XPS Study of Calcium Lanthanum Sulfide Ceramics

Brian E. Butkus
University of Central Florida
XPS STUDY OF CALCIUM LANTHANUM SULFIDE CERAMICS

by

BRIAN EDWARD BUTKUS
B.S. Illinois State University, 2005
M.S. University of Central Florida, 2019

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Department of Material Science and Engineering
in the College of Engineering and Computer Science
at the University of Central Florida
Orlando, Florida

Fall Term
2023

Major Professor: Parag Banerjee
ABSTRACT

Long wave infrared (LWIR) optics that transmit in the 8 to 14 μm wavelength range and, additionally, can withstand severe physical and thermal stresses are needed for advanced remote sensing, guidance and communication-based applications. However, most non-oxide transparent LWIR optics do not have the wider transmission range, nor the hardness and resistance to thermal shock needed for extreme environments. Because of these limitations, research is circling back to a promising material, calcium lanthanum sulfide (CLS), that could meet LWIR needs for extreme environments.

In this thesis, we will demonstrate the abilities of x-ray photoelectron spectroscopy (XPS) as a technique for characterizing CLS powders and ceramics for elemental analysis, valence state and stoichiometry evaluation. Three preliminary studies were conducted - a binary metal sulfide evaluation of lanthanum sulfide (La$_2$S$_3$) and calcium sulfide (CaS), and a calibration curve of mixtures of the two binary metal sulfide powders from a known concentration matrix. Based on these results, a methodology was developed to evaluate CLS powder and ceramics via XPS. We showcase the power of XPS to reliably determine CLS stoichiometry, identify impurities and defects as related to the presence of carbon and oxygen during processing, and predict the bonding environment of sulfur which can lead to better quality CLS ceramics.

This thesis demonstrates the use of XPS as a potential characterization tool in CLS to identify contaminants, determine if stoichiometry is met, and identify the bonding environments to assist in processing improvements for producing higher-quality ceramics.
To my family. My wife, Tracey L. Butkus, and daughter, Kaley E. Butkus. My parents, Rick B. Butkus Sr. and Madeline C. Butkus, and older brother, Rick B. Butkus Jr., have always supported me in life and my academic career.
ACKNOWLEDGMENTS

I am thankful for the support from my principal advisor, Dr. Parag Banerjee, and my committee, Dr. Kathleen Richardson, Dr. Roman Gaume, and Dr. Kris Davis. I am also grateful for the support of all my lab mates: Corbin, Jeya, Novia, Jaynlynn, Eric, Bri, Luis, and TJ. They have supported me through my research and my journey in the MSE program. I am grateful for my experience with all of them as I have learned different skills and lessons from each.

I want to thank Dr. Kathleen Richardson for her support and belief in my abilities as a scientist; she has supported my efforts ever since I returned to school.

I thank Dr. Roman Gaume for his support and guidance during my research.

I would also like to thank Dr. Richardson’s and Dr. Gaume’s group for being a great research collaboration. I have been made to feel like a critical part of the team; Myungkoo, Rashi, Matt, and Andrew have significantly influenced my material science and engineering journey.

I want to thank Alexandros Kostogiannes of Dr. Richardson’s group for providing samples and support for this work.

I want to thank Dr. Clara Rivero-Baleine; this work would not be possible without her support.

I would like to thank the UCF Materials Characterization Facility and its staff, especially Kirk Scammon.

In addition, I would also like to thank Dr. Sandra Hick and Dr. Richard Blair. They have believed in me since I told him I wanted to go back and further my education. Their trust and support helped me through some of the most challenging times in my academic journey.
Lastly, I would like to thank Dr. Parag Banerjee for taking a chance on me and always treating me respectfully and as a competent lab researcher. He made me a very proactive student in his group and taught me invaluable skills that I know will make me a better researcher and teacher.

Brian Butkus

**Funding:**

This work was made possible by funding from the Lockheed Martin University Engagement.

This research was supported, in part, by the Florida High Tech Corridor’s Matching Grant Research Program at the University of Central Florida.

And the NSF MRI: ECCS: 1726636 for the support of the XPS Instrument.
# TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................ iii

ACKNOWLEDGMENTS ....................................................................................................................... v

TABLE OF CONTENTS ....................................................................................................................... vii

LIST OF FIGURES .............................................................................................................................. x

LIST OF TABLES ............................................................................................................................... xiii

LIST OF ABBREVIATIONS ..................................................................................................................... xv

CHAPTER 1: INTRODUCTION .............................................................................................................. 1

1.1 Motivation ...................................................................................................................................... 1

1.2 Current Characterization of Calcium Lanthanum Sulfide .............................................................. 3

CHAPTER 2: LITERATURE REVIEW .................................................................................................... 5

2.1 Introduction to CLS ....................................................................................................................... 5

2.2 XPS Studies on Metal Sulfides .................................................................................................. 11

2.3 XPS Studies on CaLa$_2$S$_4$ ...................................................................................................... 12

2.4 Conclusions ............................................................................................................................... 15

CHAPTER 3: EQUIPMENT AND METHODS ........................................................................................ 17

3.1 Equipment ..................................................................................................................................... 17

3.1.2 Powder and Ceramic Custom Holder for ESCALAB Xi+ XPS ................................................. 22

7.1 3.2 Methods ............................................................................................................................... 23

3.2.1 Sample Preparation ................................................................................................................. 24

3.2.2 Ceramic Cleaning Process ..................................................................................................... 26

3.2.3 Argon ion Sputtering Process for Cleaning Powder and Ceramics ........................................ 27

3.2.4 Survey Spectrum Collection ................................................................................................. 28

3.2.5 Fine Spectra Collection ......................................................................................................... 28

3.2.6 XPS Calibration Sample Preparation .................................................................................... 29
CHAPTER 4: RESULTS – CALCIUM SULFIDE CHARACTERIZATION BY XPS .......................................................... 30
  4.1 Background Calcium Sulfide Powder ........................................................................................................ 30
  4.2 Results XPS of Calcium Sulfide Powder .................................................................................................... 31
  4.3 Discussion XPS Analysis of Calcium Sulfide Powder .............................................................................. 39
  4.4 Conclusions ............................................................................................................................................. 40

CHAPTER 5: RESULTS – LANTHANUM SULFIDE CHARACTERIZATION BY XPS ........................................ 42
  5.1 Background Lanthanum Sulfide Powder ................................................................................................... 42
      Results XPS of Lanthanum Sulfide Powder ............................................................................................... 43
  5.3 Discussion XPS Analysis of Lanthanum Sulfide Powder ........................................................................ 52
  5.4 Conclusions ............................................................................................................................................. 54

CHAPTER 6: RESULTS – CALIBRATION CURVE FOR XPS ON CALCIUM LANTHANUM SULFIDE BY VARYING
  MIXTURES OF LANTHANUM AND CALCIUM SULFIDE ................................................................................... 56
  6.1 Background Calibration Curve ................................................................................................................ 56
  6.2 Results of Calibration Curve .................................................................................................................. 57
  6.3 Discussion Calibration Curve .................................................................................................................. 62
  6.4 Conclusions ............................................................................................................................................. 63

CHAPTER 7: RESULTS – CALCIUM LANTHANUM SULFIDE 90:10 ................................................................. 65
  7.1 Background CALCIUM LANTHANUM SULFIDE 90:10 ......................................................................... 65
  7.2 Results of CALCIUM LANTHANUM SULFIDE 90:10 ............................................................................ 66
      7.2.1 XPS on Cold Isostatically Pressed CLS Powder Coupon ............................................................... 66
      7.2.2 Sintered coupon – Surface Analysis ............................................................................................... 70
      7.2.4 XPS of sintered ceramic cross-section exposed to ambient .......................................................... 75
      7.2.4 XPS of sintered ceramic cross-section inert atmosphere .............................................................. 81
      7.2.5 XPS of sintered ceramic cross-section in the atmosphere and inert atmosphere depth
            profile 87
LIST OF FIGURES

Figure 1: (A) Phase diagram of CaS – La$_2$S$_3$ as given by Chess et al., showing complete solid solution between X.CaS (1-X).La$_2$S$_3$ 0.0 ≤ X ≤ 0.5. (B) Variation of % cation vacancies in CaS:La$_2$S$_3$ as a function of CaS mole fraction, X in X.CaS : (1-X).La$_2$S$_3$ ........................ .......................................................... .......................................................... .... 7

Figure 2: (A) Emission Diagram (redrawn based on Moulder et. al.[136] (B) XPS Schematic Diagram ........ 10

Figure 3: (A): S fine spectra from elemental S, showing the position of the 2p3/2 at 164.0 eV with a SOS (i.e., $\Delta$) = 1.18 eV. (B) 2p3/2 peak ranges for a variety of compounds including sulfides, sulfates and organics. From Moulder et al., Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics, 1995; ISBN: 0-9648124-1-X........................................................................................................... 11

Figure 4: XPS Spectra Graphs from Literature (A) Lanthanum 3d XPS spectra of La$_2$S$_3$ film (1) as deposited without any cleaning, (2) as-deposited measured after sputtering, and (3) annealed, without any cleaning. The film was grown at 500°C a soda lime glass substrate covered by Al$_2$O$_3$, figure adapted from Kaupu Kukli et al. 1998 (B) XPS spectra of La3d (4), S (5), O (7) in the pellet sintered at 1100°C for 1 hr. and corresponding powders of CLS. Figure adapted from Peisen Li et al. 2010, (C) XPS spectra of CLS 50% on graphene oxide nanohybrid after adsorption of arsenate and arsenite: (7) C 1s, (8) O 1s, (9) S2p, (10) La 3d, (11) Ca 2p, and (12) As 3d figure adapted from Subbaiah Muthu Prabhu et al. 2019[108-110]...... 14

Figure 5: (A) Labeled illustration of rotatory XPS Instrument. (B) Schematic of vacuum for XPS chamber and anti-chamber rotatory ALD system. (image from Thermo Scientific 2017)[146] (C) Survey spectra as it is depicted from Advantage software........................................................................................................... 21

Figure 6: Powder and Ceramic Custom Sample Holder. (A) Front view of sample holder loads onto sample holder control arm. (B) Top view of the sample holder with powders sample wells and cut out for ceramic coupons. (C) Back view of sample holder that loads onto sample stage. (D) Side view of the sample holder and view of the cut-out. ........................................................................................................................................... 23

Figure 7: Inert Atmosphere Fracture of Ceramic (A) Inert Atmosphere Glove Box for fracture (B) XPS Portable Sample Transfer Chamber (C) ESCALAB Xi+ XPS by Thermo Scientific ........................................................................................................ 26

Figure 8: XPS Survey spectrum of as received Calcium Sulfide powder ........................................................................................................ 26

Figure 9: XPS fine spectrum of as received Calcium Sulfide powder (A) S 2s fine spectra, (B) S 2p fine spectra, (C) Ca 2s fine spectra, (D) Ca 2p fine spectra, (E) Eu 3d fine spectra, (F) C 1s fine spectra and (G) O 1s fine spectra. ........................................................................................................................................... 34
Figure 10: Deconvoluted XPS fine spectrum of as received Calcium Sulfide powder (A) S 2s fine spectra, (B) S 2p fine spectra, (C) Ca 2s fine spectra, (D) Ca 2p fine spectra, (E) Eu 3d fine spectra, (F) C 1s fine spectra, (G) O 1s fine spectra, and (F) Peak Key for (A-G). .......................................................... 37

Figure 11: XPS Survey spectrum of received lanthanum sulfide powder ......................................................... 44

Figure 12: XPS fine spectrum of as received lanthanum sulfide powder (A) S 2s fine spectra, (B) S 2p fine spectra, (C) La 4s fine spectra, (D) La 4p fine spectra, (E) La 4d fine spectra, (F) La 3p3/2 fine spectra and (G) La 3p1/2 fine spectra, (H) La 3d, (I) Na 1s fine spectra, (J) C 1s fine spectra, (K) O1s fine spectra. .......... 46

Figure 13: Deconvoluted XPS fine spectrum of as received lanthanum sulfide powder (A) S 2s fine spectra, (B) S 2p fine spectra, (C) La 4s fine spectra, (D) La 4p fine spectra, (E) La 4d fine spectra, (F) La 3p3/2 fine spectra and (G) La 3p1/2 fine spectra, (H) La 3d, (I) Na 1s fine spectra, (J) C 1s fine spectra, (K) O1s fine spectra and (I) Peak Key for (A-K) ........................................................................................................ 50

Figure 14: CIP’ed samples of Lanthanum Sulfide and Calcium Sulfide and powder compacts of the intermediate mixtures (A) Sample yellow green- yellow red La$_2$S$_3$ 100%- 60% (B) Sample yellow red-light red CaS 60%-100% (C) Table for the mixture for the ratio of La$_2$S$_3$: CaS ....................................................................................... 57

Figure 15: Composites of XPS Survey spectrums for Lanthanum Sulfide and Calcium Sulfide mixture from 100% to 50/50 mixtures as pieces of CIP’ed coupons ........................................................................................................ 58

Figure 16: Composite of XPS fine spectrum of the mixture of Lanthanum Sulfide and Calcium Sulfide from 100% to 50/50 mixtures as pieces CIP’ed (A) S 2p fine spectra, (B) Ca 2p fine spectra, (C) La 3d fine spectra ........................................................................................................ 59

Figure 17: Experimental vs Theoretical at% (A) Sulfur S 2p fine spectra at% average with standard deviation vs theoretical at% (B) Calcium Ca 2p fine spectra at% average with standard deviation vs theoretical at% (C) Lanthanum La 3d fine spectra at% average with standard deviation vs theoretical at% ........................................................................................................ 59

Figure 18: CIP’ed samples of Calcium Lanthanum Sulfide 90:10 ........................................................................ 61

Figure 19: XPS Survey spectrums for Calcium Lanthanum Sulfide as CIP’ed coupon. ................................. 67

Figure 20: XPS fine spectrum of Calcium Lanthanum Sulfide 90:10 CIP’ed (A) S 2p fine spectra, (B) Ca 2p fine spectra, (C) La 3d fine spectra, (D) C 1s fine spectra, (E) O 1s fine spectra, (F) Peak Key Table ............... 68

Figure 21: Sintered Hot Pressed Samples of Calcium Lanthanum Sulfide 90:10 ............................................. 71

Figure 22: XPS Survey Spectrum for Calcium Lanthanum Sulfide 90:10 Sintered Hot Pressed Coupon..... 72
Figure 23: XPS fine spectrum of Calcium Lanthanum Sulfide 90:10 Hot Pressed Sintered Sample (A) S 2p fine spectra, (B) Ca 2p fine spectra, (C) La 3d fine spectra, (D) C 1s fine spectra, (E) O 1s fine spectra, (F) Peak Key Table

Figure 24: Ambient Fracture of Ceramic Coupon of Calcium Lanthanum Sulfide 90:10 (A) Schematic of Coupon (B) Schematic of Cross Section with points for XPS Scan (C) Light Gray CaLa$_2$S$_4$ Coupon Cross Section in Ambient Condition located on Custom Holder (1) Bottom, (2) Middle Bottom, (3) Center, (4) Middle Top, (5) Top

Figure 25: XPS Survey Spectrum for Ambient Fracture of Sintered Hot Pressed Sample of Calcium Lanthanum Sulfide 90:10

