Analysis of the Be KLL Auger Transition on Beryllium and Beryllium Oxide by AES

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As-received beryllium, beryllium scribed in vacuum and beryllium oxide were analysed by Auger Electron Spectroscopy. As-received beryllium was analysed at low and high take off angles. Spectra produced demonstrate the change in the KLL structure with increasing oxygen concentration. Survey spectra as well as high resolution Be KLL and O KLL transitions were collected and are presented. © 2013 American Vacuum Society.
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INTRODUCTION

As a continuation of the previous XPS investigation on beryllium, the KLL Auger transition of beryllium has been examined. It is shown herein that the beryllium metal signal is highly attenuated by the thin surface oxide layer, of ~3 nm, due to the low kinetic energy of the transition. Upon removal of this oxide by scribing the metal surface in vacuum a striking increase in the beryllium signal is obtained. Little current literature is available regarding the Auger analysis of beryllium or beryllium compounds. Some of the most recent work has used Auger to monitor the oxidation of beryllium for the investigation of the electronic band structure of beryllium (Ref. 1) and a number of authors in the past have studied the KLL Auger transition in both beryllium (Refs. 2–4) and beryllium oxide (Refs. 1–5).

The earliest work on clean beryllium observed two peaks in the derivative spectrum which were identified as 1s2s2s and 1s2p2p transitions at 92 eV and 104 eV respectively (Ref. 2). Another study confirmed the presence of a large sharp peak at 104.5 eV however no peak was observed at 92 eV. In addition to the large peak at 104.5 eV two small peaks at 84 and 60 eV were observed which were believed to be first and second order plasmon losses of the main peak (Ref. 3). Oxidation of the beryllium surface leads to formation of a strong peak at 94 eV and weaker satellites at 85, 77 and 66 eV (Ref. 3). It is concluded that clean beryllium has a large Auger peak at 104.5 eV and beryllium oxide at 94 eV. Later work confirmed that no peak is observed at 92 eV on clean, oxide free, beryllium, with the main peak position at ~104 eV (Ref. 4). Beryllium oxide has also been confirmed to show a main peak at 94 eV and three satellites with positions approximately 87, 77 and 67 eV (Ref. 5).

The main peak in BeO was confirmed to shift by ~10 eV from that of Be (Refs. 1 and 5), the main peak at 95 eV and the satellite at 86 eV originate from the 1s2p2p transitions involving electrons from the top and bottom of the p-band respectively. The satellite at 78 eV is believed to be due to the 1s2p2s transition and the satellite at 68 eV is thought to be an energy loss feature (Ref. 5).

In this work spectra are presented that show the main Auger transition for beryllium and beryllium oxide. The beryllium metal differential spectrum shows the primary peak at 108.8 eV together with a loss satellite at 91 eV. The native oxide differential spectrum contains the metal component at 108.3 eV, the main oxide component at 97 eV as well as a number of satellites at 88.5, 81 and 70 eV. The spectrum of native beryllium oxide film was acquired by tilting the sample 15 degrees from the analyser, increasing the emission angle from 60 to 75 degrees relative to the sample normal. The resultant spectrum was free of the metal component. The differential spectrum showed the main oxide component at 97 eV and the satellites at 88.5, 81 and 70 eV. The differential spectrum showed the main oxide component at 97 eV and the satellites at 80.5 and 69 eV.

To the authors' knowledge this is the first time a sample of bulk beryllium oxide has been analysed. The insulating surface makes analysis difficult. A range of methods were attempted to analyse the surface including: flooding with low energy argon, tilting the sample towards the analyser, covering the sample with aluminium foil and performing analysis through a pin hole in the foil. Each of these methods proved unsuccessful. Analysis using a beam energy of 1.5 kV was partially successful with carbon contamination and oxygen peaks resolvable. The spectrum of beryllium oxide was successfully collected by tilting the sample 85 degrees from the excitation source and reducing the beam energy from 10 to 3 kV. Flooding the sample with low energy argon, <30 eV, decreases the small amount of sample charging in the spectrum observed using this method, although it is not removed entirely.

