J_ID: SSS DOI: 10.1116/1.4972828 Date: 21-December-16 Stage: Page: 1 Total Pages: 10

PROOF COPY [SSS-XPS-16-012R] 003602SSS

Samarium and europium beta"-alumina derivatives characterized by XPS

Kristian Myhre[a)]
University of Tennessee, Bredesen Center for Interdisciplinary Research and Graduate Education, 821 Volunteer Blvd, Knoxville, Tennessee 37996-3394

Harry Meyer and Miting Du
Oak Ridge National Laboratory, Nuclear Security and Isotope Technology Division, P.O. Box 2008, Oak Ridge, Tennessee 37831

(Received 25 August 2016; accepted 21 October 2016; published xx xx xxxx)

Characterization of samarium, and europium beta"-alumina derivatives has been carried out using x-ray photoelectron spectroscopy (XPS). Beta"-alumina has been widely studied as a material capable of incorporating many different cations into its lattice structure, such as sodium and many of the lanthanide elements. This unique behavior has been recently explored at Oak Ridge National Laboratory for separating samarium and europium from each other. The XPS of samarium and europium in the beta"-alumina structure are reported here. Additionally, the XPS spectra of the europium and samarium trichloride starting materials are presented in the database. © *2016 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4972828]

Keywords: *beta" -alumina; europium; samarium*

Accession #s: 01385, 01386, 01388, 01389

Technique: XPS

Host Material: #01385: $EuCl_3$ powder; #01386: $SmCl_3$ powder; #01388: europium beta"-alumina; #01389: samarium beta"-alumina

Instrument: Thermo Scientific K-Alpha XPS

Major Elements in Spectra: Eu, Sm, Al, O, Cl, Na

Minor Elements in Spectra: N, Si

Published Spectra: 4

Spectra in Electronic Record: 14

Spectral Category: technical

INTRODUCTION

Beta"-alumina (BDPA) derivatives have been investigated for their unique superionic conducting properties in numerous settings (Refs. 1–3). Sodium BDPA, for instance, continues to be investigated as a solid electrolyte for application in sodium based batteries for energy storage. Other derivatives of BDPA, such as those where the sodium content has been replaced with lanthanide ions, have been investigated for their optical properties. Recently, the use of BDPA as a separation material has been explored at Oak Ridge National Laboratory (ORNL) (Ref. 4). Early studies have focused on separating europium and samarium by selective ion exchange reactions between Eu/Sm-BDPA and molten chloride salts. An important aspect of this is the oxidation state behavior of Eu and Sm in BDPA. This is due to the separation relying upon a large difference in diffusivity of Eu(II) in BDPA compared to Sm(III). XPS has been implemented in order to better understand the oxidation state behavior of Eu and Sm in BDPA.

Lanthanide derivatives of BDPA are typically synthesized through ion exchange reactions at high temperatures (Refs. 5 and 6). This process involves a precursor material, such as sodium-BDPA, being directly immersed in a molten salt or exposed to salt vapors containing the ions to be exchanged for sodium in the BDPA material. The lanthanide BDPA derivatives described here were synthesized by surrounding a small polycrystalline sodium-BDPA chip with an excess amount of the respective lanthanide chloride salt powder. Each sample was individually sealed in a quartz ampoule while under high vacuum. The sealed samples were then heated to 650 °C and held at that temperature for 24 h. After cooling, the ampoules were opened and the samples rinsed with a small amount of water. The samples were then put into the chamber of the XPS instrument, and the spectra presented herein were acquired. A paper describing the entirety of the study that has produced the XPS spectra presented here is in preparation.

The Na-BDPA precursor material studied was composed of Al (47.1% w/w), O (46.0% w/w), Na (6.5% w/w), and Li (0.4% w/w) and has a molecular formula of $Na_{1.67}Li_{0.3}Al_{10.33}O_{17}$. The spectra for the Na-BDPA precursor material show the presence of Cl, which is likely present from contamination due to handling or the Na-BDPA production process. The Eu 3d regions show evidence of both trivalent and divalent species in the Eu-BDPA and $EuCl_3$. The Sm 3d regions show evidence only of trivalent species in Sm-BDPA and $SmCl_3$. The Eu(III) $3d_{3/2}$ peak is at 1136.37 eV, and $3d_{5/2}$ peak is at 1166.19 eV, whereas the Eu(II) $3d_{3/2}$ and $3d_{5/2}$ peaks are at 1126.26 eV and 1157.09 eV, respectively (Refs. 7–11). The Sm(III) $3d_{3/2}$ peak is at 1111.91 eV, and $3d_{5/2}$ peak is at 1084.89 eV (Refs. 12–16). Both the Eu-BDPA and Sm-BDPA samples show a small amount of Si present. This is likely from the quartz ampoules that the samples were heated in. Nitrogen can also be seen in the Sm-BDPA and $SmCl_3$ spectra. The N is likely an impurity in the $SmCl_3$ stock material, which was used to produce the Sm-BDPA sample, since it is present in both the spectra but none of the others.

SPECIMEN DESCRIPTION (ACCESSION #01385, 1 OF 4)

Host Material: $EuCl_3$ powder

CAS Registry #: 10025-76-0

Host Material Characteristics: homogeneous; polycrystalline; unknown electrical characteristics; inorganic compound; powder

Chemical Name: Europium trichloride

Source: Alfa Aesar, Europium (III) chloride, ultra-dry 99.99% (REO)

Host Composition: $EuCl_3$

Form: powder

Structure: UCl_3 motif

History & Significance: purchased from Alfa Aesar and used as a reference material

a)Author to whom correspondence should be addressed.