Figure 26: XPS fine spectrum of Calcium Lanthanum Sulfide 90:10 Hot Pressed Sintered Fractured in Ambient Conditions Sample (A) S 2p fine spectra, (B) Ca 2p fine spectra, (C) La 3d fine spectra, (D) C 1s fine spectra, (E) O 1s fine spectra, (F) Peak Key Table

Figure 27: XPS Survey Spectrum for Inert Atmosphere Fracture of Sintered Hot-Pressed Sample of Calcium Lanthanum Sulfide 90:10

Figure 28: XPS fine spectrum of Calcium Lanthanum Sulfide 90:10 Hot Pressed Sintered Fractured in Inert Atmosphere Conditions Sample (A) S 2p fine spectra, (B) Ca 2p fine spectra, (C) La 3d fine spectra, (D) C 1s fine spectra, (E) O 1s fine spectra, (F) Peak Key Table

Figure 29: Ambient Atmosphere & Inert Atmosphere Fracture Calcium Lanthanum Sulfide 90:10 Sintered Ceramic atomic % Graph without carbon quantification, (A) Ambient Atmosphere Fracture Sintered CLS 90:10 Cross-section at. % Graph (B) Inert Atmosphere Fracture Sintered CLS 90:10 Cross-section at. % Graph

Figure 30: Atomic Percent by Element for CLS 90:10 Green, Sintered, Ambient Fracture, and Inert Fracture
LIST OF TABLES

Table 1: Three Classes of Infrared Window Materials Adapted from Daniel C. Harris, 1998[39] ..................1

Table 2: Properties of Calcium Lanthanum Sulfide versus Zinc Sulfide (Cleartran™, FLIR, Multispectral)[34, 58, 67, 68, 72, 80-89] .................................................................3

Table 3: CLS properties as listed in literature .........................................................................................6

Table 4: Listing of the sulfides, the sulfur and metal BE and the orbitals to which the BE belong[1-32] ...10

Table 5: XPS Parameters for literature[108-110] ..............................................................................15

Table 6: XPS system parameters .........................................................................................................18

Table 7: Fine spectrum collection element transition from the start to the end of the collection in eV ...29

Table 8: Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor,
Concentration (at.%), and Peak Assignment. .................................................................................35

Table 9: Deconvoluted Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s),
Sensitivity Factor, Concentration (at.%), and Peak Assignment ......................................................38

Table 10: Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor,
Concentration (at %), and Peak Assignment .................................................................................47

Table 11: Deconvoluted Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s),
Sensitivity Factor, Concentration (at.%) and Peak Assignment ..........................................................51

Table 12: Ideal Theoretical composition in at% .................................................................................65

Table 13: Calcium Lanthanum Sulfide 90:10 CIP’ed Deconvoluted Spectrum ID, Peak Energy, Peak Width
FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor, Concentration (at.%), and Peak Assignment........70

Table 14: Calcium Lanthanum Sulfide 90:10 Sintered Ceramic Deconvoluted Spectrum ID, Peak Energy,
Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor, Concentration (at.%), and Peak
Assignment. ........................................................................................................................................75

Table 15: Ambient Fracture Calcium Lanthanum Sulfide 90:10 Sintered Ceramic Deconvoluted Spectrum
ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor, Concentration (at.%),
and Peak Assignment .........................................................................................................................81

Table 16: Inert Atmosphere Fracture Calcium Lanthanum Sulfide 90:10 Sintered Ceramic Deconvoluted
Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor,
Concentration (at.%), and Peak Assignment .......................................................................................87

Table 17: Ambient Atmosphere & Inert Atmosphere Fracture Calcium Lanthanum Sulfide 90:10 Sintered
Ceramic atomic % table based on the spot in the cross-section with and without carbon quantification,
(A) Ambient Atmosphere Fracture Sintered CLS 90:10 Cross-section at. % table (B) Inert Atmosphere Fracture Sintered CLS 90:10 Cross-section at. % table ..................................................................................................................................................88
LIST OF ABBREVIATIONS

Ar⁺: Argon Ion Sputtering

at. %: Atomic Percentage

BCC: Body-Centered Cubic

BE: Binding Energy

C: Carbon

Ca: Calcium

CaS: Calcium Sulfide

CIP: Cold Isostatically Pressed

CLS: Calcium Lanthanum Sulfide

CVD: Chemical Vapor Deposition

DSC: Differential Scanning Calorimetry

EDS: Energy-Dispersive X-ray Spectroscopy

EDX: Energy Dispersive X-ray Spectroscopy

Eu: Europium

FLIR: Forward-Looking Infrared

FTIR: Fourier Transform Infrared Spectroscopy

FWHM: Full Width Half Max
HIP: Hot Isostatically Pressed

IR: Infrared

KE: Kinetic Energy

La: Lanthanum

La$_2$S$_3$: Lanthanum Sulfide

LWIR: Long-Wave Infrared

Na$_2$S: Sodium Sulfide

O: Oxygen

Poly metal sulfide: poly sulfur metal sulfide

S: Sulfur

SEM: Scanning Electron Microscopy

SOS: Spin-Orbit Splitting

TGA: Thermogravimetric Analysis

UHV: Ultra-High Vacuum

XPS: X-ray Photoelectron Spectroscopy

XRD: X-ray Diffraction

ZnS: Zinc Sulfide
CHAPTER 1: INTRODUCTION

1.1 Motivation

Long-wave infrared (LWIR) optics are needed for various applications such as, aerospace, automotive, military, and smart sensors[33-38]. There are many examples of infrared (IR) windows - from single crystal and polycrystalline materials to glasses, as seen in Table 1[39]. While materials like zinc sulfide (ZnS) are produced and used in infrared optical applications, their uses are limited by mechanical and thermomechanical stability[40-56]. However, the need for IR optics is increasing, especially for use in extreme environments that require materials to have better resistance towards abrasion, erosion, thermal shock, oxidation and chemically attack[33, 38, 57-64].

Table 1: Three Classes of Infrared Window Materials Adapted from Daniel C. Harris, 1998[39]

<table>
<thead>
<tr>
<th>Single crystal</th>
<th>Polycrystalline</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>MgF₂</td>
<td>Calcium aluminate (Ca-Al-Ba-O)</td>
</tr>
<tr>
<td>NaCl</td>
<td>ZnS</td>
<td>As₂S₃</td>
</tr>
<tr>
<td>KCl</td>
<td>CaF₂</td>
<td>Fused silica (SiO₂)</td>
</tr>
<tr>
<td>AgCl</td>
<td>ZnSe</td>
<td>Germanate glass (Ge-Al-Ca-Ba-Zn-O)</td>
</tr>
<tr>
<td>MgF₂</td>
<td>MgO</td>
<td>Fluoride glass (Zr-Hf-Ba-F)</td>
</tr>
<tr>
<td>CaF₂</td>
<td>CdTe</td>
<td>Chalcogenide glasses (Ge-Si-S-Se-Te)</td>
</tr>
<tr>
<td>BaF₂</td>
<td>MgAl₂O₄ (spinel)</td>
<td>AMTIR® (Ge-As-Se)</td>
</tr>
<tr>
<td>CsI</td>
<td>9Al₂O₃:SiAlN (ALON)</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>Y₂O₃</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>Lanthana-doped Y₂O₃</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>Si</td>
<td></td>
</tr>
<tr>
<td>Sapphire</td>
<td>Ge</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>GaAs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GaP</td>
<td></td>
</tr>
</tbody>
</table>

Hot-pressed polycrystalline windows were formerly sold by Kodak under the following trade names: Irtran-1 (MgF₂), Irtran-2 (ZnS), Irtran-3 (CaF₂), Irtran-4 (ZnSe), Irtran-5 (MgO) and Irtran-6 (CdTe).
One previously developed material, calcium lanthanum sulfide (CLS), is gaining renewed interest. The production of CLS never made it to the mainstream, as its only successful production came from Raytheon Technologies in the 1980s[58]. Yet this success was limited due to material production quality, available technology for improvement, and limitations to characterization[37, 38, 65-68].

Because of limitations in the production of CLS, the development of ZnS overtook CLS[40, 41, 69-71]. The characteristics of ZnS in the infrared space had advantages over CLS that had been produced till date. The percent transmission and clarity are some of the advantages of ZnS[72]. Yet one of the most compelling reasons for ZnS to overtake CLS research and production is the ease of chemical vapor deposition (CVD) manufacturing.[45, 47, 72-75] The resulting ZnS is a milky yellow opaque material, yet when hot isostatically pressed (HIP‘ed), it is transparent and known under the trade name Cleartran™ [45, 47, 72-75].

Cleartran™ can transmit in the visible through 12 µm[45, 47, 72-75]. IR optical applications need materials that function in multispectral and forward-looking infrared (FLIR) IR applications. ZnS could fill these needs because of the ease of production and manipulation. Further, doped and coated ZnS could be used to withstand additional stresses and harsher environments compared to untreated Clear Tran[49, 72, 76-79].

It is essential to look at the current properties of CLS and ZnS to see the properties that would make CLS advantageous for new IR applications. The properties of CLS and ZnS can be seen in Table 2. It can be seen from Table 2 that CLS has advantages in hardness with a Knoop value of 570, a wider IR transmission of up to 20 µm, a higher thermal expansion coefficient of 14.7 (10⁻⁶/C°), and lower thermal conductivity of 1.7 (W/m-K) than ZnS [33-38, 65]. Understandably, therefore, CLS’s characteristics align with the needs of advanced optical applications in harsh environments. Additionally, CLS’s (-) thermo-optic coefficient (dn/dT) makes this material of interest and has led to renewed efforts for production(J.
Hall, personal communication, September 26, 2018). Correspondingly, the advancements in powder processing, sintering technology, thin film deposition processes, and, importantly metrology techniques make investigating CLS a worthwhile endeavour.

Table 2: Properties of Calcium Lanthanum Sulfide versus Zinc Sulfide (Cleartran™, FLIR, Multispectral)[34, 58, 67, 68, 72, 80-89]

<table>
<thead>
<tr>
<th>Property</th>
<th>CaLa$_2$S$_4$</th>
<th>Zinc Sulfide Cleartran</th>
<th>FLIR Grade ZnS</th>
<th>Multispectral Grade ZnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (Knoop)</td>
<td>570</td>
<td>160</td>
<td>240</td>
<td>160</td>
</tr>
<tr>
<td>Band Gap (eV)</td>
<td>~4.0</td>
<td>~3.5</td>
<td>~3.5</td>
<td>~3.5</td>
</tr>
<tr>
<td>IR Transmission (μm)</td>
<td>0.6 - 20 μm</td>
<td>0.4 - 12 μm</td>
<td>0.4 - 12 μm</td>
<td>0.4 - 12 μm</td>
</tr>
<tr>
<td>Chemical Resistance</td>
<td>Chemically Stable</td>
<td>Susceptible to Moisture</td>
<td>Susceptible to Moisture</td>
<td>Susceptible to Moisture</td>
</tr>
<tr>
<td>Heat Tolerance (°C)</td>
<td>&gt;1000°C (high-temp.)</td>
<td>~250°C (limited)</td>
<td>~250°C (limited)</td>
<td>~250°C (limited)</td>
</tr>
<tr>
<td>Electrical Conductance</td>
<td>Generally Insulating</td>
<td>Generally Insulating</td>
<td>Generally Insulating</td>
<td>Generally Insulating</td>
</tr>
<tr>
<td>Refractive Index (n)</td>
<td>~2.5</td>
<td>~2.2</td>
<td>~2.2</td>
<td>~2.2</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>~4.53</td>
<td>~4.09</td>
<td>~4.09</td>
<td>~4.09</td>
</tr>
<tr>
<td>$dn/dT$ (10^{-6} °C)</td>
<td>Varies with wavelength</td>
<td>~110</td>
<td>~110</td>
<td>~110</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>1840</td>
<td>1827</td>
<td>1872</td>
<td>1827</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (10^{-6} °C)</td>
<td>14.7</td>
<td>6.5</td>
<td>6.8</td>
<td>6.5</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m-K)</td>
<td>1.7</td>
<td>27.2</td>
<td>16.7</td>
<td>27.2</td>
</tr>
</tbody>
</table>

1.2 Current Characterization of Calcium Lanthanum Sulfide

Many different techniques are used to understand the structure-property characteristics of CLS. These techniques still need to identify what makes a powder a good candidate for producing a ceramic with good IR optical transmission, leading to lower transmittance and the presence of absorption peaks. In evaluating CLS, researchers have published the following metrology techniques to provide information on its physical and optical properties and base components. The methods most frequently reported for characterizing CLS powders and ceramics are:

i) X-ray diffraction (XRD) to study crystal structure [33-38, 59, 64-68, 78, 90-107],

ii) Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive X-ray Spectroscopy (EDS) to understand grain size, composition and stoichiometry[67, 78, 90, 102, 106]
iii) Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy to study local bonding environment, defects and impurities and[97, 102],

iv) Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) to understand thermal stability[103].

This thesis will focus on integrating x-ray photoelectron spectroscopy (XPS) as a characterization technique for CLS. This characterization technique has been reported with limited effectiveness for CLS and, more generally, has been rarely used for sulfide based materials[108-110].

We hypothesize that XPS can provide extensive knowledge of the bonding environment of CLS, including presence of impurities that may have a detrimental impact on the optical properties of CLS. A key focus of this thesis is the identification of impurities, primarily oxygen, which may be undetected or incorrectly assigned in previous investigations.

This thesis contains seven parts. Chapter 2 will cover an extensive literature review of CLS's characterization and properties. This includes an extensive survey of metal sulfides by XPS and the XPS of CLS, to date. Chapter 3 will transition into the methodology and equipment used for this investigation. Chapter 4 will illustrate the characterization results of calcium sulfide (CaS) powder via XPS. Chapter 5 will explain the results of lanthanum sulfide (La$_2$S$_3$) powder via XPS. Chapter 6 will present the results from the calibration study of powder compacts of varying mixture compositions of CaS to La$_2$S$_3$. Chapter 7 will explain the results of the hot-pressed CLS ceramic. Chapter 8 will conclude and provide directions for future work.
CHAPTER 2: LITERATURE REVIEW

2.1 Introduction to CLS

The history of CLS as a material of interest stems from the need for improved IR optics, hypersonic materials, and semiconductors.[58] CLS's physical, thermal, optical, and electrical properties make it a unique material to support these applications. CLS has good thermal stability with a melting point of \( \sim 1810 \, ^\circ\text{C} \) and a thermal conductivity of 1.70 W/m-K. It has good chemical stability compared to other IR ceramic materials like ZnS. It is resistant to detergents, mild acids, and bases. As CLS is part of the lanthanide family, it has chemical resistance to solvents and inorganic weak bases and acids, with the limiting factor being the release of sulfur from the matrix [33-38, 65-68, 111].

A detailed listing of the structural, mechanical, thermal, electronic, and optical properties of CLS for varying Ca: La ratios is presented in Table 3. The salient features are that the CLS crystallizes in the cubic Th\(^3\)P\(^4\) phase, a derivative of the body-centered cubic (BCC) structure. The lattice parameter is composition-dependent but varies from 8.54 Å to 8.72 Å. The hardness of the CLS (Knoop hardness) is 570 – 736 and the variability is grain size dependent. The electrical properties have also been studied, and the semiconductor bandgap lies between 2.5 – 2.7 eV, while the conductivity behaviour is reported to be \( p \)-type for the pure \( \text{La}_2\text{S}_3 \). The optical properties are reported in the LWIR, with the highest transmission reported at 74%. However, absorption bands are observed in the transmission spectra.