SPECIMEN DESCRIPTION (ACCESSION #01269, 1 OF 2) —

Host Material: Be foil

CAS Registry #: 7440-41-7

Host Material Characteristics: homogeneous; solid; polycrystalline; conductor; metal

Chemical Name: beryllium

Source: GoodFellow

Host Composition: Be

Form: foil 1 × 25 × 25 mm

Lot #: BE000330

Accession #s: 01269, 01270

Technique: AES

Host Material: #01269: Be foil;
#01270: BeO foil

Instrument: Thermo MicroLab 350

Major Elements in Spectra: Be, O

Minor Elements in Spectra: O, C

Published Spectra: 11

Spectra in Electronic Record: 20

Spectral Category: reference

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As Received Condition: Sample arrived vacuum packed wrapped in cardboard from GoodFellow. It was stored wrapped in aluminium foil under normal conditions. Typical analysis provided by GoodFellow (ppm) Al <500, B <3, Cd <2, Ca <100, C <700, Cr <100, Co <10, Cu <100, Fe <700, Pb <20, Li <3, Mg <500, Mn <120, Mo <20, Ni <200, N <400, Si <400, Ag <10, BeO <8000.

Analyzed Region: not specified

Ex Situ Preparation/Mounting: Sample was mounted onto an aluminium sample stub using sprung copper beryllium clips.

In Situ Preparation: Sample was argon ion etched for 60 s to remove carbonaceous contamination. After initial analysis was completed, a region was scribed with the end of a wobble stick, and the freshly exposed beryllium analysed.

Pre-Analysis Beam Exposure: Sample was previously exposed to approximately 15 h of monochromatic Al x-ray irradiation and sonically cleaned in isopropyl alcohol for 5 min.

Charge Control: not specified

Temp. During Analysis: 300 K

Pressure During Analysis: $<1 \times 10^{-7}$ Pa

SPECIMEN DESCRIPTION (ACCESSION #01270, 2 OF 2) —

Host Material: BeO foil

CAS Registry #: 1304-56-9

Host Material Characteristics: homogeneous; solid; polycrystalline; dielectric; inorganic compound; ceramic

Chemical Name: beryllium oxide

Source: GoodFellow

Host Composition: BeO

Form: foil $1 \times 25 \times 25$ mm

Lot #: 739-203-48

As Received Condition: Sample arrived vacuum packed wrapped in cardboard from GoodFellow. It was stored wrapped in aluminium foil under normal conditions.

Analyzed Region: not specified

Ex Situ Preparation/Mounting: Due to previous fault during analysis the sample had been sputtered with large amounts of magnesium and silver. These were removed by rinsing the sample in aqua regia for 5 min, then neutralised using sodium hydroxide before the sample was rinsed using deionised water. Sample was mounted onto an aluminium sample stub using sprung copper beryllium clips.

In Situ Preparation: The sample was argon ion etched for 180 s to remove carbon contamination at which point etching was no longer effective.

Pre-Analysis Beam Exposure: Sample was previously exposed to approximately 15 h of monochromatic Al x-ray irradiation and sonically cleaned in isopropyl alcohol for 5 min.

Charge Control: Sample was analysed by using a 3 kV beam energy and tilting the sample 85 degrees from the excitation source.

Temp. During Analysis: 300 K

Pressure During Analysis: $<1 \times 10^{-6}$ Pa

INSTRUMENT DESCRIPTION —

Manufacturer and Model: Thermo Microlab 350

Analyzer Type: spherical sector

Detector: multi-channel parallel detector

Number of Detector Elements: 6

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA —

■ **Spectrometer**

Analyzer Mode: constant retard ratio

Throughput ($T = E^N$): N = See comment below

Throughput Comment: The transmission function is calculated from a cubic polynomial fit to a plot of LOG (Peak Area * XSF/PE) vs. LOG (RR) RR = KE/PE (Retard Ratio = Kinetic Energy/Pass Energy). XSF is a term to account for the difference in absolute sensitivities of the Ag MNN and Ag 3d peaks.