ID: rajeshp Time: 18:38 I Path: //chenas03.cadmus.com/Home$/rajeshp$/AI-SSS#160512

As Received Condition: powder in glass container

Analyzed Region: 400 μm × 400 μm

***Ex Situ* Preparation/Mounting:** The powder was attached to double-sided carbon tape for analysis.

***In Situ* Preparation:** none

Pre-Analysis Beam Exposure: The sample was not exposed to the beam prior to analysis.

Charge Control: A dual-beam low energy electron/ion source was used for charge neutralization (Thermo Scientific FG-03). The ion gun current was 150 μA and the voltage was 45 V.

Temp. During Analysis: 300 K

Pressure During Analysis: $<2 \times 10^{-7}$ Pa

SPECIMEN DESCRIPTION (ACCESSION #01386, 2 OF 4) —

Host Material: $SmCl_3$ powder

CAS Registry #: 10361-82-7

Host Material Characteristics: homogeneous; polycrystalline; unknown electrical characteristics; inorganic compound; powder

Chemical Name: Samarium trichloride

Source: Alfa Aesar, Samarium (III) chloride, ultra-dry 99.99% (REO)

Host Composition: $SmCl_3$

Form: powder

Structure: UCl_3 motif

History & Significance: Purchased from Alfa Aesar and used as a reference material.

As Received Condition: powder in glass container

Analyzed Region: 400 μm × 400 μm

***Ex Situ* Preparation/Mounting:** The powder was attached to double-sided carbon tape for analysis.

***In Situ* Preparation:** none

Pre-Analysis Beam Exposure: The sample was not exposed to the beam prior to analysis.

Charge Control: A dual-beam low energy electron/ion source was used for charge neutralization (Thermo Scientific FG-03). The ion gun current was 150 μA and the voltage was 45 V.

Temp. During Analysis: 300 K

Pressure During Analysis: $<2 \times 10^{-7}$ Pa

SPECIMEN DESCRIPTION (ACCESSION #01388, 3 OF 4) —

Host Material: europium beta”-alumina

Host Material Characteristics: homogeneous; solid; polycrystalline; unknown electrical characteristics; inorganic compound; ceramic

Chemical Name: europium beta”-alumina

Source: Ionotec Ltd

Host Composition: not specified

Form: solid ceramic chip

Structure: polycrystalline ceramic consisting of spinel blocks separated by a conduction plane

History & Significance: The sample was produced using an ion exchange reaction between a sodium beta”-alumina ceramic chip and molten lanthanide chloride salt. Specifically, a sodium-BDPA chip was buried in solid $EuCl_3$ powder inside of a quartz tube. The quartz tube was then sealed under high vacuum. The sealed ampoule containing the $EuCl_3$ and sodium-BDPA was then heated to 650 °C for 24 h. The ampoule was opened and a small amount of water was used to dissolve adhered salt on the ceramic chip now containing europium. The europium-BDPA chip was then dried using a wipe and immediately put in the analysis chamber.

As Received Condition: solid ceramic chip

Analyzed Region: 400 μm × 400 μm

***Ex Situ* Preparation/Mounting:** The ceramic chip was attached to double-sided carbon tape for analysis.

***In Situ* Preparation:** none

Pre-Analysis Beam Exposure: The sample was not exposed to the beam prior to analysis.

Charge Control: A dual-beam low energy electron/ion source was used for charge neutralization (Thermo Scientific FG-03). The ion gun current was 150 μA and the voltage was 45 V.

Temp. During Analysis: 300 K

Pressure During Analysis: $<2 \times 10^{-7}$ Pa

SPECIMEN DESCRIPTION (ACCESSION #01389, 4 OF 4) —

Host Material: samarium beta”-alumina

Host Material Characteristics: homogeneous; solid; polycrystalline; unknown electrical characteristics; inorganic compound; ceramic

Chemical Name: samarium beta”-alumina

Source: Ionotec Ltd

Host Composition: not specified

Form: solid ceramic chip

Structure: polycrystalline ceramic consisting of spinel blocks separated by a conduction plane

History & Significance: The sample was produced using an ion exchange reaction between a sodium beta”-alumina ceramic chip and molten lanthanide chloride salt. Specifically, a sodium-BDPA chip was buried in solid $SmCl_3$ powder inside of a quartz tube. The quartz tube then sealed under high vacuum. The sealed ampoule containing the $SmCl_3$ and sodium-BDPA was then heated to 650 °C for 24 h. The ampoule was opened and a small amount of water was used to dissolve adhered salt on the ceramic chip now containing europium. The europium-BDPA chip was then dried using a wipe and immediately put in the analysis chamber.

As Received Condition: solid ceramic chip

Analyzed Region: 400 μm × 400 μm

***Ex Situ* Preparation/Mounting:** The ceramic chip was attached to double-sided carbon tape for analysis.

***In Situ* Preparation:** none

Pre-Analysis Beam Exposure: The sample was not exposed to the beam prior to analysis.

Charge Control: A dual-beam low energy electron/ion source was used for charge neutralization (Thermo Scientific FG-03). The ion gun current was 150 μA and the voltage was 45 V.