Since the cation:anion ratio of the \( \text{La}_2\text{S}_3 \) is 2:3 and the Th\(^3\)P\(^4\) structure has a cation:anion ratio of 3:4, it is important to understand that the \( \gamma \)-\( \text{La}_2\text{S}_3 \) structure inherently contains vacancies.
Table 3: CLS properties as listed in literature.

<table>
<thead>
<tr>
<th>Composition &amp; Structure</th>
<th>Mechanical and thermal</th>
<th>Electrical and Optical</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaS:La,S2</td>
<td>La/Ca ratio</td>
<td>Crystal Type</td>
</tr>
<tr>
<td>48.52</td>
<td>2.2</td>
<td>Th₂P₁</td>
</tr>
<tr>
<td>50.90</td>
<td>2</td>
<td>Th₂P₁</td>
</tr>
<tr>
<td>30.70</td>
<td>4.7</td>
<td>Th₂P₁</td>
</tr>
<tr>
<td>10.90</td>
<td>18</td>
<td>Th₂P₁</td>
</tr>
<tr>
<td>unknown</td>
<td>Th₂P₁</td>
<td>4.61</td>
</tr>
<tr>
<td>unknown</td>
<td>Th₂P₁</td>
<td>8.681</td>
</tr>
<tr>
<td>42.55</td>
<td>1.35</td>
<td>Th₂P₁</td>
</tr>
<tr>
<td>43.57</td>
<td>2.7</td>
<td>Th₂P₁</td>
</tr>
<tr>
<td>44.56</td>
<td>2.5</td>
<td>Th₂P₁</td>
</tr>
<tr>
<td>12.88</td>
<td>15</td>
<td>Th₂P₁</td>
</tr>
<tr>
<td>46.53</td>
<td>2.3</td>
<td>Th₂P₁</td>
</tr>
<tr>
<td>0.100</td>
<td>-</td>
<td>Th₂P₁</td>
</tr>
</tbody>
</table>

Footnote:
2. K.J. Saunders SPIE 28th ATS 1984
3. Y Li, RSC Adv., 2016, 6, 34935
15. Theoretical density from refined lattice constant a, 8.6872 Å= 4.574 gm/cm³
16. J.S. McCloy Proc. of SPIE Vol. 8708
* Converted from Vickers Hardness to Knoop
Figure 1:(A) Phase diagram of CaS – La$_2$S$_3$ as given by Chess et al., showing complete solid solution between X.CaS (1-X).La$_2$S$_3$ 0.0 ≤ X ≤ 0.5. (B) Variation of % cation vacancies in CaS:La$_2$S$_3$ as a function of CaS mole fraction, X in X.CaS : (1-X).La$_2$S$_3$

By assuming that all anion sites are filled, one can create defect reactions which predict presence of cation vacancies.[99] For site balance, we write La$_{2.67}$$\nu_{0.33}$S$_4$ indicating that (0.33 / 3.00 ) 11% sites are occupied by cation vacancies given as, ‘v’; where, in Kroger Vink notation, the vacancies can be described as, $V''_{La}$.

Systematically eliminating $V''_{La}$ allows for changes to properties of the parent $\gamma$-La$_2$S$_3$ The reduction of vacancies is most effectively achieved using doping.[112] As shown in Figure 1A, the phase diagram in this system predicts a continuous solid solution at T > 900 °C between 50:50 CaS: La$_2$S$_3$ and La$_2$S$_3$. While other dopants have been added to $\gamma$-La$_2$S$_3$[24, 88, 110, 113-132], adding CaS can, in theory, reduce the vacancies. Thus, the formula unit X$_{CaS}$ : (1-X)$_{La2S3}$, where X is the mole fraction of CaS added, can be used to predict % cation vacancies in CLS as a function of mole fraction CaS added. The variation of vacancies with the addition of CaS is shown in Figure 1B. It can be seen that $\gamma$-La$_2$S$_3$ has a 11% vacancy concentration, whereas, for equimolar concentration of CaS to La$_2$S$_3$ the vacancies are expected to be reduced to near zero. Thus, 50:50 CaS:La$_2$S$_3$ are commonly found in technological applications.
Given CLS’s complex bonding environment consisting of multiple cations, vacancies, and sulfur, it is imperative to conduct extensive materials characterization. Materials characterization helps to understand the structure of the materials and correlate it with its properties. As briefly stated in Chapter 1, a wide range of characterization techniques have been used for CLS including, x-ray diffraction, electron microscopy, FTIR and Raman and thermogravimetry analysis. However, the use of XPS for CLS characterization has been rather limitedly.

XPS as a technique is based on the photoelectric effect. The photoelectric effect was discovered by Heinrich Hertz in 1887. The physics that explains the photoelectric effect was developed by Albert Einstein in 1905. The photoelectric effect is described as many materials emitting electrons when light shines. The modern-day XPS, also first known as electron spectroscopy for chemical analysis (ESCA) was invented by Kai Siegbahn, with the first recorded spectrum being collected in 1954, for which he won the Nobel Prize for this work in physics in 1981. This work involves the process of a core electron with kinetic energy (KE) being ejected by incident X-rays the emitted electrons being counted by a spectrometer and the date being plotted as a spectrum for evaluation. These spectra are used for qualitative analysis of atoms along with the quantitative determination of atomic composition and chemistry. Every element has unique XPS spectra that are detected. XPS collection and analysis can determine elemental composition, stoichiometry, electrical/ Chemical states, and surface contamination.

XPS is extensively used for probing the surface of a material. The principal advantage of XPS is that this technique provides detailed information on the elements' bonding environment and valence states. This information is obtained by probing the surface of interest with a monochromatic x-ray beam (usually Al K-α with a beam energy of 1486.6. eV)[133-135]. The x-ray photon energy is high enough to excite core electrons from atoms which reside in the material’s top few tens of monolayers Figure 2 (A). The electrons are ejected from the surface with a fixed kinetic energy (KE) and knowing the original x-ray
photon energy (i.e., of the Al K-α beam), the binding energy (BE) of the core electrons can be obtained from a pure conservation of energy analysis as,

\[ BE = h\nu - KE - \phi \]

Where \( h\nu \) is the x-ray photon energy and \( \phi \) is the work function of the spectrometer. The absolute value of the BE and its shifts can provide detailed information on the charged state of the atom and the bonding environment in which the atom resides. The methods on atomic presentation quantifications are in Appendix A. The schematic of an XPS is shown in Figure 2 (B).
Figure 2: (A) Emission Diagram (redrawn based on Moulder et. al.[136] (B) XPS Schematic Diagram

Table 4: Listing of the sulfides, the sulfur and metal BE and the orbitals to which the BE belong[1-32]

<table>
<thead>
<tr>
<th>Metal Sulfide</th>
<th>Sulfur 2p Binding Energy (eV)</th>
<th>Metal Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Sulfide (Li₂S)</td>
<td>~160.5 - 162.5</td>
<td>~55.0 - 57.0 (Li 1s)</td>
</tr>
<tr>
<td>Cadmium Sulfide (CdS)</td>
<td>~161.0 - 163.0</td>
<td>~405.0 - 406.0 (Cd 3d)</td>
</tr>
<tr>
<td>Arsenic Sulfide (As₂S₃)</td>
<td>~161.0 - 163.0</td>
<td>~46.0 - 47.0 (As 3d)</td>
</tr>
<tr>
<td>Potassium Sulfide (K₂S)</td>
<td>~161.0 - 163.0</td>
<td>~292.0 - 294.0 (K 2p)</td>
</tr>
<tr>
<td>Iron Sulfide (FeS)</td>
<td>~161.0 - 163.0</td>
<td>~706.0 - 709.0 (Fe 2p)</td>
</tr>
<tr>
<td>Zinc Sulfide (ZnS)</td>
<td>~161.5 - 163.5</td>
<td>~1022.0 - 1024.0 (Zn 2p)</td>
</tr>
<tr>
<td>Copper Sulfide (Cu₂S)</td>
<td>~161.0 - 163.0</td>
<td>~932.0 - 935.0 (Cu 2p)</td>
</tr>
<tr>
<td>Lead Sulfide (PbS)</td>
<td>~162.0 - 164.0</td>
<td>~137.0 - 140.0 (Pb 4f)</td>
</tr>
<tr>
<td>Nickel Sulfide (Ni₂S₃)</td>
<td>~161.0 - 164.0</td>
<td>~853.0 - 855.0 (Ni 2p)</td>
</tr>
<tr>
<td>Molybdenum Disulfide (MoS₂)</td>
<td>~161.0 - 143.0</td>
<td>~228.0 - 230.0 (Mo 3d)</td>
</tr>
<tr>
<td>Calcium Sulfide (CaS)</td>
<td>~161.0 - 163.0</td>
<td>~345.0 - 349.0 (Ca 2p)</td>
</tr>
<tr>
<td>Lanthanum Sulfide (La₂S₃)</td>
<td>~160.0 - 163.0</td>
<td>~826.0 - 834.0 (La 3d)</td>
</tr>
</tbody>
</table>

While details on XPS as a surface characterization technique can be found in standard textbooks [136-139] and many review articles,[140-144] here we describe the use of XPS specifically targeting metal–sulfides and in particular, survey the use of XPS for CLS.
2.2 XPS Studies on Metal Sulfides

XPS of metal sulfides has been extensively reported in literature[1-30]. Table 4 provides a list of sulfides that have been evaluated using XPS. The primary elements – sulfur and the cation are evaluated for their BE positions. This information is presented in the form of a “fine spectrum” i.e., localized regions in the spectrum which contain high resolution data on the BE of electrons ejected from a specific orbital within an element. For sulfur the 2p 3/2 orbital is reported to vary from 160.5 eV to 164.0 eV.

To understand the position and placement of sulfur BE, it is important to note the characteristics of the sulfur XPS fine spectrum. The sulfur BE has a spin-orbit splitting (SOS) due to ionization which causes a characteristic split S 2p_{3/2} and 2p_{1/2}, separated by 1.18 eV. A typical fine spectrum of S 2p obtained from elemental sulfur and detailing the above features are shown in Figure 3A.[136] The 2p3/2 is positioned at 164.0 eV. The area ratio of the 2p3/2 and 2p1/2 is 2:1[145]. On the other hand, for cations the primary BE peaks vary depending on factors such as sensitivity and overlap with other BE’s.

The typical variability in sulfur BE is shown in Figure 3B. Elemental sulfur has a narrow BE reported between 163.5 – 164.0 eV. In sulfides, the peak position is attributed to changes in the bonding character of the sulfur with cations[136].

![Figure 3](image-url)
Thus, highly electropositive elements such as Li, tend to donate their electrons to the electronegative sulfur, raising the ionic character of the metal-sulfur bond. The excess electrons in the sulfur results in the lowering of the BE for electrons in a sulfur bonded to Li, as compared to elemental S. Thus, a Li$_2$S compound has a sulfur BE between 160.5 – 162.5 eV. On the contrary, metals with lower electropositivity have higher covalent character in the cation-sulfur bond and, as a result, the BE’s tend to be higher. A compound like MoS$_2$ has a sulfur BE from 161.0 – 163.0 eV.

The variability in the sulfur BE position can be further highlighted by studying sulfur bonding to other highly electronegative elements. For example, it can be seen that adding oxygen (a competing anion and with a higher electronegativity) to the compounds dramatically shifts the sulfur BE to a higher value. Indeed for (SO$_3$)$_2^-$ and (SO$_4$)$_2^-$ the BE shifts are between 3 – 10 eV. Along the same lines, fluorine, which has one of the highest electronegativities, can cause the sulfur BE to ~ +15 eV. Thus, studying the sulfur fine spectra can yield important information on the bonding environment of sulfides and can be a valuable tool to characterize the structure and purity of metal sulfides.

2.3 XPS Studies on CaLa$_2$S$_4$

The references for the XPS characterization of CLS come from three distinct sources. The first recorded source is by Kaupo Kukli et. al., but does not contain the spectra from CLS but the spectra of γ-La$_2$S$_3$, as seen in Figure 4. The article is on the deposition of La$_2$S$_3$ by atomic layer epitaxy in the form of thin films of γ-La$_2$S$_3$[108]. The second reference comes from Peisen Li et. al. Hot-pressed optical ceramic of γ-La$_2$S$_3$ doped with calcium in various ratios are fabricated[110]. The fine spectra shown were for La3d, S2p, and O1s as seen in Figure 4. The work of Subbaiah Muthu Prabhu et. al. analyses of CLS 50% on graphene oxide mixture for trapping arsenite and arsenate[109]. The XPS data shown in this article is of the fine spectra for C1s, O1s, S2p, La3d, Ca2p, and As3d, as seen in Figure 4. The Figures represent the spectra
after adsorption of arsenic and arsenite with no pre-characterization of the materials before testing.

While this article does provide all of the elements in fine spectra scans, it does not provide a pre-treatment scan that would give more insight into the bonding of the CLS 50% on graphene oxide.
Figure 4: XPS Spectra Graphs from Literature (A) Lanthanum 3d XPS spectra of La$_2$S$_3$ film (1) as deposited without any cleaning, (2) as-deposited measured after sputtering, and (3) annealed, without any cleaning. The film was grown at 500$^\circ$C a soda lime glass substrate covered by Al$_2$O$_3$, figure adapted from Kauku Kukli et al. 1998 (B) XPS spectra of La3d (4), S (5), O (7) in the pellet sintered at 1100$^\circ$C for 1 hr. and corresponding powders of CLS. Figure adapted from Peisen Li et al. 2010, (C) XPS spectra of CLS 50% on graphene oxide nanohybrid after adsorption of arsenate and arsenite: (7) C 1s, (8) O 1s, (9) S2p, (10) La 3d, (11) Ca 2p, and (12) As 3d figure adapted from Subbaiah Muthu Prabhu et al. 2019[108-110]

The methods, results, and conclusions through literature varied greatly between the three articles, yet the articles did have a common theme that oxygen was more than just surface contamination[108-110]. XPS was used to study the samples' contamination level and chemical state.

The measurements were done; similarly, the parameters are listed in Table 5. A common excitation source of monochromated Al Ka radiation was used. However, the pass energy, if reported, varied from reference to reference. For example, Kauku Kukli et. al. stated using 0.5 eV step and 80 eV analyser pass energy[108]. The sample preparation varies from author to author but is very similar in that the sample
was fit onto a holder and taped with carbon or ultra-high vacuum (UHV) tape[108-110]. The chamber was then brought to a standard operating vacuum. The details on some articles did state the use of charge compensation, while others did not add that level of detail. Still, as the material is insulating, they need some charge compensation. In the methods, two articles stated that overcompensation of the charge resulted in a shift to the higher BE that needed to be corrected[108, 110]. While only one article included depth profiling in the methods, the results did not indicate that the depth profile and the time the depth profile was conducted, differed. The stated parameter used argon ions at 4.5 KeV and with a beam current of 20 mA[108].

