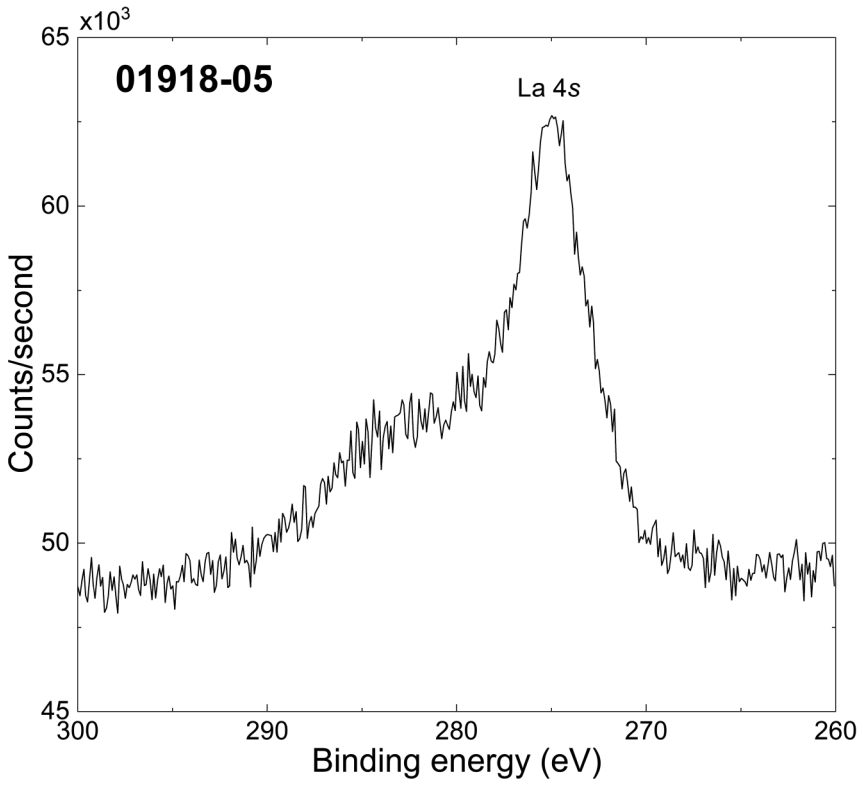
- **Accession #:** 01918-03
- **Specimen:** La
- **Technique:** XPS
- **Spectral Region:** La 4*d*

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size:0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 72 s
Total Elapsed Time: 272 s
Number of Scans: 4
Effective Detector Width:6.8 eV
Comments: Spectra were collected after a 30 s sputter after collection of the prior spectrum to minimize any oxidation. Total elapsed time includes previous scans and sputtering time.



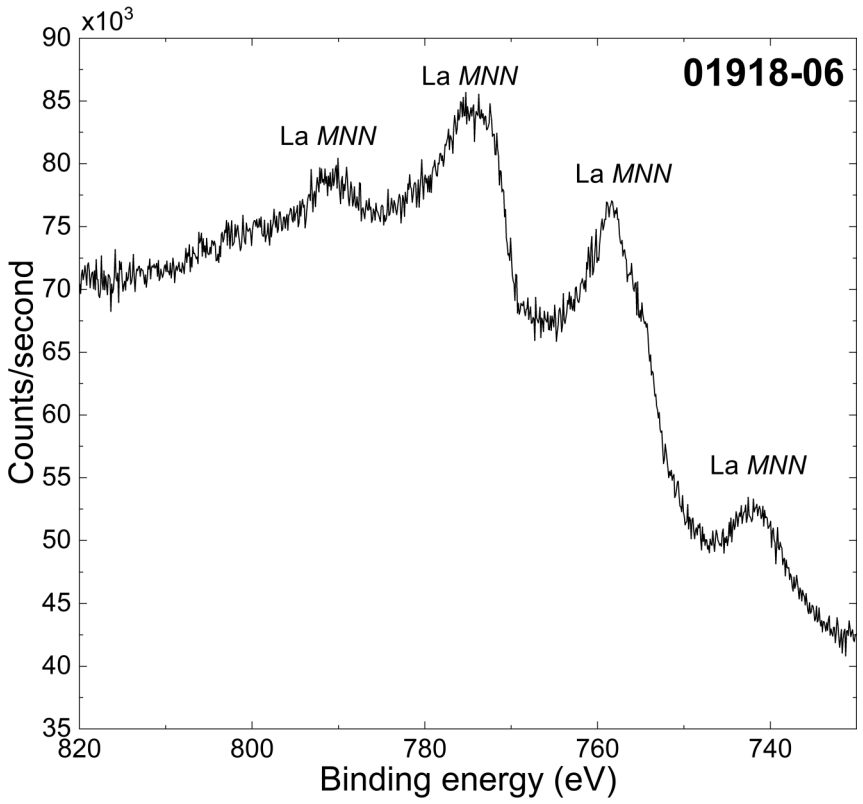
- **Accession #:** 01918-04
- **Specimen:** La
- **Technique:** XPS
- **Spectral Region:** La 4*p*