Excitation Source Window: none

Excitation Source: electron beam

Source Beam Size: $0.1 \mu\text{m} \times 0.1 \mu\text{m}$

Source Beam Size at Specimen Surface: $0.11 \mu\text{m} \times 0.11 \mu\text{m}$

Signal Modulation: none

Signal Mode: pulse single channel

■ **Geometry**

Incident Angle: 60°

Source to Analyzer Angle: 60°

Emission Angle: 60°

Specimen Azimuthal Angle: 0°

Acceptance Angle from Analyzer Axis: $50/+25^\circ$

Analyzer Angular Acceptance Width: $25^\circ \times 25^\circ$

■ **Ion Gun**

Manufacturer and Model: Thermo EX05

Energy: 3000 eV

Current: 1 mA

Current Measurement Method: biased stage

Sputtering Species: Ar^+

Spot Size (unrastered): $200 \mu\text{m}$

Raster Size: $2000 \mu\text{m} \times 2000 \mu\text{m}$

Incident Angle: 67.5°

Polar Angle: 43°

Azimuthal Angle: 228°

DATA ANALYSIS METHOD —

Energy Scale Correction: The Be KLL, O KLL and survey spectra from beryllium oxide have been shifted to correct for charging. Each is shifted to align the maximum peak intensity with that seen in the equivalent spectra obtained from the tilted beryllium metal.

Recommended Energy Scale Shift: The Be KLL spectra has been shifted by +6.5 eV and the O KLL and survey spectra have been shifted by +5 eV.

Peak Shape and Background Method: A Shirley background was used for fitting peaks.

Quantitation Method: Peak height was used to measure peak amplitude and the FWHM of each peak measured using a Shirley background. Peaks were fitted using Thermo Scientific Advantage v3.75 software.

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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
01269-02	Be KLL	103.3	8.7	14726	...	...	Be metal
01269-09	O KLL	510.3	10.5	1690	...	...	O in BeO
01269-04	Be KLL	102.1, 94.5	7.7	9324	...	...	Be in BeO and metal
01269-05	O KLL	508.2	12.3	8471	...	...	O in BeO
01269-03	C KLL	262.7	16.7	880	...	...	C in contamination
01269-07	Be KLL	94.5	5.9	4153	...	...	Be in BeO
01269-08	O KLL	506.9	8.4	11416	...	...	O in BeO
01269-06	C KLL	267.8	19.0	2271	...	...	C in contamination
01270-02 ^a	Be KLL	86.0	8.0	49621	...	...	Be in BeO
01270-03 ^b	O KLL	501.0	11.4	152881	...	...	O in BeO
01270-01	C KLL	259.0	24.0	33896	...	...	C in contamination
01270-01	Ar LMM	209.0	5.6	7290	...	...	Implanted argon

^a Peak energy not adjusted for charging which is believed to be ~6.5 eV

^b Peak energy not adjusted for charging which is believed to be ~5 eV

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
15	Au M ₅ N _{6,7} N _{6,7}	2014.0	22	19676	...	...	Au metal
14	Au N _{6,7} VV	69.5, 71.5	7.4	38605	...	...	Au metal
20	Ag M ₄ NN	351.75, 357.5	4.4	111196	...	...	Ag metal
18	Cu L ₃ VV	60.2, 62.3	6.2	19337	...	...	Cu metal
17	Cu M _{2,3} VV	917.3	7.2	41899	...	...	Cu metal

GUIDE TO FIGURES					
Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
1269-01	Be KLL, O KLL	−5	1	0	1
1269-02	Be KLL	−6.5	1	0	1
1269-03	Be KLL, C KLL, O KLL	−5	1	0	1
1269-04	Be KLL	−6.5	1	0	1
1269-05	O KLL	−5	1	0	1
1269-06	Be KLL, C KLL, O KLL	−5	1	0	1
1269-07	Be KLL	−6.5	1	0	1
1269-08	O KLL	−5	1	0	1
1270-01	Be KLL, C KLL, O KLL	−5	1	0	2
1270-02	Be KLL	−6.5	1	0	2
1270-03	O KLL	−5	1	0	2
1269-09 [NP]**	O KLL	−5	1	0	1
1271-01 [NP]	Au NVV, Au MNN	-	1	0	3
1271-02 [NP]	Au NVV	-	1	0	3
1271-03 [NP]	Au MNN	-	1	0	3
1272-01 [NP]	Cu MVV, Cu LVV	-	1	0	4
1272-02 [NP]	Cu MVV	-	1	0	4
1272-03 [NP]	Cu LVV	-	1	0	4
1273-01 [NP]	Ag MNN	-	1	0	5
1273-02 [NP]	Ag MNN	-	1	0	5