Table 5: XPS Parameters for literature[108-110]

<table>
<thead>
<tr>
<th>XPS Parameters</th>
<th>Article</th>
<th>Article</th>
<th>Article</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kaupo Kukli et. al.</td>
<td>Peisen Li et. al.</td>
<td>Subbaiha Muthu Prabhu et. al.</td>
</tr>
<tr>
<td>Radiation Source</td>
<td>Monochromated Al Ka</td>
<td>monochromated Al Ka</td>
<td>Monochromated Al Ka</td>
</tr>
<tr>
<td>Step Size</td>
<td>0.5 eV</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Pass Energy</td>
<td>80 eV</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Sample Adhesion</td>
<td>UHV</td>
<td>Carbon Tape</td>
<td>Unknown</td>
</tr>
<tr>
<td>Depth Profile</td>
<td>Ar+ 4.5KeV and 20mA</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Charge Compensation</td>
<td>Yes</td>
<td>Yes</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

2.4 Conclusions

In the literature review, we have surveyed the literature surrounding CLS. There is extensive body of knowledge on CLS’s physical, chemical, electrical, and optical properties. With the current body of knowledge, we have also identified a technique underutilized in the characterization process that can identify unique properties in the CLS system. We have identified the need for understanding XPS as a system and tool for characterization and its limitations.
The key finding from the literature is that CLS exhibits excellent thermal stability, high thermal conductivity $\sim 1.7$ W/m.K, has a high hardness value compared to other IR optics in the range of 570-736 Kg/mm$^2$ on the Knoop hardness scale, and is resistant to various chemical agents and water, making it a promising material for demanding applications. Its phase stability shows a continuous solid solution between CaS and La$_2$S$_3$, up to 50:50. The phase diagram also indicates that the cation vacancies can be reduced for additional stability with doping.

XPS offers valuable insights into the bonding environment and valence states of elements, which are crucial for understanding the chemistry of CLS. The literature on XPS of metal sulfides has given the foundational guidelines that will be the basis for characterizing CLS. The information on core electron binding energies offers insights into the bonding states of sulfur and cations in metal sulfides, aiding structural analysis.

From the existing CLS literature on XPS, there is a need for a more comprehensive collection of XPS data. The available data only provides a few spectra and BE notation without a complete list of the fine spectra or quantification. There is a need for more extensive XPS characterization to understand CLS thoroughly. Overall, the characterization of CLS by XPS would benefit from having standard procedures, additional documentation of survey spectra along with a wider breadth of fine spectra, the addition of peaks for common contaminants, and the post-processing of fine spectra to produce quality peak assignments and quantifications for stoichiometry.
CHAPTER 3: EQUIPMENT AND METHODS

3.1 Equipment

3.1.1 Thermo Scientific ESCALAB Xi+

Throughout this study, the Thermo Scientific ESCALAB Xi+ was used for collecting photoelectron spectra and for argon ion milling on the surface of powders and ceramics. The system parts, components, and software are shown in Figure 5. The following information on the ESCALAB Xi+ system parameters is consistent for all spectra shown unless otherwise specified.

HARDWARE PARAMETERS: The analyzer type is a spherical sector with a detector type of channeltron having 6 detector elements, as seen in Table 6. The standard parameters configured for the spectrometer are constant pass energy with an electron throughput calculated from a polynomial fit.

The excitation source used Al Kα monochromatic at 1486.6 eV at 200 W with a beam size of 650 x 650 μm² with the signal in a single channel direction, as seen in Table 6. The instrumentation geometry is at an incident angle of 58° also known as the source-to-analyzer angle, as seen in Table 6. While the specimen electron take-off angle is 90° and its acceptance angle from the analyzer axis is 45°, these geometrical parameters allow for the capture and analysis of both the fine and survey spectra during acquisition as seen in Table 6. The systems ion gun is a Thermo Scientific EX03 Ion gun system with an energy setting range between 500 eV and 4000 eV, dependent on sample and sputter duration, as seen in Table 6. The ion gun is set to a current of 0.02 mA with a biased stage, and the sputtering species is Ar⁺ as seen in Table 6. The spot size unrastered is 500 μm while the raster size is 4500 x 4500 μm² with an angle of incident of 40° as seen in Table 6. The azimuthal angle is at 270° (reference plan for azimuth is true north measured at 0° moving clockwise on a 360° circle east is at 90° south is at 180° and west is 270°) as seen in Table 6. These parameters only correspond to the ion-cleaning methods used in powder
and ceramic sample cleaning, with details on evaluating sputtering to remove surface carbon (Appendix B).

**Table 6:** XPS system parameters

<table>
<thead>
<tr>
<th>Chamber Conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. During Analysis:</td>
<td>300 K</td>
</tr>
<tr>
<td>Pressure During Analysis:</td>
<td>$5 \times 10^{-8}$ Pa</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Instrument Description</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer and Model:</td>
<td>Thermo Scientific ESCALAB Xi+</td>
</tr>
<tr>
<td>Analyzer Type:</td>
<td>Spherical sector</td>
</tr>
<tr>
<td>Detector:</td>
<td>Channeltron</td>
</tr>
<tr>
<td>Number of Detector Elements:</td>
<td>6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spectrometer</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyzer Mode:</td>
<td>Constant pass energy</td>
</tr>
<tr>
<td>Excitation Source:</td>
<td>Al Ka monochromatic</td>
</tr>
<tr>
<td>Source Energy:</td>
<td>1486.6 eV</td>
</tr>
<tr>
<td>Source Strength:</td>
<td>200 W</td>
</tr>
<tr>
<td>Source Beam Size:</td>
<td>$200 \times 200$ µm²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Geometry</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Incident Angle:</td>
<td>58°</td>
</tr>
<tr>
<td>Source-to-Analyzer Angle:</td>
<td>58°</td>
</tr>
<tr>
<td>Emission Angle:</td>
<td>0°</td>
</tr>
<tr>
<td>Specimen Azimuthal Angle:</td>
<td>90°</td>
</tr>
<tr>
<td>Acceptance Angle from Analyzer Axis:</td>
<td>45°</td>
</tr>
<tr>
<td>Analyzer Angular Acceptance Width:</td>
<td>$22.5° \times 22.5°$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ion Gun</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer and Model:</td>
<td>Thermo Scientific EX03 Ion Gun System</td>
</tr>
<tr>
<td>Energy:</td>
<td>500-4000 eV</td>
</tr>
<tr>
<td>Current:</td>
<td>0.02 mA</td>
</tr>
<tr>
<td>Time:</td>
<td>120s-1200s</td>
</tr>
<tr>
<td>Current Measurement Method:</td>
<td>Biased stage</td>
</tr>
<tr>
<td>Sputtering Species:</td>
<td>Ar⁺</td>
</tr>
<tr>
<td>Spot Size (un rastered):</td>
<td>500 µm</td>
</tr>
<tr>
<td>Raster Size:</td>
<td>$4500 \times 4500$ µm²</td>
</tr>
<tr>
<td>Incident Angle:</td>
<td>40°</td>
</tr>
<tr>
<td>Azimuthal Angle:</td>
<td>270°</td>
</tr>
</tbody>
</table>

All samples had charge compensation. This was achieved by an in-lens electrostatic electron flood source (1 eV, 100µA) and a dual beam low-energy electron and ion coaxial flood source (2 eV, 100µA). During the analysis, the temperature was approximately 300K at a pressure of $5 \times 10^{-8}$ Pa, as seen in Figure 5 B. Before spectrum collection, there was no pre-analysis beam exposure.
Figure 5: (A) Labeled illustration of rotatory XPS Instrument. (B) Schematic of vacuum for XPS chamber and anti-chamber rotatory ALD system. (image from Thermo Scientific 2017)[146] (C) Survey spectra as it is depicted from Advantage software.

SOFTWARE: Thermo Scientific Avantage software version 5.9902 sets all parameters for each experiment. The Avantage software runs all aspects of data collection and processing. The data analysis method starts with collecting and processing data through Avantage software. Figure 5C shows the survey spectra but can also be similarly done on any fine spectra. The processing begins with energy scale correction by binding energy scale being a reference to C 1s at 284.8 eV fine spectra pre- and post-sputter. The Peak shape and background method was done through Avantage software through the smart feature that uses the Shirley function to subtract the background from the peaks. The smart feature unitizes revised constraints that limit the background from having greater intensity than data from points in the collection region. Atomic percentages can quantify the data collected through the Avantage software. The software has built-in sensitivity factors in the database, and the peak library is ALWAG[147].
GENERAL PROCEDURE: The general process for loading samples is to load samples onto the stage if the solid load is attached with carbon tape if the sample is loaded into a powder well. Release the vacuum from the anti-chamber, and while pressure is coming down, take a picture of the sample holder at the computer workstation. When the vacuum is released, load the sample through the load lock door onto the sliding sample arm, close the load lock door, and pull a vacuum. The sample must hit a pressure of $5 \times 10^{-8}$ Pa before the gate valve to the analysis chamber can be opened, and the sample can be transferred to the XPS stage for evaluation.

3.1.2 Powder and Ceramic Custom Holder for ESCALAB Xi+ XPS

For this study, a custom sample holder was made at the University of Central Florida CECS Machine Shop. Brian Butkus designed the sample holder. The sample holder was modelled in Auto Cad 2021 software. All dimensions are listed in inches per machine shop guidelines for machining. The dimension of the holder is 1 and 8/10th inches long by 5.5/10th inches wide and 3/10th of an inch high. The features that attach the holder to the transfer arm and the XPS stage, as seen in Figures 6 A and C, are modelled from the dimension of a standard holder from Thermo Scientific ESCALAB Xi+. The sample holder powder wells are a depth of 2/32nd of an inch by 2/10th of an inch in diameter. There are 6 wells and one large cut-out. The cut-out dimensions are 1 inch wide long by 3/10th of an inch and a depth of 1/16th of an inch. This can be seen in Figure 6 B. The sample holder was used for all powder and ceramic samples unless otherwise specified in the results. Powders and ceramic coupon samples were mounted on a stainless-steel sample holder, shown in Figure 6.

The custom sample holder avoids using carbon tape on powder samples and allows for an even surface for spectral collection. The holder was designed to accommodate larger samples than standard sample holders. This holder enables spectra to be collected from intact ceramic coupons. The XPS stage system
reaches the height upper limits with the standard holder; this causes the Z height requirements not to be within spec for collection with intact ceramic coupons.

![Figure 6: Powder and Ceramic Custom Sample Holder.](image)

(A) Front view of sample holder loads onto sample holder control arm. (B) Top view of the sample holder with powders sample wells and cut out for ceramic coupons. (C) Back view of sample holder that loads onto sample stage. (D) Side view of the sample holder and view of the cut-out.

The custom sample holder was designed to reduce carbon contamination from carbon tape on powder samples and provide a consistent surface for the powders. The cut-out was designed to hold a standard ceramic coupon to keep the ceramic mounted safely and within height limitation. The overall design of the holder was made to allow for optimal sample collection parameters and a consistent powder sampling method that allowed for multiple powders to be sampled in a single session. Sample holder is composed of 316 stainless steel as per material specs of other holders well spacing and depth sizing to reduce cross contamination with acquired data.

**7.1 3.2 Methods**
3.2.1 Sample Preparation

**Powder preparation for analysis by XPS.** Powers are stored in an inert atmosphere glove box after receiving from commercial manufacturers until a small vial 1 gram of powder is aliquoted into a glass vial to be brought to the XPS room for mounting, image capture, and loading into the XPS anti-chamber for being brought down to base pressure. The powders are scooped from the vial and placed into a well in the sample holder. The time from removal from the vacuum pouch to loading and pulling a vacuum in the anti-chamber is less than 1 minute of exposure to the atmosphere. Powder samples are pumped in the load lock to a 5 x 10⁻⁸ Pa pressure before being transferred into the XPS acquisition chamber.

**Green body preparation for analysis by XPS.** Green body samples are powder samples pressed into coupons and loaded into a 3/4” stainless steel die compressed uniaxially under an applied force of 3 tons while under vacuum. This process was completed in an inert atmosphere, and the samples were in vacuum bags stored in an inert atmosphere glove box until they were brought for XPS analysis. Green bodies are brought to the XPS room for mounting, image capture, and loading into the XPS anti-chamber for being brought down to base pressure. The green body is removed from the vacuum pouch and placed on the sample holder on carbon tape. The time from removal from the vacuum pouch to loading and pulling a vacuum in the anti-chamber is less than 1 minute of exposure to the atmosphere. Powder samples are pumped in the load lock to a 5 x 10⁻⁸ Pa pressure before being transferred into the XPS acquisition chamber.

**Ceramic preparation for XPS analysis.** Ceramics are stored in an ambient atmosphere after hot-pressing or hot-pressing and hot isostatic pressing (HIP’ing) after polishing in plastic sample bags until the ceramic cleaning process is done directly before being brought to the XPS room for mounting, image capture, and loading into the XPS anti-chamber for being brought down to base pressure. The ceramics
are placed on carbon tape on the sample holder to maintain stability during loading. The time from cleaning to loading and pulling the vacuum in the anti-chamber is less than 5 minutes of exposure to the atmosphere. The ceramics are stored in covered dishes during the transfer process from lab cleaning until mounting on the sample holder. Ceramics samples are pumped in the load lock to a 5x 10⁻⁸ Pa pressure before being transferred into the XPS acquisition chamber.

**Ceramic ambient fracture preparation for XPS analysis.** Ceramic ambient fractures are stored in the ambient atmosphere after hot-pressing or Hot-pressing and HIP’ing after polishing in plastic sample bags until they are fractured and mounted with a cross-section facing up on the sample holder. No ceramic cleaning step was done before being brought to the XPS room for mounting, image capture, and loading into the XPS anti-chamber for being brought down to base pressure. The ceramics are placed on carbon tape on the sample holder to maintain stability during loading. The time from fracture to pulling a vacuum in an anti-chamber is less than 48 hours of exposure to the atmosphere. The ceramics are stored in covered dishes during the transfer process from the lab until mounting on the sample holder. Ceramics samples are pumped in the load lock to a 5x 10⁻⁸ Pa pressure before being transferred into the XPS acquisition chamber.

**Ceramic inert atmosphere fracture preparation for XPS analysis.** Ceramic inert atmosphere fracture preparation is stored in the ambient atmosphere after hot-pressing or Hot-pressing and HIP’ing after polishing in plastic sample bags until they are returned to the inert atmosphere glove box with XPS portable transfer chamber. The sample was fractured and mounted with a cross-section facing up on the sample holder. The ceramics are placed on carbon tape on the sample holder (a more miniature sample holder is used; the custom holder will not fit in the transfer chamber) to maintain stability during loading. The sample was loaded in an inert atmosphere glove box and was brought to the XPS system. The XPS antechamber was brought to ambient pressure, and the transfer chamber was attached to the
load lock see Figure 7. The XPS anti-chamber was then brought under vacuum before the transfer chamber was opened and loaded into the anti-chamber. There was No ceramic cleaning step or sample picture on the sample holder, as it was in the transfer chamber. The time from fracture to pulling a vacuum in the anti-chamber is less than 15 minutes, yet an inert atmosphere is maintained in the transfer chamber. Ceramics samples are pumped in the load lock to a $5 \times 10^{-8}$ Pa pressure before being transferred into the XPS acquisition chamber.