Author Proof

PROOF COPY [SSS-XPS-16-012R] 003602SSS

Temp. During Analysis: 300 K

Pressure During Analysis: $<2 \times 10^{-7}$ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Thermo Scientific K-Alpha XPS

Analyzer Type: Other

Detector: position sensitive detector

Number of Detector Elements: 128

Analyzer Description: double-focusing hemispherical analyzer

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ Spectrometer

Analyzer Mode: constant pass energy

Throughput ($T = E^N$): N = −1

Excitation Source Window: 0.25 m Rowland circle monochromator with micro-focused x-ray source

Excitation Source: Al K_α, monochromatic

Source Energy: 1486.68 eV

Source Strength: 72 W

Source Beam Size: 5 μm × 5 μm

Source Raster Rate: 60

Analyzer Width:: 60000 μm × 60000 μm

Signal Mode: direct analog

Number of Scans: 10

■ Geometry

Incident Angle: 0°

Source to Analyzer Angle: 45°

Emission Angle: 45°

Specimen Azimuthal Angle: 0°

Acceptance Angle from Analyzer Axis: 0°

Analyzer Angular Acceptance Width: 45° × 45°

■ Ion Gun

Manufacturer and Model: Thermo Scientific EX-06

Energy: 1000 eV

Current: 10 mA

Current Measurement Method: Faraday cup

Sputtering Species: Ar^+

Spot Size (unrastered): 400 μm

Comment: The ion gun was utilized to clean the surfaces of the calibration standards.

DATA ANALYSIS METHOD

Energy Scale Correction: The sample was not charging, and no energy scale correction is needed.

Recommended Energy Scale Shift: none

Peak Shape and Background Method: Thermo Avantage software version 4.61 was used to carry out the background subtraction using the Shirley function as well as the determinations of peak positions and full width at half maximum (FWHM) values. The peaks were fitted using Gaussian-Lorentzian functions.

Quantitation Method: The atomic concentrations were calculated using the Al Scofield sensitivity factors in the Thermo Avantage software version 4.61.

ACKNOWLEDGMENTS

The authors thank Jason Craig for sealing samples in quartz tubes and Randy Parten for cutting and grinding various samples. This Research is sponsored by the Laboratory Directed Research and Development Program at Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy.

REFERENCES

1. G. Chen, J. Lu, L. Li, L. Chen, and X. Jiang, J. Alloys Compd. **673**, 295 (2016).
2. A. Mali and A. Petric, J. Eur. Ceram. Soc. **32**, 1229 (2012).
3. J. Prakash, L. Redey, and D. R. Vissers, J. Power Sources **87**, 195 (2000).
4. K. G. Myhre and M. Du, oral presentation at Pacifichem 2015, Honolulu, HI, December (2015).
5. S. Sattar, B. Ghosal, M. L. Underwood, H. Mertwoy, M. A. Saltzberg, W. S. Frydrych, G. S. Rohrer, and G. C. Farrington, J. Solid State Chem. **65**, 231 (1986).
6. W. Carrillo-Cabrera, J. O. Thomas, and G. C. Farrington, Solid State Ionics **19**, 645 (1986).
7. P. Maslankiewicz, J. Szade, A. Winiarski, and P. Daniel, Cryst. Res. Technol. **40**, 410 (2005).
8. H. C. Swart, I. M. Nagpure, O. M. Ntwaeaborwa, G. L. Fisher, and J. J. Terblans, Opt. Express **20**, 17119 (2012).
9. W. B. Im, J. H. Kang, D. C. Lee, S. Lee, D. Y. Jeon, Y. C. Kang, and K. Y. Jung, Solid State Commun. **133**, 197 (2005).
10. M. Taheri, M. Konuma and F. S. Razavi, Surf. Interface Anal. ■, ■ (2016). AQ1
11. L. A. Zavala-Sanchez, G. A. Hirata, E. Novitskaya, K. Karandikar, M. Herrera, and O. A. Graeve, ACS Biomater. Sci. Eng. **12**, 1306 (2015).
12. G. Krill, J. P. Senateur, and A. Amamou, J. Phys. F: Met. Phys. **10**, 1889 (1980).
13. J. D. Burns, K. G. Myhre, N. J. Sims, D. W. Stracener, and R. A. Boll, Nucl. Instrum. Methods Phys. Res., A **830**, 95 (2016).
14. K. Myhre, J. Burns, H. Meyer, N. Sims, and R. A. Boll, Surf. Sci. Spectra **23**, 70 (2016).
15. Y. Yan, K. Li, Y. Dai, X. Chen, J. Zhao, Y. Yang, and J. M. Lee, Electrochim. Acta **208**, 231 (2016).
16. V. S. Kumbhar, A. C. Lokhande, N. S. Gaikwad, and C. D. Lokhande, Chem. Phys. Lett. **645**, 112 (2016).