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size:0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 79 s
Total Elapsed Time: 381 s
Number of Scans: 4
Effective Detector Width: 6.8 eV
Comments: See comments on the Spectral Features Table section. Spectra were collected after a 30 s sputter after collection of the prior spectrum to minimize any oxidation. Total elapsed time includes previous scans and sputtering time.



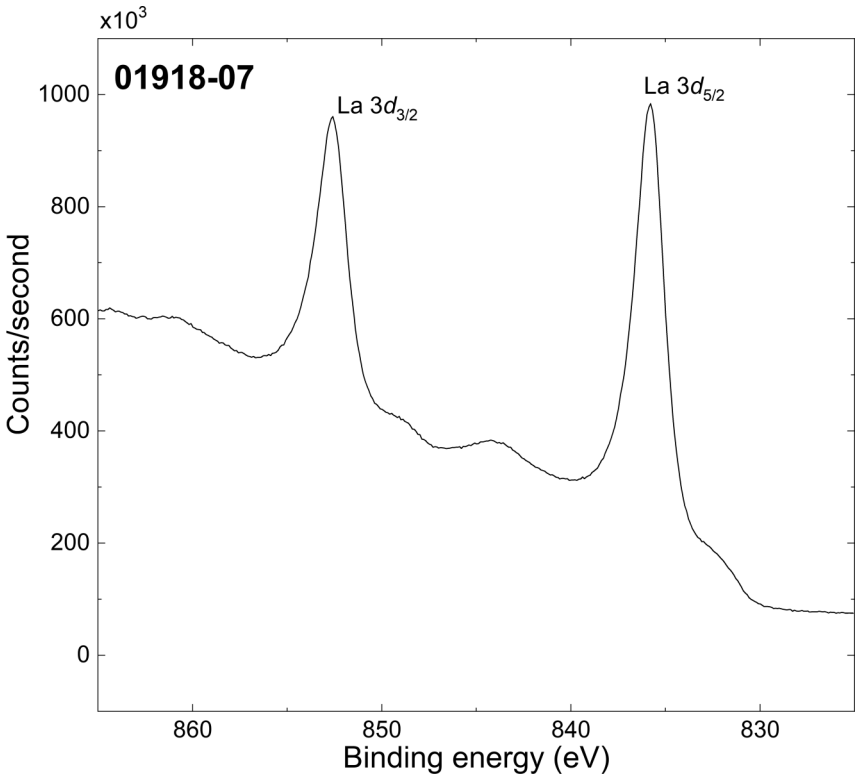
- **Accession #:** 01918-05
- **Specimen:** La
- **Technique:** XPS
- **Spectral Region:** La 4*s*

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size:0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 79 s
Total Elapsed Time: 490 s
Number of Scans: 4
Effective Detector Width: 6.8 eV
Comments: Loss structure of 4 *s* peak overlaps C1*s* region. Spectra were collected after a 30 s sputter after collection of the prior spectrum to minimize any oxidation. Total elapsed time includes previous scans and sputtering time.



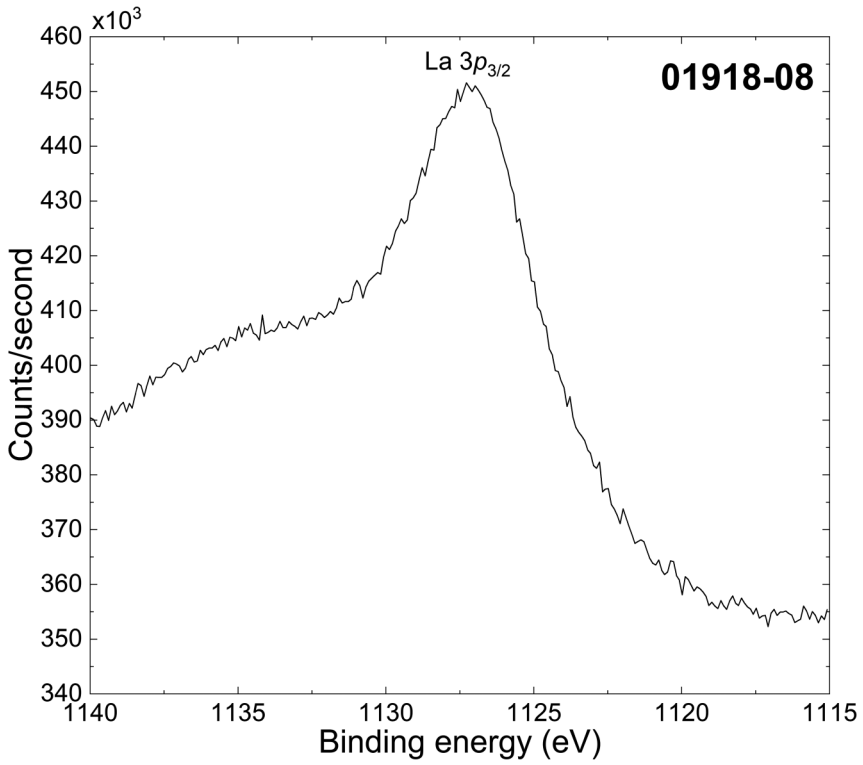
- **Accession #:** 01918-06
- **Specimen:** La
- **Technique:** XAES
- **Spectral Region:** La *MNN*