**Figure 7**: Inert Atmosphere Fracture of Ceramic (A) Inert Atmosphere Glove Box for fracture (B) XPS Portable Sample Transfer Chamber (C) ESCALAB Xi+ XPS by Thermo Scientific

### 3.2.2 Ceramic Cleaning Process

Sonication based cleaning of ceramics before XPS analysis. Samples are placed in a beaker of 100 ml hexane > 85% Optima Fisher Chemical that covers the sample's surface and is sonicated for 5 minutes. The sample was taken out of hexane and placed in a beaker of 100 ml of IPA 70% Fisher Chemical, and then sonication was repeated for an additional 5 minutes. The sample is removed from the IPA and placed in a 100 ml beaker of DI Water for the final sonication for 5 minutes. The sample is removed from the DI Water, dried with compressed HEPA-filtered air, and placed in a closed dish to be brought to XPS. Ceramics were visually inspected in an optical microscope before and after cleaning with no signs of visual damage.
3.2.3 Argon ion Sputtering Process for Cleaning Powder and Ceramics

Surface levels of nitrogen, oxygen, and carbon naturally contaminate all surfaces exposed to the atmosphere. This surface-level contamination can significantly impact the stoichiometry of spectral calculation for atomic percentage by XPS analysis since XPS is a surface-level technique that only penetrates the 1-10 nm of a sample surface for analysis. During this thesis, the argon ion sputtering (Ar⁺) was done with three distanced recipes for data collection. For the collection of spectra of powder samples, the process was to collect spectra before sputtering and then sputter for 8 minutes. To determine sputter timing and intensity, a series of experiments on duration and power was run to find at what lever the carbon content was diminished to baseline for powders (Appendix B). The information on sputtering studies is in the appendices. The system ion gun is a Thermo Scientific EX03 Ion gun system with an energy setting of 500 eV.

For the collection of spectra of ceramic samples, the process was to collect spectra before sputtering and then sputter for 20 minutes. As with the powder sputtering process, similar experiments were conducted to determine sputter timing and intensity; a series of experiments on duration and power was run to find at what lever the carbon content was diminished to baseline for ceramics. The information on sputtering studies is in the appendices. The ion gun settings for ceramics were with an energy setting of 500 eV a separate protocol was used for fracture cross-sections.

The collection spectra of ceramic fracture cross-section samples were collected spectra before sputtering and then sputtering for 2 minutes. Unlike the ceramics' surface sputtering process, no experiments were run to determine sputter timing and intensity; a standard sputtering protocol was used. The ion gun settings for ceramics fracture cross-section had an energy setting of 4000 eV.
3.2.4 Survey Spectrum Collection

Survey Spectrum collection was done with the same parameters for all samples. The spectrum was collected from 0-1361 eV. The pass energy for the survey was set to 150 eV with an analyzer resolution of 1.000 eV. The number of scans would vary between 3 and 5 per sample collection. The effective detector for survey scans was set at 25.441 eV. The total number of energy steps for each survey was 1361.

3.2.5 Fine Spectra Collection

Fine Spectrum collection was done with the same parameters for all samples. The fine spectrum collected for this thesis is represented in Table 7. The pass energy for all fine spectrums was set to 20eV with an analyzer resolution of 0.100eV. The number of scans would vary between 10 and 45 per sample collection. The effective detector for fine spectrum scans was set at 3.392 eV. The total number of energy steps for each fine spectrum equals the width of the spectrum divided by the analyzer resolution.
Table 7: Fine spectrum collection element transition from the start to the end of the collection in eV.

<table>
<thead>
<tr>
<th>Element/Transition</th>
<th>Spectrum Start in eV</th>
<th>Spectrum End in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>La4d</td>
<td>93</td>
<td>116</td>
</tr>
<tr>
<td>S2p</td>
<td>154</td>
<td>185</td>
</tr>
<tr>
<td>La4p</td>
<td>188</td>
<td>221</td>
</tr>
<tr>
<td>S2s</td>
<td>219</td>
<td>237</td>
</tr>
<tr>
<td>La4s</td>
<td>268</td>
<td>281</td>
</tr>
<tr>
<td>C1s</td>
<td>280</td>
<td>300</td>
</tr>
<tr>
<td>Ca2p</td>
<td>341</td>
<td>365</td>
</tr>
<tr>
<td>Ca2s</td>
<td>430</td>
<td>446</td>
</tr>
<tr>
<td>O1s</td>
<td>521</td>
<td>540</td>
</tr>
<tr>
<td>La3d</td>
<td>825</td>
<td>881</td>
</tr>
<tr>
<td>Na1s</td>
<td>1061</td>
<td>1086</td>
</tr>
<tr>
<td>La3p3/2</td>
<td>1119</td>
<td>1141</td>
</tr>
<tr>
<td>Eu3d</td>
<td>1121</td>
<td>1161</td>
</tr>
<tr>
<td>La3p1/2</td>
<td>1195</td>
<td>1221</td>
</tr>
</tbody>
</table>

3.2.6 XPS Calibration Sample Preparation

Powder preparation for binary metal sulfide mixtures from 100%-50%. Powders were stored in an inert atmosphere glove box after being received from the manufacturer. Powders of Na: La$_2$S$_3$ (99.9%) and Eu: CaS (99.9%) were purchased from Lorad Corporation. Simple mixtures of these powders were prepared across the entire range of solid solutions between La$_2$S$_3$ and CaS (0 mol % CaS to 50 mol % CaS). Powder mixtures were loaded into a 3/4” stainless steel die compressed uniaxially under an applied force of 3 tons while under vacuum.
CHAPTER 4: RESULTS – CALCIUM SULFIDE CHARACTERIZATION BY XPS

4.1 Background Calcium Sulfide Powder

CLS is a ternary sulfide with a complex bonding environment. The Ca ion is expected to either, occupy the La vacancies or, substitute the La ion. In this way, both Ca and La bond to the sulfur (S). Since the parent lattice for 10:90 CaS:La$_2$S$_3$ (i.e., 10:90 CLS) is the cubic La$_2$S$_3$ structure (which in turn is a Th$_3$P$_4$ structure), there are ~11 at % of La vacancies present in the Ca free structure, necessary to match the sites to the stoichiometry. Thus, the nature and location of Ca addition is important to understand. To disambiguate any effects of the parent material (i.e., La$_2$S$_3$), it is first prudent to understand the bonding environment of pure CaS. By comparing XPS fine spectra of CLS (which will contain the structural unit “Ca-S”) and pure CaS, differences in the bonding environment can be potentially unraveled.

XPS was performed on as-received CaS powder (98.0%), doped with Europium (Eu) 2.0% wt%. The scans provide photoelectron spectroscopy investigation data for CaS to help identify sulfide compounds. This chapter includes charge-corrected scans for the survey along with S 2s, S 2p, O 1s, Eu 3d, Ca 2s, Ca 2p, and C 1s surface photoelectron signals.

While CLS does not contain europium, we must note why we chose this compound for evaluation. The same manufacturer produced the CaS studied as the studied CLS powders that are transformed into ceramics. CaS has historically been used as a phosphor. CaS doped with Europium (Eu) is a typical red phosphor with an emission at 645 nm[148]. Along with the enhanced color emission, doping increases the material’s thermal stability. The Eu doping should not affect the fine spectra for calcium or sulfur and still give a good representation of the bonding environment and peak positions for later comparison and calibration. Other historical uses include the production of pharmaceutical sulfur-based drugs. However, new interest has broadened the uses and research in electronics, optical glasses, and ceramics, along
with its use in catalysis. Examples of applications in each area include nanocrystals for LED production, broadband glasses, and ceramic application (i.e., U.V. and IR glass and ceramics) [148-150]. Catalysis research includes using CaS for the removal of heavy metals from groundwater[151] and the conversion of drywall (gypsum board) to sulfur[152]. While some reports include XPS of CaS[153, 154], the data included in the reports have missing survey spectra and do not identify peaks in the fine spectra.

Herein, we present charge-corrected scans for the survey spectrum, along with S 2s, S 2p, Ca 2s, Ca 2p, S 2s, S 2p, Eu 3d, O 1s, and C 1s surface photoelectron signals. The peak fitting aims to identify the bonding states of CaS. Atomic % are also calculated and additional constituent elements and non-trace level impurities are reported.

4.2 Results XPS of Calcium Sulfide Powder

CaS powder analysis by XPS was conducted on loose powder attached to carbon tape. The sample was in-situ processed by Ar+ ion sputtering at 4000 eV for 120 seconds prior to collecting spectra on a single spot of 650 μm. For additional information on preparation and collections specification, please refer to the materials and methods section. A survey spectrum was taken to identify elements present in the sample, which can be seen in Figure 8. The survey scan was taken from 0 to 1300 eV. After scans were taken and before analysis, the survey spectrum was calibrated to the C 1s to 284.8 eV binding energy. The survey was analyzed for the unique peaks because each element has a unique binding energy that can be identified. From the survey, we found peaks that could be identified as calcium, sulfur, europium, carbon, and oxygen. While it is significant to point out that XPS is a surface technique that probes the surface 1-10 nm in depth. The surface of a material is not always representative of the bulk. If the surface of the powder is highly contaminated with carbon and oxygen, that material can be brought into the bulk of materials produced from this powder.
High-resolution scans, also known as fine spectra scans, were taken for sulfur and calcium and can be seen as S 2s, S 2p, Ca 2s, and Ca 2p in Figure 9. Additionally, fine spectra were collected for Eu 3d, O 1s, and C 1s as minor elements and contaminants that can also be seen in Figure 9 as part of the elemental lines for europium, carbon, and oxygen.

**Figure 8**: XPS Survey spectrum of as received Calcium Sulfide powder.
Figure 9: XPS fine spectrum of as received Calcium Sulfide powder (A) S 2s fine spectra, (B) S 2p fine spectra, (C) Ca 2s fine spectra, (D) Ca 2p fine spectra, (E) Eu 3d fine spectra, (F) C 1s fine spectra and (G) O 1s fine spectra.

From Figure 9, we can see the primary peak positions and shapes of each of the elements. With Thermo Scientific Advantage software, we can calculate the peak positions and atomic parentage for each of the elementals. That is done by dividing the peak area by the sensitivity factor over the sum of all the element's peak area divided by the sensitivity factors (atomic percentage eq.1):

\[ n_i = \frac{I_{ij}S_i}{\sum I_jS_i} \]  

(1)

In the atomic percentage calculation, the variable \( n_i \) represents the atomic percentage of element \( i \) in the sample. This is calculated using the peak area of element \( i \) (\( I_{ij} \)), where \( j \) represents the peak or element \( i \) and the sensitivity factor of element \( i \) (\( S_i \)), which accounts for differences in the XPS sensitivity of different elements. The sum of peak areas of all elements in the sample (\( \sum I_i \)) is also included in the denominator to normalize the calculation. The sensitivity factor (\( S_i \)) is determined experimentally using a known reference sample and represents the efficiency of the XPS instrument in detecting a given element. The peak area (\( I_{ij} \)) is obtained by integrating the XPS spectrum for the element \( i \) and represents the total number of electrons emitted from that element.
This formula makes it possible to accurately determine the atomic percentages of different elements in a sample, which is vital for understanding the material's chemical composition and electronic structure.

Along with the peak energy and atomic percentage, we have the full-width half maximum (FWHM) in eV, and the peak is in eV by counts per second for ease of use. This information can be seen in Table 8. From Figure 9, the seven fine spectra bonding states can be identified by their binding energy peak position and peak shape visually and numerically by FWHM listed in Table 8.

**Table 8: Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor, Concentration (at.%), and Peak Assignment.**

<table>
<thead>
<tr>
<th>Figure Label</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV x cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at.%)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B)</td>
<td>S2s</td>
<td>224.54</td>
<td>2.63</td>
<td>13864.86</td>
<td>1.294</td>
<td>...</td>
<td>CaS</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p</td>
<td>160.78</td>
<td>2.45</td>
<td>21373.11</td>
<td>1.681</td>
<td>32.7</td>
<td>CaS</td>
</tr>
<tr>
<td>(G)</td>
<td>C1s</td>
<td>530.89</td>
<td>2.31</td>
<td>15477.98</td>
<td>2.881</td>
<td>16.96</td>
<td>Metal Oxide/Carbonates</td>
</tr>
<tr>
<td>(E)</td>
<td>Eu3d3/2</td>
<td>1133.83</td>
<td>3.56</td>
<td>12820.81</td>
<td>48.796</td>
<td>1.18</td>
<td>Eu</td>
</tr>
<tr>
<td>(C)</td>
<td>Ca2s</td>
<td>437.46</td>
<td>3.3</td>
<td>17085.82</td>
<td>2.106</td>
<td>...</td>
<td>CaS, CaO, CaCO3</td>
</tr>
<tr>
<td>(D)</td>
<td>Ca2p</td>
<td>345.78</td>
<td>1.52</td>
<td>57501.87</td>
<td>5.97</td>
<td>28.86</td>
<td>CaS, CaO, CaCO3</td>
</tr>
<tr>
<td>(F)</td>
<td>C1s</td>
<td>284.64</td>
<td>2.22</td>
<td>6873.88</td>
<td>1</td>
<td>20.3</td>
<td>C-C, C-H, Carbonates</td>
</tr>
</tbody>
</table>

Spectrum ID (A) sulfur S 2s is at binding energy 224.54, corresponding to a metal sulfide [136], in this case, CaS. Spectrum ID (D) calcium Ca 2p contains 3/2 and ½ peaks. For identification purposes, the 3/2 peak is used with a B.E. of 345.78, corresponding to CaS. This spectrum has split peaks and plasmon loss peaks. This information shows that additional states are possible but not seen from the single peak positions. It can also be identified as containing calcium oxide or carbonate by looking at the spectrum I.D. (F) and (G) the peaks for Carbon C 1s and Oxygen O 1s with peak shapes that indicate carbonate and metal oxide but will require deconvolution to identify the additional bonding states. The prominent peak
for carbon is at 284.64, which indicates carbon-carbon bonding or the advantages of carbon. In comparison, oxygen B.E. peak is at 530.89 and can be representative of hydroxides, carbonates, and metal oxides. Using the Advantage software by Thermo Scientific, deconvolution of fine spectra (A-F) was done and can be seen in Figure 10 and corresponding deconvoluted features in Table 9.
Figure 10: Deconvoluted XPS fine spectrum of as received Calcium Sulfide powder (A) S 2s fine spectra, (B) S 2p fine spectra, (C) Ca 2s fine spectra, (D) Ca 2p fine spectra, (E) Eu 3d fine spectra, (F) C 1s fine spectra, (G) O 1s fine spectra, and (F) Peak Key for (A-G).
Table 9: Deconvoluted Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor, Concentration (at.%), and Peak Assignment.