* 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. Be
2. BeO
3. Au calibration
4. Cu calibration
5. Ag calibration

Accession #	01269-01
Host Material	Be foil
Technique	AES
Spectral Region	survey
Instrument	Thermo Microlab 350
Excitation Source	electron beam
Source Energy	10000 eV
Source Strength	1.22 nA
Source Size	$0.1 \mu\text{m} \times 0.1 \mu\text{m}$
Analyzer Type	spherical sector
Incident Angle	60°
Emission Angle	60°
Analyzer Retard Ratio:	4
Analyzer Resolution	2%
Total Signal Accumulation Time	495 s
Total Elapsed Time	720 s
Number of Scans	5
Effective Detector Width	1 eV
Comment	Survey of Be metal after scribing in vacuum

■ Accession #: 01269-02
 ■ Host Material: Be foil
 ■ Technique: AES
 ■ Spectral Region: Be KLL

Instrument: Thermo Microlab 350
 Excitation Source: electron beam
 Source Energy: 10000 eV
 Source Strength: 1.22 nA
 Source Size: $0.1 \mu\text{m} \times 0.1 \mu\text{m}$
 Analyzer Type: spherical sector
 Incident Angle: 60°
 Emission Angle: 60°
 Analyzer Retard Ratio: 4
 Analyzer Resolution: 2%
 Total Signal Accumulation Time: 604 s
 Total Elapsed Time: 900 s
 Number of Scans: 100
 Effective Detector Width: 0.5 eV

Accession #	01269-03
Host Material	Be foil
Technique	AES
Spectral Region	survey
Instrument	Thermo Microlab 350
Excitation Source	electron beam
Source Energy	10000 eV
Source Strength	1.22 nA
Source Size	0.1 μm $\times$ 0.1 μm
Analyzer Type	spherical sector
Incident Angle	60°
Emission Angle	60°
Analyzer Retard Ratio:	4
Analyzer Resolution	2%
Total Signal Accumulation Time	495 s
Total Elapsed Time	727 s
Number of Scans	5
Effective Detector Width	1 eV
Comment	Survey of as-received metal surface showing both oxide and metal Be KLL components

■ Accession #: 01269-04
 ■ Host Material: Be foil
 ■ Technique: AES
 ■ Spectral Region: Be KLL

Instrument: Thermo Microlab 350
 Excitation Source: electron beam
 Source Energy: 10000 eV
 Source Strength: 1.22 nA
 Source Size: $0.1 \mu\text{m} \times 0.1 \mu\text{m}$
 Analyzer Type: spherical sector
 Incident Angle: 60°
 Emission Angle: 60°
 Analyzer Retard Ratio: 4
 Analyzer Resolution: 2%
 Total Signal Accumulation Time: 465 s
 Total Elapsed Time: 555 s
 Number of Scans: 50
 Effective Detector Width: 0.5 eV

■ Accession #: 01269-05
 ■ Host Material: Be foil
 ■ Technique: AES
 ■ Spectral Region: O KLL

Instrument: Thermo Microlab 350
 Excitation Source: electron beam
 Source Energy: 10000 eV
 Source Strength: 1.22 nA
 Source Size: $0.1 \mu\text{m} \times 0.1 \mu\text{m}$
 Analyzer Type: spherical sector
 Incident Angle: 60°
 Emission Angle: 60°
 Analyzer Retard Ratio: 4
 Analyzer Resolution: 2%
 Total Signal Accumulation Time: 402 s
 Total Elapsed Time: 925 s
 Number of Scans: 50
 Effective Detector Width: 0.5 eV