Author Proof

PROOF COPY [SSS-XPS-16-012R] 003602SSS

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
01385-01[a]	Eu 5p	23.8	...	...	...	...	Eu in Eu-Cl
01385-01[a]	Eu 5s	35.1	...	...	...	...	Eu in Eu-Cl
01385-01[a]	Eu 4d	137.4	...	...	...	...	Eu in Eu-Cl
01385-01[b]	Cl 2p	200.0	3.88	231957.0	2.285	49.2	Cl in M-Cl
01385-01[a]	Eu $4p_{3/2}$	261.8	...	...	...	...	Eu in Eu-Cl
01385-01[b]	Cl 2s	270.33	...	...	...	...	Cl in Eu-Cl
01385-01[c]	C 1s	285.4	4.66	59057.5	1.000	29.8	C in C-O
01385-01[a]	Eu 4s	366.5	...	...	...	...	Eu in Eu-Cl
01385-01[d]	O 1s	533.0	2.88	59590.6	2.930	11.8	O in C-O
01385-01[d]	O KLL	980.1	...	...	...	...	O in C-O
01385-01[a]	Eu $3d_{5/2}$	1136.4	4.91	374445.0	43.240	9.2	Eu in Eu-Cl
01385-01[a]	Eu $3d_{3/2}$	1166.2	...	...	...	...	Eu in Eu-Cl
01385-01[c]	C KLL	1218.5	...	...	...	...	C in C-O
01385-01[b]	Cl LMM	1305.76	...	...	...	...	Cl in Eu-Cl
01385-02[b]	Cl 2p	199.7	...	...	...	...	Cl in $EuCl_3$ and/or EuOCl
01385-03[c]	C 1s	285.5	...	...	...	...	Residual C
01385-04[e]	Eu $3d_{5/2}$	1126.3	...	...	...	...	Eu(II) in Eu-Cl
01385-04[f]	Eu $3d_{5/2}$	1136.4	...	...	...	...	Eu(III) in Eu-Cl
01385-04[a]	Eu $3d_{5/2}$ satellite	1145.02	...	...	...	...	Eu in Eu-Cl
01385-04[e]	Eu $3d_{3/2}$	1157.1	...	...	...	...	Eu(II) in Eu-Cl
01385-04[f]	Eu $3d_{3/2}$	1166.2	...	...	...	...	Eu(III) in Eu-Cl
01386-01[g]	Sm 5p	22.1	...	...	...	...	Sm in Sm-Cl
01386-01[g]	Sm 5s	42.3	...	...	...	...	Sm in Sm-Cl
01386-01[g]	Sm 4d	132.2	...	...	...	...	Sm in Sm-Cl
01386-01[h]	Cl 2p	199.4	3.72	468857.96	2.285	46.9	Cl in Sm-Cl
01386-01[g]	Sm $4p_{3/2}$	250.8	...	...	...	...	Sm in Sm-Cl
01386-01[h]	Cl 2s	269.96	...	...	...	...	Cl in Sm-Cl
01386-01[c]	C 1s	285.3	4.34	127085.52	1.000	30.3	Residual C
01386-01[g]	Sm 4s	349.0	...	...	...	...	Sm in Sm-Cl
01386-01[i]	N 1s	402.23	3.02	44350.84	1.8000	6.2	Contaminant N
01386-01[a0]	O 1s	532.4	3.77	91484.40	2.930	8.54	Residual O and/or O in SmOCl
01386-01[a0]	O KLL	978.2	...	...	...	...	Residual O and/or O in SmOCl
01386-01[g]	Sm $3d_{5/2}$	1084.6	4.77	709116.64	40.370	8.1	Sm in Sm-Cl
01386-01[g]	Sm $3d_{3/2}$	1111.8	...	...	...	...	Sm in Sm-Cl
01386-01[c]	C KLL	1221.8	...	...	...	...	Residual C
01386-01[h]	Cl LMM	1305.37	...	...	...	...	Cl in Sm-Cl
01386-02[h]	Cl 2p	199.2	...	...	...	...	Cl in Sm-Cl
01386-03[c]	C 1s	285.0	...	...	...	...	Residual C
01386-04[g]	Sm $3d_{5/2}$	1084.9	...	...	...	...	Sm in Sm-Cl
01386-04[g]	Sm $3d_{3/2}$	1111.9	...	...	...	...	Sm in Sm-Cl
01388-01[aa]	Eu 5p	23.3	...	...	...	...	Eu as Eu-O
01388-01[aa]	Eu 5s	36.1	...	...	...	...	Eu as Eu-O
01388-01[ab]	Al 2p	74.4	3.35	23387.17	0.537	3.0	Al as Al-O

Author Proof

PROOF COPY [SSS-XPS-16-012R] 003602SSS

SPECTRAL FEATURES TABLE (CONT.)