<table>
<thead>
<tr>
<th>Figure Label</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV x cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at.%)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B)</td>
<td>S 2p½/2 III</td>
<td>160.81</td>
<td>1.76</td>
<td>9528.09</td>
<td>1.245</td>
<td>32.7</td>
<td>CaS</td>
</tr>
<tr>
<td>(B)</td>
<td>S 2p½/2 III</td>
<td>161.95</td>
<td>1.76</td>
<td>4867.05</td>
<td>0.636</td>
<td>...</td>
<td>CaS</td>
</tr>
<tr>
<td>(B)</td>
<td>S 2p½/2 IV</td>
<td>159.93</td>
<td>1.3</td>
<td>4681.39</td>
<td>1.245</td>
<td>...</td>
<td>CaS</td>
</tr>
<tr>
<td>(B)</td>
<td>S 2p½/2 IV</td>
<td>161.03</td>
<td>1.3</td>
<td>2391.31</td>
<td>0.636</td>
<td>...</td>
<td>CaS</td>
</tr>
<tr>
<td>(A)</td>
<td>S 2s I</td>
<td>224.39</td>
<td>2.52</td>
<td>8485</td>
<td>1.294</td>
<td>...</td>
<td>CaS</td>
</tr>
<tr>
<td>(A)</td>
<td>S 2s II</td>
<td>225.03</td>
<td>3.18</td>
<td>5340.33</td>
<td>1.294</td>
<td>...</td>
<td>CaS</td>
</tr>
<tr>
<td>(G)</td>
<td>O 1s XIX</td>
<td>530.84</td>
<td>2.77</td>
<td>15308.96</td>
<td>2.881</td>
<td>16.96</td>
<td>Hydroxides</td>
</tr>
<tr>
<td>(G)</td>
<td>O 1s XX</td>
<td>527.69</td>
<td>1</td>
<td>367.44</td>
<td>2.881</td>
<td>...</td>
<td>Metal Oxide/Carbonate</td>
</tr>
<tr>
<td>(E)</td>
<td>Eu 3d½/2 X</td>
<td>1154.36</td>
<td>3.05</td>
<td>1798.38</td>
<td>80.59</td>
<td>...</td>
<td>Eu</td>
</tr>
<tr>
<td>(E)</td>
<td>Eu 3d½/2 X</td>
<td>1152.17</td>
<td>2.3</td>
<td>877.43</td>
<td>80.59</td>
<td>...</td>
<td>Eu</td>
</tr>
<tr>
<td>(E)</td>
<td>Eu3d Multiplet XIX</td>
<td>1141.49</td>
<td>2.91</td>
<td>650.89</td>
<td>80.59</td>
<td>...</td>
<td>Eu</td>
</tr>
<tr>
<td>(E)</td>
<td>Eu 3d½/2 XII</td>
<td>1134.13</td>
<td>3.37</td>
<td>8561.26</td>
<td>80.59</td>
<td>1.18</td>
<td>Eu</td>
</tr>
<tr>
<td>(E)</td>
<td>Eu 3d½/2 XIV</td>
<td>1124.67</td>
<td>3.37</td>
<td>2776.41</td>
<td>80.59</td>
<td>...</td>
<td>Eu</td>
</tr>
<tr>
<td>(E)</td>
<td>Eu 3d½/2 XV</td>
<td>1131.15</td>
<td>3.37</td>
<td>1625.38</td>
<td>80.59</td>
<td>...</td>
<td>Eu</td>
</tr>
<tr>
<td>(E)</td>
<td>Eu 3d½/2 XVI</td>
<td>1122.85</td>
<td>1.63</td>
<td>676.36</td>
<td>80.59</td>
<td>...</td>
<td>Eu</td>
</tr>
<tr>
<td>(C)</td>
<td>Ca 2s V</td>
<td>437.4</td>
<td>3.37</td>
<td>16713.92</td>
<td>2.106</td>
<td>...</td>
<td>CaS, CaO, CaCO3</td>
</tr>
<tr>
<td>(C)</td>
<td>Ca 2s VI</td>
<td>434.19</td>
<td>2.7</td>
<td>1261.81</td>
<td>2.106</td>
<td>...</td>
<td>CaS, CaO, CaCO3</td>
</tr>
<tr>
<td>(D)</td>
<td>Ca 2p½/2 VII</td>
<td>345.86</td>
<td>1.65</td>
<td>33134.52</td>
<td>3.944</td>
<td>28.86</td>
<td>CaS, CaO, CaCO3</td>
</tr>
<tr>
<td>(D)</td>
<td>Ca 2p½/2 VIII</td>
<td>345.59</td>
<td>0.85</td>
<td>3835.01</td>
<td>3.944</td>
<td>...</td>
<td>CaS, CaO, CaCO3</td>
</tr>
<tr>
<td>(D)</td>
<td>Ca 2p1/2 VI</td>
<td>349.46</td>
<td>1.65</td>
<td>17012.35</td>
<td>2.027</td>
<td>...</td>
<td>CaS, CaO, CaCO3</td>
</tr>
<tr>
<td>(D)</td>
<td>Ca 2p1/2 VII</td>
<td>348.95</td>
<td>0.85</td>
<td>1969.02</td>
<td>2.027</td>
<td>...</td>
<td>CaS, CaO, CaCO3</td>
</tr>
<tr>
<td>(D)</td>
<td>Ca 2p Plasmon IX</td>
<td>352.78</td>
<td>1.21</td>
<td>1954.63</td>
<td>5.97</td>
<td>...</td>
<td>CaS, CaO, CaCO3</td>
</tr>
<tr>
<td>(D)</td>
<td>Ca 2p Plasmon IX</td>
<td>356.36</td>
<td>1.6</td>
<td>1659.86</td>
<td>5.97</td>
<td>...</td>
<td>CaS, CaO, CaCO3</td>
</tr>
<tr>
<td>(F)</td>
<td>C 1s XVII</td>
<td>284.71</td>
<td>2.29</td>
<td>5945.54</td>
<td>1</td>
<td>20.3</td>
<td>Carbon-Carbon</td>
</tr>
<tr>
<td>(F)</td>
<td>C 1s XVIII</td>
<td>288.91</td>
<td>3.13</td>
<td>1051.87</td>
<td>1</td>
<td>...</td>
<td>O-C=O</td>
</tr>
</tbody>
</table>

With the deconvoluted fine spectra, we now see that sulfur in Figure 10 (A) and (B) shows two distinct bonding states. The procedure for deconvolution using Avantage® software is illustrated in Appendix C.

In Figure 10 (B), the sulfur 2p fine spectrum, the single peak from Figure 9 (B), is deconvoluted to show two sets of overlapping 3/2 and ½ peaks. Looking at Table 9, the primary 3/2 peak is at 160.81, and the secondary 3/2 peak is at 159.93. This shows that sulfur has two distinct bonding environments the metal sulfide at the lower binding energy and the poly sulfide at the higher binding energy [155]. While looking at the fine spectra for calcium, we see two binding states in the Ca 2s and the Ca 2p. From Table 9, the Ca 2p 3/2 scan A is 345.86, and the scan B is 345.59. Therefore, the lower binding energy can be
assigned to an oxygen or carbonate environment, while the higher binding energy can be assigned to binding with sulfur [136]. On the fine carbon spectra in Figure 10 (F), we see scan (B) with a B.E. of 288.91 that can be identified as carbonate and assigned to carbonate.

Furthermore, looking at Figure 10 (G), the fine spectra for oxygen, you see the central peak of 530.94 eV of adsorbed oxygen and then on the lower binding energy side scan (B) of table 9 at 527.69 eV BE that is indicative of metal oxide and metal carbonate. With europium as a phosphor dopant in the CaS powder, we look at Figure 10 (E) the fine spectra, and we see a higher binding energy peak of 5/2 at 1134.13 eV as scan D of Table 9. This shows as Eu³⁺ consistent with other compounds with Eu as a phosphor dopant.

The stoichiometry of CaS should be 1 to 1. The stoichiometry as calculated experimentally is Ca₀.₈₉S₁.₀₀. While this ratio for CaS is slightly off compared to theoretical, there may be many reasons for this off-stoichiometry. We can compare these results to our previously reported results for zinc sulfide where the stoichiometry is within the error ratio of XPS given as, Zn₁.₀₀S₀.₉₈[26]. The possible reasons for off-stoichiometry in CaS may be results of specific chemistries that lie on the surface of this powder (O affinity for Ca), the addition of the EuS as part of the matrix, and the formation of sulfur linkages as part of the bonding environment seen in the S2p spectra seen as two distinct bonding environments.

4.3 Discussion XPS Analysis of Calcium Sulfide Powder

The X-ray photoelectron spectroscopy (XPS) results presented in this chapter demonstrate the chemical and electronic structure of CaS powder doped with europium, a starting point for comparison of calcium La₂S₃ as CaS is one of the two parts of the tertiary system for the formation of CLS. As expected, the main elements present in the powder were identified as calcium, sulfur, and europium. Furthermore, the XPS spectra showed the presence of CaS as the main component of the powder and calcium oxide and
calcium carbonate as a minor composition as surface oxidation, even though an Ar⁺ sputter was done at 120 seconds at 3000eV.

The Ca 2p3/2 and S 2p 3/2 spectra of the CaS powder showed a strong peak at 345.86 eV and 159.931 eV, respectively, corresponding to the Ca-S bond. The presence of CaO and CaCO₃ was confirmed by the peaks at 345.86 eV in the Ca 2p3/2 spectra. Furthermore, in the O 1s and C 1s spectra, the presence of CaO and CaCO₃ can be seen by 527.69 and 288.91 eV, respectively, corresponding to Ca-O and O-C=O. The S 2p spectra showed the presence of polysulfide- species, which can be attributed to sulfur atoms displaced by the oxidation of Ca with oxygen from the atmosphere during sample handling. The presence of Ca-O and Ca-CO₃ species was also observed, which could be attributed to the polysulfide concentration in the powder.

In addition, the XPS spectra showed the presence of carbon and oxygen contamination on the surface of the powder; this surface contamination is very hard to remove from loose powder with sputtering due to uneven surface. Most of this contamination can be attributed to the adsorption of atmospheric gases during sample production and handling. Therefore, these contaminants could be minimized by optimizing the sample preparation process and using a controlled atmosphere during production and handling.

4.4 Conclusions

In summary, the XPS analysis of the CaS powder showed the presence of CaS as the main component (at % Ca:S = 25.29:32.7), with calcium oxide/ calcium carbonate as 3 at% minor components of the powder. The Ca 2p3/2 and S 2p spectra confirmed the presence of the Ca-S bond and the polysulfide- species, respectively. The presence of calcium-oxygen and calcium-carbon-oxygen species can be attributed to the reaction of calcium with oxygen on the surface of the powder. While the presence of europium is
confirmand by XPS, the +3/ +2-state indicated it is not contributing to binding with calcium or sulfur and is not playing a part in the binding energy shifts of calcium or sulfur. In addition to the known elements of CaS -Eu powder, the XPS spectra revealed the presence of carbon and oxygen contamination within the powder, which could be minimized by optimization during the production process and with additional precaution within the sample handling process and by using a controlled atmosphere during transfer and analysis.

Overall, the XPS analysis of CaS provided valuable insight into photoelectric lines expectation that can be expected from the binary compound that can translate to the tertiary CLS material. In addition, the chemical and electronic structure of the CaS powder can help compare CLS to aid in identifying shifts in the binding energy that can be indicative of contamination or defects and therefore help improve the performance of ceramics made from base powders on this material. Further studies are needed to investigate the binary compound La₂S₃ to correlate base binding energies that affect compositional parameters on the chemical and electronic structure of the ceramics, as well as to explore the use of alternative production techniques to minimize the presence of contaminants and reduce oxygen incorporation into the CLS lattice potently.
 CHAPTER 5: RESULTS – LANTHANUM SULFIDE CHARACTERIZATION BY XPS

5.1 Background Lanthanum Sulfide Powder

This Chapter focuses on the XPS of commercially available $\gamma$-La$_2$S$_3$ doped with 0.1 wt% sodium sulfide (Na$_2$S) powder to understand the nature of bonding between the major species (i.e., La and S) in CLS. While CLS does not contain Na$_2$S, $\gamma$-La$_2$S$_3$ is unstable in atmospheric conditions without a stabilizing cation. The proposed stabilization mechanism is that the presence of the dopant ion in the lattice reduces the ability of La or S atom migration. The migration of La or S is one of the considerations for phase transformation in the La$_2$S$_3$ system. Therefore, 0.1 wt. % Na$_2$S is added to La$_2$S$_3$, and it is expected that this will not significantly affect the XPS peak position or shapes of the $\gamma$-La$_2$S$_3$.

La$_2$S$_3$ is a binary metal sulfide that belongs to the greater chalcogenide materials known for their electronic applications. La$_2$S$_3$ produces arsenic-free, chalcogenide glasses and ceramics[148]. Along with it being a wide bandgap semiconductor with a bandgap of ~2.6 eV, the material is optically transparent in the visible wavelength (380-750 nm) through the infrared ~8 $\mu$m[24, 35, 38, 71, 108, 156]. Historical uses for La$_2$S$_3$ include catalysts for wastewater reclamation, arsenic-free chalcogenides glasses, and optical windows and domes for IR applications[18, 108, 157-166]. While this material has been studied since the early 1970’s an exhaustive characterization by XPS has not been available.

Herein, we present charge-corrected scans for the survey spectrum, along with S 2s, S 2p, La 4s, La 4p, La 4d, La 3p$_{3/2}$, La 3p$_{1/2}$, La 3d, Na 1s, O 1s, and C 1s surface photoelectron signals. The peak fitting aims to identify the bonding states of $\gamma$-La$_2$S$_3$. Atomic % are also calculated and additional constituent elements and non-trace level impurities are reported.
Results XPS of Lanthanum Sulfide Powder

Like with the previous sample $\gamma$-La$_2$S$_3$ powder analysis by XPS was conducted on loose powder attached to carbon tape. The sample was in-situ processed by Ar$^+$ ion sputtering at 4000 eV for 120 seconds before collecting spectra on a single spot of 650 $\mu$m for additional information on preparation and collections specification. Please refer to the materials and methods. A survey spectrum was taken to identify elements in the sample, as seen in Figure 11. The survey scan was taken from 0 to 1300 eV. After scans were taken and before analysis, the survey spectrum was calibrated to the O 1s to 531 eV binding energy. The survey was analyzed for the unique peaks because each element has a unique binding energy that can be identified. From the survey, we found peaks that could be identified as lanthanum, sulfur, sodium, carbon, and oxygen. In the previous Chapter, we discussed the limitation of XPS as a surface-only technique with only a few nanometers of probing depth. Some features of the surface may only sometimes be representative of the bulk. The presence of contaminates in the form of oxides in bulk can be present in the physical and electrical properties of the ceramic made from the powders.

High-resolution scans, also known as fine spectra scans, were taken for sulfur and lanthanum and can be seen as S 2s, S 2p, La 4s, La 4p, La 4d, La 3p3/2, La 3p1/2, La 3d, in Figure 12. Additionally, fine spectra were collected for Na 1s, C 1s, and O1s as minor elements and contaminants that can also be seen in Figure 12 as part of the elemental lines for sodium, carbon, and oxygen as part of the elemental lines for sodium, carbon, and oxygen.
Figure 11: XPS Survey spectrum of received lanthanum sulfide powder.
La 4s

La 4p

La 4d

La 3p

La 3d
Figure 12: XPS fine spectrum of as received lanthanum sulfide powder (A) S 2s fine spectra, (B) S 2p fine spectra, (C) La 4s fine spectra, (D) La 4p fine spectra, (E) La 4d fine spectra, (F) La 3p_{3/2} fine spectra and (G) La 3p_{1/2} fine spectra, (H) La 3d, (I) Na 1s fine spectra, (J) C 1s fine spectra, (K) O1s fine spectra.

From Figure 12, we can see the primary peak positions and shapes of each of the elements. As with the previous Chapter, we calculate peak position and atomic parentage using Thermo Scientific Advantage software for each elemental collected.

In Table 10, we have tabulated the information from the spectra of Figure 12, the peak energy, peak width as FWHM, peak area in eV x counts per second, atomic percentage, the sensitivity factors used for calculation, atomic concentrations, and peak assignments. This information is produced by calculations
from the Thermo Scientific Advantage software. From Figure 12, the eleven fine spectra bonding states can be identified by their binding energy peak position and peak shape visually and numerically by FWHM listed in Table 10.

Table 10: Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor, Concentration (at %), and Peak Assignment.