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size:0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 90 s
Total Elapsed Time: 610 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 30 s sputter after collection of the prior spectrum to minimize any oxidation. Total elapsed time includes previous scans and sputtering time.



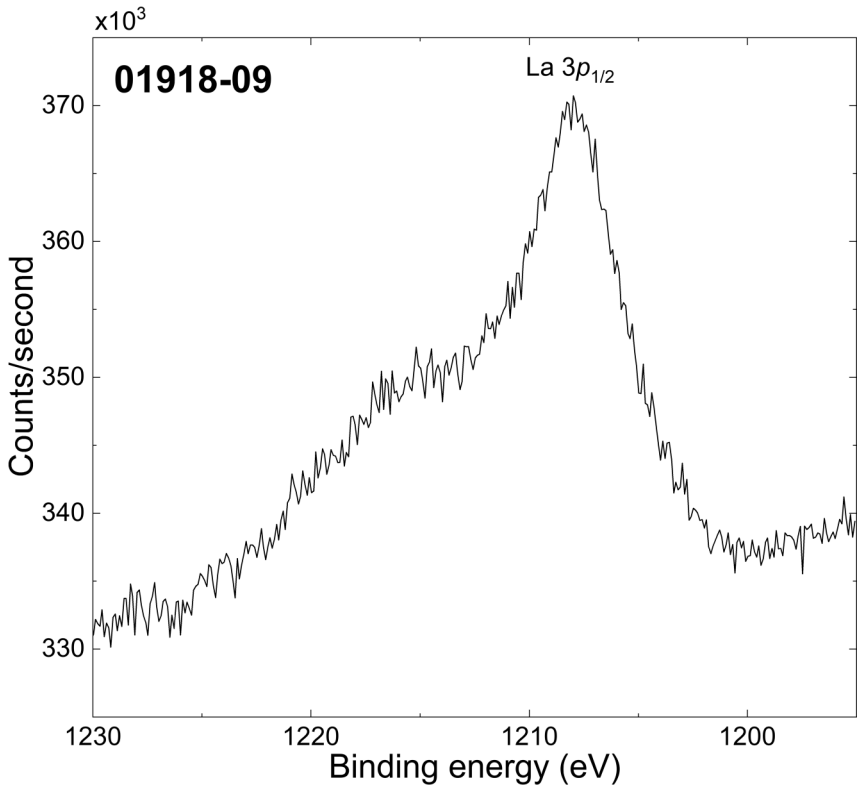
- **Accession #:** 01918-07
- **Specimen:** La
- **Technique:** XPS
- **Spectral Region:** La 3*d*

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 79 s
Total Elapsed Time: 719 s
Number of Scans: 4
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 30 s sputter after collection of the prior spectrum to minimize any oxidation. Total elapsed time includes previous scans and sputtering time. Background subtraction is complicated by overlap of La *MNN* Auger features, see comments in the Data Analysis section.



- **Accession #:** 01918-08
- **Specimen:** La
- **Technique:** XPS
- **Spectral Region:** La $3p_{3/2}$

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 76 s
Total Elapsed Time: 825 s
Number of Scans: 6
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 30 s sputter after collection of the prior spectrum to minimize any oxidation. Total elapsed time includes previous scans and sputtering time.



- **Accession #:** 01918-09
- **Specimen:** La
- **Technique:** XPS
- **Spectral Region:** La $3p_{1/2}$

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size:0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 76 s
Total Elapsed Time: 959 s
Number of Scans: 6
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 30 s sputter after collection of the prior spectrum to minimize any oxidation. Total elapsed time includes previous scans and sputtering time