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV × cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
01388-01[ac]	Si 2s	102.46	...	...	...	...	Residual Si
01388-01[ab]	Al 2s	119.22	...	...	...	...	Al in Al-O
01388-01[aa]	Eu 4d	136.8	...	...	...	...	Eu as Eu-O
01388-01[ad]	Cl 2p	199.1	3.54	626230.94	2.285	33.0	Residual Cl
01388-01[aa]	Eu $4p_{3/2}$	261.4	...	...	...	...	Eu as Eu-O
01388-01[ad]	Cl 2s	269.55	...	...	...	...	Residual Cl
01388-01[c]	C 1s	285.0	3.67	247319.21	1.000	31.1	Residual C
01388-01[aa]	Eu 4s	365.3	...	...	...	...	Eu in Eu-O
01388-01[ae]	O 1s	532.0	3.69	481882.43	2.930	23.7	O in Eu-O and Al-O
01388-01[ae]	O KLL	980.1	...	...	...	...	O in Eu-O and Al-O
01388-01[aa]	Eu $3d_{5/2}$	1135.4	4.83	1082820.94	43.240	6.6	Eu as Eu-O
01388-01[aa]	Eu $3d_{3/2}$	1165.24	...	...	...	...	Eu in Eu-O
01388-01[ad]	Cl LMM	1304.68	...	...	...	...	Residual Cl
01388-02[c]	C 1s	284.9	...	...	...	...	Residual C
01388-03[af]	Eu $3d_{5/2}$	1125.6	...	...	...	...	Eu(II) as Eu-O
01388-03[aa]	Eu $3d_{5/2}$	1135.9	...	...	...	...	Eu(III) as Eu-O
01388-03[aa]	Eu $3d_{5/2}$ satellite	1144.27	...	...	...	...	Eu in Eu-O
01388-03[af]	Eu $3d_{3/2}$	1156.4	...	...	...	...	Eu(II) as Eu-O
01388-03[aa]	Eu $3d_{3/2}$	1165.6	...	...	...	...	Eu(III) as Eu-O
01389-01[ag]	Sm 5p	22.4	...	...	...	...	Sm as Sm-O
01389-01[ag]	Sm 5s	42.3	...	...	...	...	Sm as Sm-O
01389-01[ah]	Al 2p	74.4	3.09	56339.59	0.537	12.6	Al as Al-O
01389-01[ai]	Si 2p	102.93	...	...	...	...	Residual Si
01389-01[ah]	Al 2s	102.93	...	...	...	...	Al in Al-O
01389-01[ag]	Sm 4d	132.2	...	...	...	...	Sm as Sm-O
01389-01[b0]	Cl 2p	199.2	3.01	309555.18	2.285	17.2	Residual Cl
01389-01[ag]	Sm $4p_{3/2}$	250.8	...	...	...	...	Sm as Sm-O
01389-01[b0]	Cl 2s	269.68	...	...	...	...	Residual Cl
01389-01[c]	C 1s	285.0	3.31	312433.15	1.000	41.3	Residual C
01389-01[ag]	Sm 4s	349.1	...	...	...	...	Sm as Sm-O
01389-01[i]	N 1s	401.84	...	...	...	...	Residual N
01389-01[ba]	O 1s	531.9	3.71	478164.1	2.930	24.8	O in Sm-O and Al-O
01389-01[bb]	O KLL	979.8	...	...	...	...	Metal to O
01389-01[ag]	Sm $3d_{5/2}$	1084.1	4.74	653577.52	40.37	4.1	Sm as Sm-O
01389-01[ag]	Sm $3d_{3/2}$	1110.6	...	...	...	...	Sm as Sm-O
01389-01[c]	C KLL	1222.7	...	...	...	...	Residual C
01389-01[b0]	Cl LMM	1304.38	...	...	...	...	Residual Cl
01389-02[c]	C 1s	284.6	...	...	...	...	Residual C
01389-03[ag]	Sm $3d_{5/2}$	1084.4	...	...	...	...	Sm as Sm-O
01389-03[ag]	Sm $3d_{3/2}$	1111.4	...	...	...	...	Sm as Sm-O

[a] Europium present as $EuCl_3$. Small amounts of $EuCl_2$ and EuOCl may be present.
[b] Chlorine present as $EuCl_3$. Small amounts of $EuCl_2$ and EuOCl may be present.
[c] Residual carbon contamination
[d] Residual oxygen contamination and possibly very small amounts of EuOCl

Author Proof

PROOF COPY [SSS-XPS-16-012R] 003602SSS

[e] Small amounts of $EuCl_2$
[f] Europium present as $EuCl_3$. Small amounts of EuOCl may be present.
[g] Samarium present as $SmCl_3$. Small amounts of SmOCl may be present.
[h] Chlorine present as $SmCl_3$. Small amounts of SmOCl may be present.
[i] Residual nitrogen contamination
[a0] Residual oxygen contamination and possibly very small amounts of SmOCl
[aa] Europium present as oxide in Eu-BDPA; likely some residual $EuCl_3$ contamination
[ab] Aluminum present as oxide in Eu-BDPA
[ac] Residual silicon contamination from the ampoule that the Eu-BDPA sample was prepared in
[ad] Residual chlorine contamination, likely from residual $EuCl_3$ contamination.
[ae] Oxygen present as oxide in Eu-BDPA
[af] Europium present as oxide in Eu-BDPA
[ag] Samarium present as oxide in Sm-BDPA. Likely some residual $SmCl_3$ contamination.
[ah] Aluminum present as oxide in Sm-BDPA
[ai] Residual silicon contamination from the ampoule that the Sm-BDPA sample was prepared in
[b0] Residual chlorine contamination, likely from residual $SmCl_3$ contamination.
[ba] Oxygen present as oxide in Sm-BDPA
[bb] Oxygen as metal oxide in Sm-BDPA

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
a	Ag $3d_{5/2}$	368.2	0.92	818043	11.054	>95%	Ag $3d_{5/2}$
b	Cu $2p_{3/2}$	932.6	1.08	1049700	15.425	>95%	Cu $2p_{3/2}$
c	Au $4f_{7/2}$	83.9	1.02	529237	8.839	>95%	Au $4f_{7/2}$

[a] Ar^+ ion sputter cleaned high-purity Ag foil
[b] Ar^+ ion sputter cleaned high-purity Cu foil
[c] Ar^+ ion sputter cleaned high-purity Au foil