<table>
<thead>
<tr>
<th>Figure Label</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV x cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at %)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>S2s</td>
<td>224.62</td>
<td>2.78</td>
<td>8074.73</td>
<td>1.294</td>
<td>...</td>
<td>La2S3</td>
</tr>
<tr>
<td>B</td>
<td>S2p</td>
<td>161</td>
<td>2.58</td>
<td>12818.31</td>
<td>1.881</td>
<td>...</td>
<td>La2S3</td>
</tr>
<tr>
<td>K</td>
<td>O1s</td>
<td>528.14</td>
<td>1.33</td>
<td>13393.67</td>
<td>2.881</td>
<td>...</td>
<td>La2O3/Sulfate, Carbonates/Hydroxyl</td>
</tr>
<tr>
<td>I</td>
<td>Na1s</td>
<td>1071.23</td>
<td>1.85</td>
<td>4161.84</td>
<td>10.588</td>
<td>3.33</td>
<td>Na2S</td>
</tr>
<tr>
<td>C</td>
<td>La4s</td>
<td>274.09</td>
<td>6.3</td>
<td>4010.16</td>
<td>1.19</td>
<td>...</td>
<td>La3S/La2O3</td>
</tr>
<tr>
<td>D</td>
<td>La4p</td>
<td>195.29</td>
<td>5.5</td>
<td>19642.48</td>
<td>4.33</td>
<td>...</td>
<td>La2S/La2O3</td>
</tr>
<tr>
<td>E</td>
<td>La4d</td>
<td>104.27</td>
<td>5.95</td>
<td>51987.48</td>
<td>10.731</td>
<td>27.74</td>
<td>La3S/La2O3</td>
</tr>
<tr>
<td>F</td>
<td>La3p12</td>
<td>1127.2</td>
<td>7.53</td>
<td>46502.55</td>
<td>14</td>
<td>...</td>
<td>La2O3</td>
</tr>
<tr>
<td>G</td>
<td>La3p12</td>
<td>1208.72</td>
<td>7.26</td>
<td>18993.02</td>
<td>6.1</td>
<td>...</td>
<td>La2S/La2O3</td>
</tr>
<tr>
<td>H</td>
<td>La3d12</td>
<td>837.11</td>
<td>2.28</td>
<td>196155.2</td>
<td>32.944</td>
<td>...</td>
<td>La2S/La2O3</td>
</tr>
<tr>
<td>J</td>
<td>C1s</td>
<td>284.43</td>
<td>1</td>
<td>838.92</td>
<td>1</td>
<td>...</td>
<td>C=C/Carbonates/Carboxyl</td>
</tr>
</tbody>
</table>

Spectrum ID (A) sulfur S 2s is at binding energy 224.62, corresponding to a metal sulfide [136], in this case, La2S3. Spectrum ID (E) Lanthanum La 4d contains 3/2 and 5/2 peaks. For identification purposes, the 5/2 peak is used with a B.E. of 104.27 eV, corresponding to La2S3. This spectrum has split peaks yet is not as complicated as La 3d, which has plasmons and is also convoluted with auger peaks making quantification more straightforward for the La 4d spectra. This information from the peak shapes shows that additional states are possible but not seen in Table 10 for the main binding energy peak from the single positions. The O 1s and C 1s peaks show that the La2S3 can also be identified as containing oxide, carbonate, or carboxyl. Still, the C 1s peak is so tiny and close to the baseline that quantification is the carbon concentration would be inaccurate and not added into the atomic present calculations. To dive deeper into the material's makeup, a deconvolution of the peaks is necessary to see the contribution of
lattice oxygen in the spectrum. The residual peak for carbon is at 284.43 eV, indicating carbon-carbon bonding or carbon's advantages.

In comparison, the oxygen B.E. peak is at 528.14 eV and can be representative of lanthanum oxide. At the same time, there is a secondary peak in the range of hydroxides, carbonates, and metal oxides. Using the Advantage software by Thermo Scientific, deconvolution of fine spectra (A-K) was done and can be seen in Figure 13 and corresponding deconvoluted features in Table 11.
Figure 13: Deconvoluted XPS fine spectrum of as received lanthanum sulfide powder (A) S 2s fine spectra, (B) S 2p fine spectra, (C) La 4s fine spectra, (D) La 4p fine spectra, (E) La 4d fine spectra, (F) La 3p<sub>3/2</sub> fine spectra and (G) La 3p<sub>1/2</sub> fine spectra, (H) La 3d, (I) Na 1s fine spectra, (J) C 1s fine spectra, (K) O1s fine spectra and (I) Peak Key for (A-K).
Table 11: Deconvoluted Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor, Concentration (at.%), and Peak Assignment

<table>
<thead>
<tr>
<th>Figure Label</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV x cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at.%)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>S2s I</td>
<td>223.95</td>
<td>3.37</td>
<td>3952.04</td>
<td>1.294</td>
<td>...</td>
<td>Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2s II</td>
<td>224.99</td>
<td>2.59</td>
<td>4904.91</td>
<td>1.294</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
<tr>
<td>(B)</td>
<td>S2p3/2 III</td>
<td>160.23</td>
<td>1.84</td>
<td>4964.18</td>
<td>1.245</td>
<td>40.42</td>
<td>Metal Sulfide</td>
</tr>
<tr>
<td>(B)</td>
<td>S3p3/2 III</td>
<td>161.37</td>
<td>1.84</td>
<td>2535.76</td>
<td>0.636</td>
<td>...</td>
<td>Metal Sulfide</td>
</tr>
<tr>
<td>(B)</td>
<td>S3p3/2 IV</td>
<td>161.18</td>
<td>1.53</td>
<td>3537.84</td>
<td>1.245</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
<tr>
<td>(B)</td>
<td>S2p3/2 IV</td>
<td>162.39</td>
<td>1.53</td>
<td>1807.17</td>
<td>0.636</td>
<td>...</td>
<td>Poly Sulfide</td>
</tr>
<tr>
<td>(K)</td>
<td>O1s XVII</td>
<td>528.11</td>
<td>1.22</td>
<td>6618.3</td>
<td>2.881</td>
<td>32.12</td>
<td>Metal Oxide</td>
</tr>
<tr>
<td>(K)</td>
<td>O1s XXIX</td>
<td>530.13</td>
<td>1.72</td>
<td>6358.32</td>
<td>2.881</td>
<td>...</td>
<td>Hydroxide/ Other Oxygen</td>
</tr>
<tr>
<td>(K)</td>
<td>O1s XXX</td>
<td>532.62</td>
<td>1.71</td>
<td>404.17</td>
<td>2.881</td>
<td>...</td>
<td>Carboxyl/ Carbonates</td>
</tr>
<tr>
<td>(I)</td>
<td>Na1s XXV</td>
<td>1071.24</td>
<td>2.1</td>
<td>3718.81</td>
<td>10.588</td>
<td>3.15</td>
<td>Sodium Sulfide</td>
</tr>
<tr>
<td>(C)</td>
<td>La4s V</td>
<td>272.81</td>
<td>3.37</td>
<td>1971.9</td>
<td>1.19</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(C)</td>
<td>La4s VI</td>
<td>274.55</td>
<td>2.03</td>
<td>638.75</td>
<td>1.19</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(C)</td>
<td>La4s VII</td>
<td>276.82</td>
<td>3.02</td>
<td>1646.05</td>
<td>1.19</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(D)</td>
<td>La4p VIII</td>
<td>194.57</td>
<td>2.69</td>
<td>6429.44</td>
<td>4.33</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(D)</td>
<td>La4p IX</td>
<td>198.67</td>
<td>2.16</td>
<td>2505.49</td>
<td>4.33</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(D)</td>
<td>La4p X</td>
<td>196.77</td>
<td>2.88</td>
<td>4311.76</td>
<td>4.33</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(E)</td>
<td>La4d3/2 XII</td>
<td>105.02</td>
<td>2.06</td>
<td>6041.76</td>
<td>4.216</td>
<td>25.3</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(E)</td>
<td>La4d5/2 XII</td>
<td>108</td>
<td>2.06</td>
<td>4190</td>
<td>2.928</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(E)</td>
<td>La4d3/2 XI</td>
<td>101.45</td>
<td>2.62</td>
<td>16218.28</td>
<td>4.216</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(E)</td>
<td>La4d5/2 XI</td>
<td>104.61</td>
<td>2.61</td>
<td>11247.48</td>
<td>2.928</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(E)</td>
<td>La4d1/2 XI</td>
<td>103.27</td>
<td>2.5</td>
<td>8528.4</td>
<td>4.216</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(E)</td>
<td>La4d3/2 XII</td>
<td>106.17</td>
<td>2.5</td>
<td>5914.5</td>
<td>2.928</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(F)</td>
<td>La3p3/2 XIV</td>
<td>1127.16</td>
<td>3.37</td>
<td>18134.11</td>
<td>14</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(F)</td>
<td>La3p3/2 XV</td>
<td>1123.95</td>
<td>3.37</td>
<td>14698.52</td>
<td>14</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(F)</td>
<td>La3p3/2 XVI</td>
<td>1129.7</td>
<td>3.37</td>
<td>11450.73</td>
<td>14</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(G)</td>
<td>La3p1/2 XVIII</td>
<td>1204.19</td>
<td>3.37</td>
<td>5681.1</td>
<td>6.1</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(G)</td>
<td>La3p3/2 IX</td>
<td>1209.65</td>
<td>3.37</td>
<td>6947.31</td>
<td>6.1</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(G)</td>
<td>La3p5/2 XVIII</td>
<td>1206.71</td>
<td>2.98</td>
<td>5474.58</td>
<td>6.1</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(H)</td>
<td>La3d3/2 XX</td>
<td>837.37</td>
<td>1.85</td>
<td>6259.34</td>
<td>32.944</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(H)</td>
<td>La3d5/2 XX</td>
<td>854.17</td>
<td>1.85</td>
<td>4340.75</td>
<td>22.588</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(H)</td>
<td>La3d3/2 XXI</td>
<td>832.85</td>
<td>2.29</td>
<td>68097.45</td>
<td>32.944</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(H)</td>
<td>La3d5/2 XXI</td>
<td>841.76</td>
<td>2.29</td>
<td>4722.62</td>
<td>22.588</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(H)</td>
<td>La3d3/2 XXII</td>
<td>835.56</td>
<td>3.37</td>
<td>6571.95</td>
<td>32.944</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(H)</td>
<td>La3d5/2 XXII</td>
<td>852.2</td>
<td>3.37</td>
<td>45568.39</td>
<td>22.588</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(H)</td>
<td>La3dXXIII</td>
<td>846.96</td>
<td>5.77</td>
<td>40165.32</td>
<td>55.532</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(H)</td>
<td>La3dXXIV</td>
<td>862.07</td>
<td>13.5</td>
<td>112367.65</td>
<td>55.532</td>
<td>...</td>
<td>La2O3/ La2S3</td>
</tr>
<tr>
<td>(J)</td>
<td>Cls XXVI</td>
<td>284.56</td>
<td>2.36</td>
<td>560.57</td>
<td>1</td>
<td>...</td>
<td>Carbon- Carbon</td>
</tr>
<tr>
<td>(J)</td>
<td>Cls XXVII</td>
<td>289.31</td>
<td>3.37</td>
<td>408.75</td>
<td>1</td>
<td>...</td>
<td>Carboxyl/ Carbonates</td>
</tr>
</tbody>
</table>

With the deconvoluted fine spectra, we now see that sulfur in Figure 13 (A) and (B) shows two distinct bonding states. In Figure 13 (B), the sulfur 2p fine spectrum, the single peak from Figure 12 (B), is deconvoluted to show two sets of overlapping 3/2 and ½ peaks. Looking at Table 11, the primary 3/2 peak is at 160.23 eV, and the secondary 3/2 peak is at 161.18 eV. This shows that sulfur has two distinct
bonding environments the metal sulfide at the lower BE and the poly sulfide at the higher binding energy[167]. While looking at the fine spectra for lanthanum, we see three binding states throughout the different lanthanum photoelectric fine spectra. From Table 11, the La 3d 5/2 peak XX is 837.37 eV, the peak XXI is 832.85 eV, and the mid peak XXII is 835.56 eV. These three binding outcomes can be attributed to La$_2$S$_3$ and La$_2$O$_3$. If we investigate the literature, we can see that peak XXII is the primary peak position, peak XX is the bonding peak, and peak XXII is the anti-bonding peak [168]. The La 3d fine spectra also have plasmon peaks that form in front of the 3/2 and hide the 3/2 peak. This, coupled with being near the Auger lines, makes for a complicated deconvolution. This peak can still give insightful information on the bonding state of La sulfide and La oxide by looking at the peak position and ratio[168-170]. For purposes of atomic calculation, Figure 13 (E) La 4d 5/2 is used as the reference peak due to being a simpler peak for measures. Yet when comparing the deconvoluted spectra Figure 13 (C-H) for lanthanum, each spectra fitting reflects the same story that there is a primary peak with a bonding and anti-bonding peak, giving further stability of the argument for the material being a mixture of La$_2$S$_3$ and La$_2$O$_3$[24, 67, 168, 169, 171]. In Figure 13 (I), the Na 1s peak is a single peak at B.E. 1071.24 eV and can be assigned to Na$_2$S. Along with minor elements in Figure 13, spectrum (J), C 1s is collected and can be deconvoluted into two peaks, XXVI 284.56 eV. and XXVII 289.31 eV, being assigned to carbon-carbon and carboxyl/carbonates. The final spectrum collected in Figure 13(K) O 1s has three peaks XXVIII 528.11eV., XXIX 530.11 eV, and XXX 532.62 eV being assigned to lanthanum and oxygen, oxygen/ hydroxide, and carboxyl/ carbonate.

5.3 Discussion XPS Analysis of Lanthanum Sulfide Powder

The results of this Chapter show the electronic and chemical structure of the as-received powder γ-La$_2$S$_3$ stabilized with Na$_2$S. γ-La$_2$S$_3$ is the majority component in the tertiary CLS matrix. For this reason, it is
imported to deconvolute and identify the energy signature of the base material and crystal structure for CLS. From the survey spectrum, Figure 11, the major elements in the powder are identified as lanthanum, sulfur, sodium, and the minor element sodium, which contaminates carbon and oxygen. Furthermore, the XPS spectra showed the presence of La$_2$S$_3$ as the main component of the powder and lanthanum oxide as a secondary component with carboxyl/ carbonates as a minor composition as surface oxidation, even though an Ar$^+$ sputter was done at 120 seconds at 3000eV.

The La 3d 5/2 higher binding energy peak XX is 837.37 eV, is associated with sulfide, and the lower binding energy peak XXI is 832.85 eV from the literature. This satellite peak indicates an oxide bond and would be consistent with the mixed phase of lanthanum being bound to sulfur and oxygen. While looking at the La 3d 5/2, we have a distance of 4.56 eV between the mainline peak and the satellite peak, consistent with the literature on the separation identified in lanthanum oxysulfide [108, 110, 169, 170, 172-176]. The La 3d 5/2 mainline peak B.E. range for lanthanum oxygen is reported between ~833.5-835.25 eV by looking at the XPS Handbook, and the lower binding energy peak XXI has been identified as La$_2$O$_3$ [108, 110, 169, 170, 172-176] as, the less intense of the peaks. Secondly, we looked at the S 2p 3/2 spectra for the γ-La$_2$S$_3$ powder, which showed peaks at 160.23 eV and 161.18 eV. These peaks both indicate binding energy for metal sulfide, with the higher binding energy peaks indicative of a more sulfur-rich binding metal sulfide environment. This could be because of the two types of binding environment that sulfur and lanthanum can have in the possible crystal orientation, as these measurements take over an average size of 650μm and not over a single crystal. And thirdly, looking at the O 1s spectra, we see three peaks, the lower binding peak of 528.11 eV, historically assigned to lanthanum-oxygen bonding. A second peak at 530.13 can be attributed to other oxygen or a hydroxide-boding environment, and the highest of the binding energy peaks at 532.62 as carboxyl/carbonate surface contamination. Furthermore, C 1s spectra confirm the presence of carbonate
and carboxyl, as seen by the peak at 289.31 eV, which coincides with the O 1s peak at 532.62 eV. While the lower binding energy peaks O 1s are attributed to lanthanum oxide, and this oxygen is part of the lattice, the higher binding energy carbonate and carboxyl can be attributed to powder handling and carbon contamination from the atmosphere during sample handling.