Accession #	01269-06
Host Material	Be foil
Technique	AES
Spectral Region	survey
Instrument	Thermo Microlab 350
Excitation Source	electron beam
Source Energy	10000 eV
Source Strength	1.22 nA
Source Size	0.1 μm $\times$ 0.1 μm
Analyzer Type	spherical sector
Incident Angle	60°
Emission Angle	75°
Analyzer Retard Ratio:	4
Analyzer Resolution	2%
Total Signal Accumulation Time	495 s
Total Elapsed Time	710 s
Number of Scans	5
Effective Detector Width	1 eV
Comment	Survey of as-received metal taken with lower take-off angle to isolate surface oxide and collect just BeO KLL component

■ Accession #: 01269-07
 ■ Host Material: Be foil
 ■ Technique: AES
 ■ Spectral Region: Be KLL

Instrument: Thermo Microlab 350
 Excitation Source: electron beam
 Source Energy: 10000 eV
 Source Strength: 1.22 nA
 Source Size: $0.1 \mu\text{m} \times 0.1 \mu\text{m}$
 Analyzer Type: spherical sector
 Incident Angle: 60°
 Emission Angle: 75°
 Analyzer Retard Ratio: 4
 Analyzer Resolution: 2%
 Total Signal Accumulation Time: 604 s
 Total Elapsed Time: 866 s
 Number of Scans: 100
 Effective Detector Width: 0.5 eV

■ Accession #: 01269-08
 ■ Host Material: Be foil
 ■ Technique: AES
 ■ Spectral Region: O KLL

Instrument: Thermo Microlab 350
 Excitation Source: electron beam
 Source Energy: 10000 eV
 Source Strength: 1.22 nA
 Source Size: $0.1 \mu\text{m} \times 0.1 \mu\text{m}$
 Analyzer Type: spherical sector
 Incident Angle: 60°
 Emission Angle: 75°
 Analyzer Retard Ratio: 4
 Analyzer Resolution: 2%
 Total Signal Accumulation Time: 402 s
 Total Elapsed Time: 648 s
 Number of Scans: 50
 Effective Detector Width: 0.5 eV

Accession #	01270-01
Host Material	BeO foil
Technique	AES
Spectral Region	survey
Instrument	Thermo Microlab 350
Excitation Source	electron beam
Source Energy	3000 eV
Source Strength	0.04 nA
Source Size	0.1 μm $\times$ 0.1 μm
Analyzer Type	spherical sector
Incident Angle	60°
Emission Angle	60°
Analyzer Retard Ratio:	4
Analyzer Resolution	2%
Total Signal Accumulation Time	899 s
Total Elapsed Time	1217 s
Number of Scans	5
Effective Detector Width	0.5 eV
Comment	Survey collected from bulk BeO

■ Accession #: 01270-02
 ■ Host Material: BeO foil
 ■ Technique: AES
 ■ Spectral Region: Be KLL

Instrument: Thermo Microlab 350
 Excitation Source: electron beam
 Source Energy: 3000 eV
 Source Strength: 0.04 nA
 Source Size: $0.1 \mu\text{m} \times 0.1 \mu\text{m}$
 Analyzer Type: spherical sector
 Incident Angle: 60°
 Emission Angle: 60°
 Analyzer Retard Ratio: 4
 Analyzer Resolution: 2%
 Total Signal Accumulation Time: 376 s
 Total Elapsed Time: 552 s
 Number of Scans: 50
 Effective Detector Width: 0.5 eV

■ Accession #: 01270-03
 ■ Host Material: BeO foil
 ■ Technique: AES
 ■ Spectral Region: O KLL

Instrument: Thermo Microlab 350
 Excitation Source: electron beam
 Source Energy: 3000 eV
 Source Strength: 0.04 nA
 Source Size: $0.1 \mu\text{m} \times 0.1 \mu\text{m}$
 Analyzer Type: spherical sector
 Incident Angle: 60°
 Emission Angle: 60°
 Analyzer Retard Ratio: 4
 Analyzer Resolution: 2%
 Total Signal Accumulation Time: 502 s
 Total Elapsed Time: 790 s
 Number of Scans: 50
 Effective Detector Width: 0.5 eV