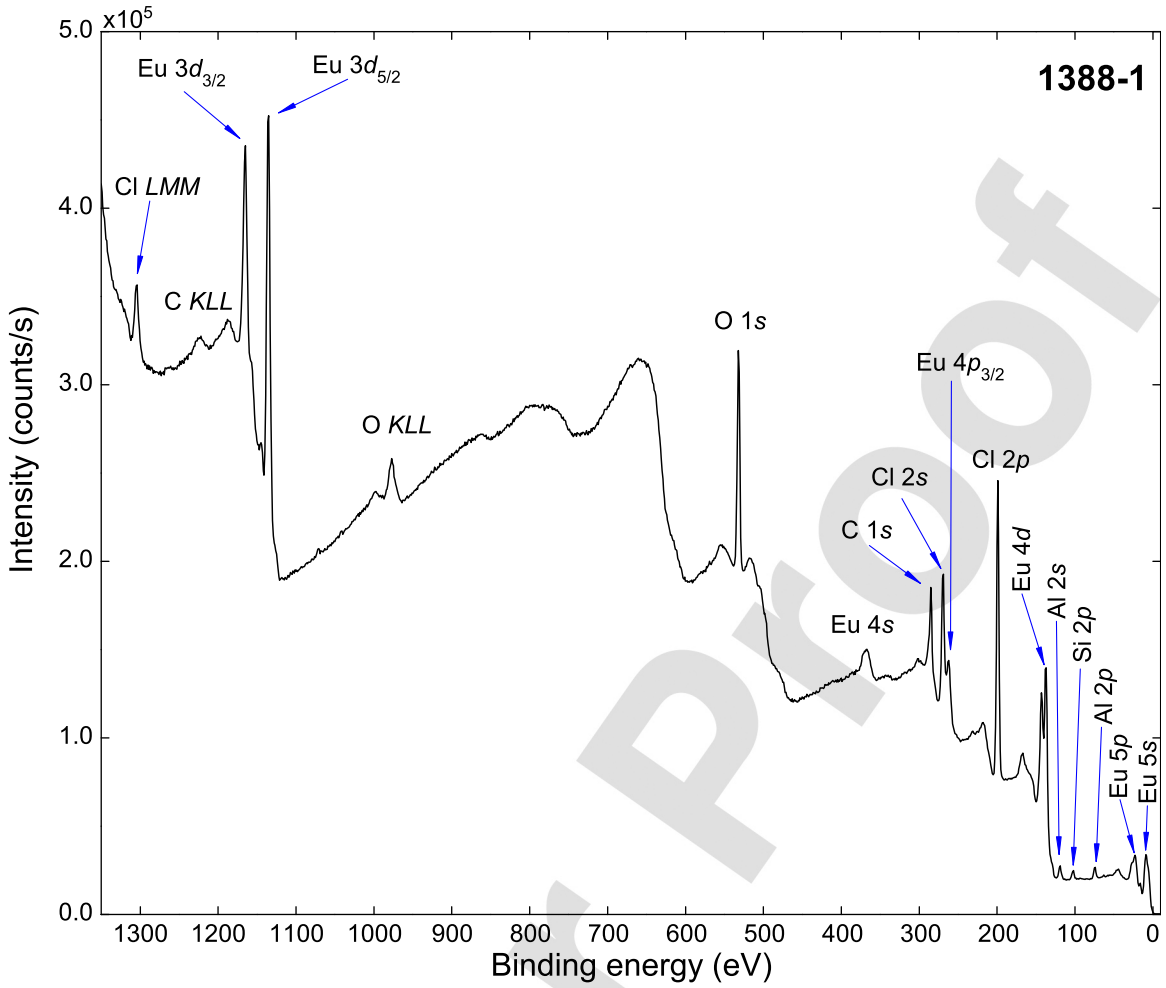
GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
1385-01 [NP]**	survey	0	1	0	1
1385-02 [NP]	Cl 2p	0	1	0	1
1385-03 [NP]	C 1s	0	1	0	1
1385-04 [NP]	Eu(III) $3d_{3/2}$, Eu(II) $3d_{3/2}$, Eu(II)	0	1	0	1
1386-01 [NP]	survey	0	1	0	2
1386-02 [NP]	Cl 2p	0	1	0	2
1386-03 [NP]	C 1s	0	1	0	2
1386-04 [NP]	Sm $3d_{3/2}$, Sm $3d_{5/2}$	0	1	0	2
1388-01	survey	0	1	0	3
1388-02 [NP]	C 1s	0	1	0	3
1388-03	Eu(III) $3d_{3/2}$, Eu(II) $3d_{3/2}$, Eu(II)	0	1	0	3
1389-01	survey	0	1	0	4
1389-02 [NP]	C 1s	0	1	0	4
1389-03	Sm $3d_{3/2}$, Sm $3d_{5/2}$	0	1	0	4

* 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.
** [NP] signifies not published; digital spectra are archived in *SSS* database but not reproduced in the printed journal.
1. $EuCl_3$ powder
2. $SmCl_3$ powder
3. europium beta"-alumina
4. samarium beta"-alumina

Author Proof

PROOF COPY [SSS-XPS-16-012R] 003602SSS

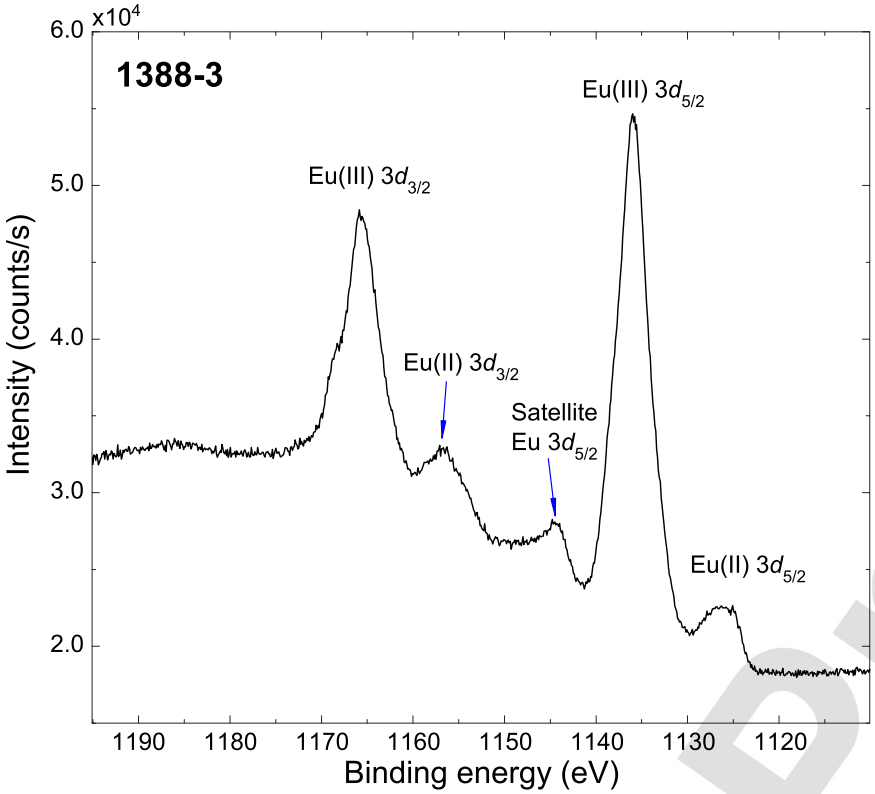


Accession #	01388–01
Host Material	europium beta”-alumina
Technique	XPS
Spectral Region	survey
Instrument	Thermo Scientific K-Alpha XPS
Excitation Source	Al K_α monochromatic
Source Energy	1486.68 eV
Source Strength	72 W
Source Size	0.005 mm × 0.005 mm
Analyzer Type	double-focusing hemispherical analyzer
Incident Angle	0°
Emission Angle	45°
Analyzer Pass Energy:	200 eV
Analyzer Resolution	0.01 eV
Total Signal Accumulation Time	680.5 s
Total Elapsed Time	833 s
Number of Scans	10
Effective Detector Width	1 eV

Author Proof

J_ID: SSS DOI: 10.1116/1.4972828 Date: 21-December-16 Stage: Page: 8 Total Pages: 10

PROOF COPY [SSS-XPS-16-012R] 003602SSS



- **Accession #:** 01388–03
- **Host Material:** europium beta"-alumina
- **Technique:** XPS
- **Spectral Region:** Eu(III) $3d_{3/2}$; Eu(II) $3d_{3/2}$; Eu(III) $3d_{5/2}$; Eu(II) $3d_{5/2}$

Instrument: Thermo Scientific K-Alpha XPS

Excitation Source: Al K_α monochromatic

Source Energy: 1486.68 eV

Source Strength: 72 W

Source Size: 0.005 mm × 0.005 mm

Analyzer Type: double-focusing hemispherical analyzer

Incident Angle: 0°

Emission Angle: 45°

Analyzer Pass Energy: 50 eV

Analyzer Resolution: 0.001 eV

Total Signal Accumulation Time: 425.5 s

Total Elapsed Time: 493 s

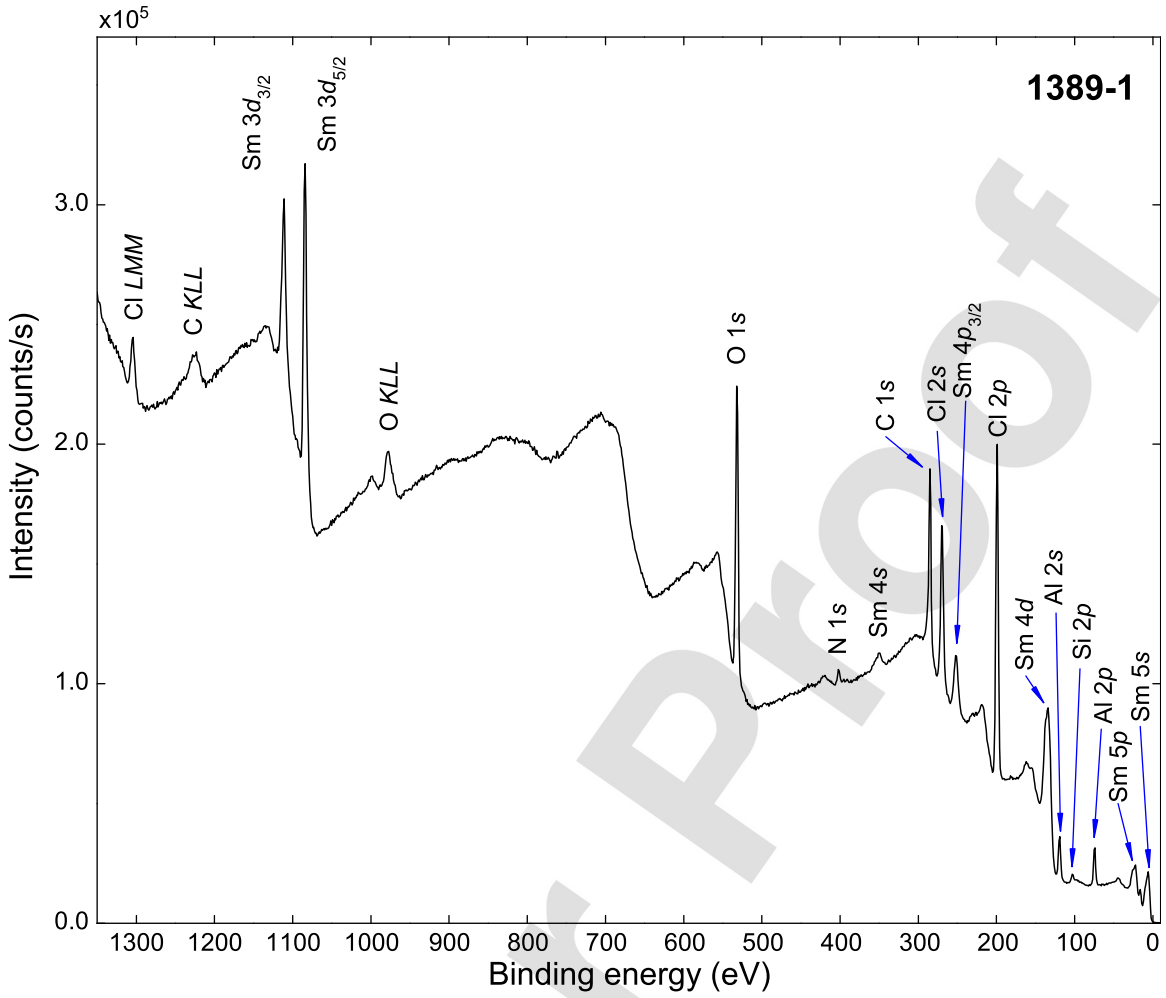
Number of Scans: 10

Effective Detector Width: 0.1 eV

Author Proof

ID: rajeshp Time: 18:39 I Path: //chenas03.cadmus.com/Home$/rajeshp$/AI-SSS#160512

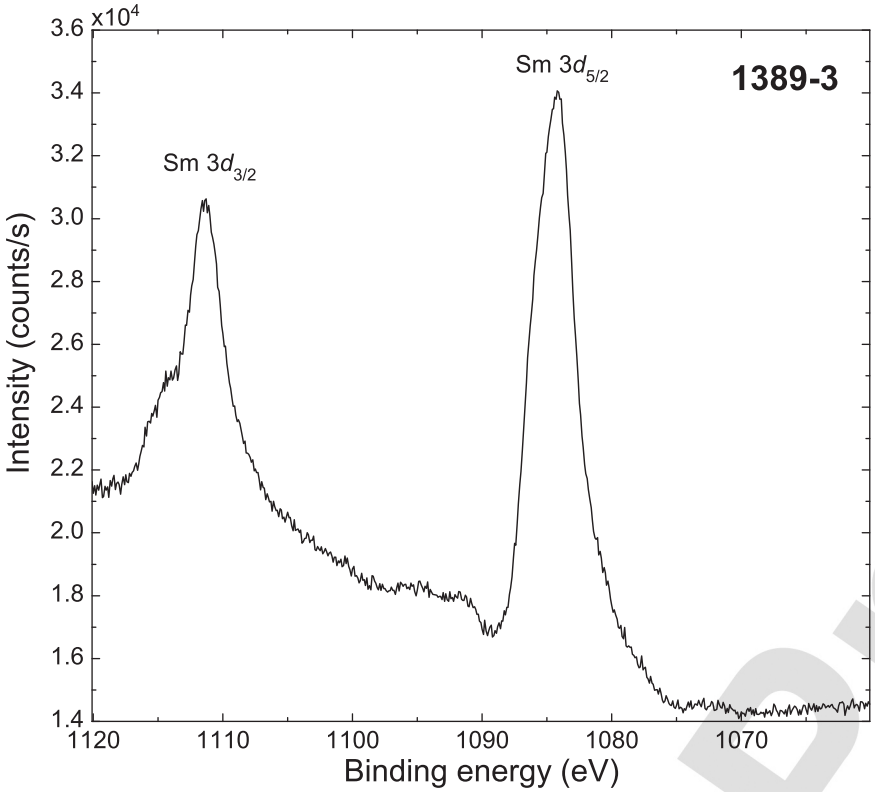
PROOF COPY [SSS-XPS-16-012R] 003602SSS



Accession #	01389–01
Host Material	samarium beta”-alumina
Technique	XPS
Spectral Region	survey
Instrument	Thermo Scientific K-Alpha XPS
Excitation Source	Al K_α monochromatic
Source Energy	1486.68 eV
Source Strength	72 W
Source Size	0.005 mm × 0.005 mm
Analyzer Type	double-focusing hemispherical analyzer
Incident Angle	0°
Emission Angle	45°
Analyzer Pass Energy:	200 eV
Analyzer Resolution	0.01 eV
Total Signal Accumulation Time	680.5 s
Total Elapsed Time	831 s
Number of Scans	10
Effective Detector Width	1 eV

Author Proof

PROOF COPY [SSS-XPS-16-012R] 003602SSS



- **Accession #:** 01389–03
- **Host Material:** samarium beta"-alumina
- **Technique:** XPS
- **Spectral Region:** Sm $3d_{3/2}$; Sm $3d_{5/2}$

Instrument: Thermo Scientific K-Alpha XPS

Excitation Source: Al K_α monochromatic

Source Energy: 1486.68 eV

Source Strength: 72 W

Source Size: 0.005 mm × 0.005 mm

Analyzer Type: double-focusing hemispherical analyzer

Incident Angle: 0°

Emission Angle: 45°

Analyzer Pass Energy: 50 eV

Analyzer Resolution: 0.001 eV

Total Signal Accumulation Time: 300.5 s

Total Elapsed Time: 361 s

Number of Scans: 10

Effective Detector Width: 0.1 eV

Author Proof