As in the previous Chapter, the XPS spectra showed the presence of carbon and oxygen contamination on the surface of the powder, along with a significant amount of oxide that would be attributed to a second phase and not just surface contamination. The residual carbonate and carboxyl surface contamination are very hard to remove from loose powder with sputtering due to uneven surface. The carboxyl and carbonate contamination can be attributed to the adsorption of atmospheric gases during sample production and handling. But the significance of the oxide presence is that just contamination cannot be managed by simple handling and cleaning protocols. Because the oxide is a more significant majority of the atomic percentage of the material, these contaminants may only be handled by additional production steps and sulfurization processes.

5.4 Conclusions

In summary, the XPS analysis of the $\gamma$-La$_2$S$_3$ powder showed the presence of La$_2$S$_3$ as the main component (at % La:S = 25.31:40.42), with O at ~32.12 at%, sodium at ~3.15 at %, and carboxyl/carbonates as less than~1 at% minor components of the powder. The La 3d 5/2 and S 2p spectra confirmed the presence of the La-S bond and the second poly sulfur metal sulfide- species, respectively. The O 1s spectra confirmed the presence of a significant lanthanum oxide contamination in the powder. Lanthanum-oxygen bonding can be attributed to an incomplete sulfonation reaction during powder conversion from lanthanum oxide to $\gamma$-La$_2$S$_3$. The presence of carbonate/carboxyl peak in the C 1s and O 1s as carbon-oxygen species can be attributed to the reaction of La$_2$S$_3$ with oxygen on the surface of the
powder. For this analysis, the atomic % calculation was not done for carbon due to the low counts of the peaks and the signal-to-noise ratio.

In contrast, atomic percentage calculation would not be accurate; we still can gather information about the bonding environment by fitting these spectra and matching them with coinciding information in the oxygen spectra. While the presence of sodium as sodium sulfide is confirmed by XPS, the spectra would indicate that it is not participating in the bonding environment for lanthanum. While the peak intensity for sodium was greater than that of carbon, the overall count would still be considered low and could be attributed to the noise of the single and peak shape. This evidence is with the low weight presence as this is not meant to participate in the reaction but to stabilize the $\gamma$-La$_2$S$_3$ crystal shape as the lanthanum has approximately $\sim$11 % vacancy on a Th3P4 lattice [113]. Stabilizing the $\gamma$-phase for La$_2$S$_3$ is necessary as, under ambient condition, the lattice can convert to one of several other phases in the presence of an atmosphere and, therefore, change the optical and electronic properties [113, 177, 178]. The peak position of sodium is a single peak that can be entirely attributed to the binding with sulfur.

Overall, the XPS analysis of $\gamma$-La$_2$S$_3$ provided valuable insight into photoelectric lines expectation that can be expected from the majority component and the crystal lattice base for tertiary CLS material. In addition, the chemical and electronic structure of the La$_2$S$_3$ powder can help compare CLS to aid in identifying shifts in the binding energy. It can help to identify inherent contamination of oxygen in the lattice. Identifying the secondary oxide phase that is not seen in XRD can help in ceramic production by working on initial powders to reduce or eliminate the oxide, therefore helping improve the performance of ceramics. With a full investigation into calcium and La$_2$S$_3$, the next steps in XPS analysis are confidence in accurately quantifying the components elements. A further study of the two binary compounds as mixtures in ratios of 100% to 50/50% will be needed to calibrate the XPS measurements for atomic quantification for future investigation of the 90:10 CLS formula.
CHAPTER 6: RESULTS—CALIBRATION CURVE FOR XPS ON CALCIUM LANTHANUM SULFIDE BY VARYING MIXTURES OF LANTHANUM AND CALCIUM SULFIDE

6.1 Background Calibration Curve

In the previous chapters, we looked at the XPS of CaS and $\gamma$-La$_2$S$_3$ powder to understand the bonding environment of binary metal sulfides. CLS can be considered a solid solution of $\gamma$-La$_2$S$_3$ and CaS mixed in the appropriate ratio, yielding many of the desired optical and mechanical properties. However, as shown in Chapter 2, there is limited XPS data availability for CLS. Therefore, calibration curves containing varying physically missed amounts of CaS and $\gamma$-La$_2$S$_3$ are a necessary and logical next step to understand XPS data of CLS better.

Calibration curves, in which individual components are premixed in desired ratios, provide simultaneous baseline spectra and help gauge instrument capabilities and sensitivity in detecting various elements. While not representative of a solid-solution of CaS and $\gamma$-La$_2$S$_3$, i.e., CLS, these curves provide fine spectra of Ca, S, La and other trace elements. Extracting compositions (e.g., in terms of atomic %) from these mixtures imparts a high level of confidence in the analysis technique. Moreover, quantification in XPS can be challenging due to variability in factors associated with collection and analysis. These variations include X-ray source intensity, detector efficiency, and signal attenuation [133, 134]. Additional variabilities, such as material charging and matrix effects, complicate the quantitative analysis [133, 134, 136, 179, 180]. To overcome these challenges, calibration procedures using $\gamma$-La$_2$S$_3$ and CaS mixtures have been adapted from other elemental calibration quantification methodologies [133-135]. Thus, this Chapter takes a significant step towards conducting consistent and repeatable XPS analyses of CLS as a material system.

$\gamma$-La$_2$S$_3$ powder (99.9 wt%) doped with Na$_2$S 0.1% wt% was mixed with CaS powder (98.0 wt%), doped with Eu 2.0% wt% to calibrate the quantification of La, Ca, and S using XPS. The samples were
mechanically mixed from 100 mol% $\gamma$-La$_2$S$_3$ to 100 mol% CaS with 10 mol% composition intervals between samples, i.e., 90/10, 80/20, 70/30, 60/40, 50/50, etc., and so on. Thus, the entire composition spectrum was covered. The samples were prepared in an inert atmosphere inside a glove box by mechanically mixing using mortar and pestle. The mixed powders were then CIP’ed, and additional information on the procedure is in Chapter 3, Material and Methods. The peak fitting done in this Chapter aims to identify elements and quantify atomic percentages across the calibration curve to determine the confidence factor of XPS in quantifying CLS. Along with the quantification, we aim to identify the presence of the constituent elements and non-trace level impurities, if present.

**6.2 Results of Calibration Curve**

Premixed samples are shown in Figure 14. The samples had no *in situ* processing before collecting spectra at 5 spots given as a sample’s north, south, east, west, and center regions. A spot size of 200 $\mu$m was used, and all 5 spots were used and averaged with standard deviation for additional information on preparation and collections specification.

![Figure 14](image)

**Figure 14:** CIP’ed samples of Lanthanum Sulfide and Calcium Sulfide and powder compacts of the intermediate mixtures (A) Sample yellow green- yellow red La$_2$S$_3$ 100%- 60% (B) Sample yellow red-light red CaS 60%-100% (C) Table for the mixture for the ratio of La$_2$S$_3$: CaS

A survey spectrum was taken for elemental identification for each sample and spot, as seen in Figure 15. The survey scan was taken from 0 to 1300 eV, but for elemental analysis, 0 to 900 eV is shown in Figure
15. Because no in situ process was done and carbon is at the received levels, the survey spectrum was calibrated to the C 1s to 284.8 eV binding energy. The survey found peaks that could be identified as lanthanum, calcium, sulfur, carbon, and oxygen. Carbon and oxygen were removed from further analysis as they appear to be products of the preparation process. These elements have been removed from the calculation for this calibration, and only Ca, La, and S have been used for analysis to be more representative of CLS.

As with previous chapters and high-resolution scans, the fine spectra of sulfur, calcium, and lanthanum can be seen as S 2p, Ca 2p, and La 3d composites in Figure 16. Additionally, fine spectra were collected for sodium, europium, carbon, and oxygen as Na 1s, Eu 3d C 1s, and O 1s as minor elements and contaminants not shown in this Chapter.

![Figure 15: Composites of XPS Survey spectrums for Lanthanum Sulfide and Calcium Sulfide mixture from 100% to 50/50 mixtures as pieces of CIP’ed coupons](image)
From Figure 15, we see that in the 100% $\gamma$-$\text{La}_2\text{S}_3$ sample, the presence of the La 3d peaks along with a peak for sulfur S 2p, O1s, and C 1s, but we do not see a peak for Ca 2p as no CaS is present in the sample. Also, we see in the 100% CaS sample the presence of the Ca 2p peak along with the S 2p peak and the peaks for O 1s and C 1s but have an absence of the peaks for La 3d.

When looking at the mixture, we see the peaks for calcium, lanthanum, sulfur, oxygen, and carbon. Still, we can see the intensities of the peaks change for the elements as the percentage of CaS present in the sample is changed.

**Figure 16:** Composite of XPS fine spectrum of the mixture of Lanthanum Sulfide and Calcium Sulfide from 100% to 50/50 mixtures as pieces CIP’ed (A) S 2p fine spectra, (B) Ca 2p fine spectra, (C) La 3d fine spectra
Figure 16 shows the fine spectra for sulfur, calcium, and lanthanum for various mixtures. We can see each element's primary peak positions and shapes. From Figure 16 (A), we see the S 2p fine spectra for the various mixtures. The S 2p 3/2 is centered at 161.23 eV for $\gamma$-La$_2$S$_3$ and 160.83 eV for CaS. The mixtures show slight variation to the peak positions but all lie within the expected range from 160.20 to 163.50 eV for sulfides[136]. In Figure 16 (B), we see a clear trend that as the percentage of calcium is decreased, we see a decrease in intensity and an increase in the FWHM of the peaks. The peak position of the Ca 2p 3/2 is present at 345.86 eV and does not significantly change as the CaS fraction is decreased in the mixture. Figure 16 (C) shows a more gradual decrease in peak intensity as the mole percent La$_2$S$_3$ is decreased this may be because of the sensitivity of XPS for the La 3d fines spectra vs. the Ca 2p fine spectra.

The fine spectra are used to calculate at% using Thermo Scientific Advantage software for each spectrum collected. For the calibration curve, there are 11 samples. Each sample had 5 data points collected, and from these 5 points, the mean was calculated along with the standard deviation for each element's atomic percentage and plotted vs. the theoretical calculations, as seen in Figure 17.
Figure 17: Experimental vs Theoretical at% (A) Sulfur S 2p fine spectra at% average with standard deviation vs theoretical at% (B) Calcium Ca 2p fine spectra at% average with standard deviation vs theoretical at% (C) Lanthanum La 3d fine spectra at% average with standard deviation vs theoretical at%.

These plots also have a 95% confidence interval and a line for slope of ~1, indicating perfect correlation.

From these plots, we have to look at the points and their proximity to the 95% confidence interval and the proximity to the slope. From each of the plots, we see they fall in the 95% confidence interval and are in proximity to the ~1 slope giving a good sign that the experimental at % are in line with the theoretical within a percentage of error.
6.3 Discussion Calibration Curve

The results of this Chapter show that XPS is sensitive to the concentration of all three major elements and has a good confidence factor for identifying the mixture ratios of CaS to La$_2$S$_3$. Looking at Figure 14 (A) and (B), we can see that the individual CIP’ed samples are not entirely uniform in color. Nonuniformity can be attributed to incomplete mechanical mixing. This can cause variation in at% in the 5-point collection scheme for each sample, and therefore the predicted % can be outside the 95% confidence interval as seen in Figures 17 B and C.

While looking at Figure 15, the stacked survey spectra graphs starting at La$_2$S$_3$ 100% to CaS 100%, the images show the strong presence of the La 3d spectra in a decreasing fashion in contrast to Ca 2p spectra is absent in C:L 0:100. Still, this peak increases in intensity as the percentage of CaS is increased. At the same time, the S 2p peak remains relatively consistent with minor changes in intensity over Figure 15. This leads to Figure 16, the stacked fine spectra for (A) S 2p that shows a relatively consistent intensity, but a change is broadening in the primary peak associated with sulfide ~161 eV and a smaller peak for sulfate or SO$_2$ at the higher binding energy ~168 eV on the sample with a greater concentration of CaS indicating oxidation of the powder sample[37, 136]. For Figure 16 (B), the Ca 2p spectra, we see a difference in peak intensity as the percentage of Ca is decreased in the sample, indicating the difference in the sensitivity of Ca to La and showing a need for increased accumulation needed for resolution in future samples to achieve accurate quantification. Finally, for Figure 16 (C), La 3d spectra show the most transparent and consistent decrease in intensity and peak shape as the percentage of lanthanum is decreased in the sample, indicating the sensitivity of La detection yet the complexity of the peak shape combined with the presence of shake-up and plasmon peaks increases the difficulty of deconvolving the peaks for accurate quantification through XPS[168].
Looking at Figure 17 (A) sulfur, we see a wider band for the 95% confidence interval that shows as a wider standard deviation in the sample that can be attributed to incomplete mixing of the two binary compounds, and this puts the linear trend just above the ~1 slope line. In Figure 17(B) for calcium falls closest to the ~1 slope line but has a broad confidence interval band. This can be attributed to the Ar$^+$ sputtering before accumulation to reduce surface carbon and oxygen and the need to increase the number of accumulations for the sensitivity of Ca in the XPS at a lower concentration. However, the graph shows reasonable confidence in delivering the atomic % in line with the theoretical calculations for the mixtures. Finally, in Figure 17 (C) lanthanum, data points are just below the slope but still linear, and all but one of the points is in the 95% confidence interval band. A better fit and spread is possible with better homogeneous sample mixing and cleaning before acquisition.

6.4 Conclusions

The XPS analysis of various mechanically premixed and CIP’ed pellets of $\gamma$-La$_2$S$_3$ and CaS powders was conducted. This effort aimed to generate a calibration dataset that would guide the interpretation and understanding of sample and instrumental effects when looking at solid solutions of $\gamma$-La$_2$S$_3$ and CaS (i.e., CLS). Data collected showed La$_2$S$_3$ and CaS in all mixtures of the two binary metal sulfides in close accordance with the premixed ratios used to prepare the samples.

The XPS system provides a baseline accuracy of composition to ±2 at% instrumentation. However, the calibration effort emphasized surface cleaning before accumulation [133, 134]. Furthermore, this study shows the need for increased accumulation of the fine spectra, particularly the Ca 2p fine spectra, to achieve expanded peak definition and atomic percentage calculations [135]. While the collection of the survey spectra has the definition to show all the major elements and contaminates elements like carbon and oxygen, and it can give an excellent visual trend, the atomic percentage calculation based solely on the peak identification on the survey is further outside the theoretical
prediction and therefore indicate the need for high-definition scans and analysis [135]. However, even with high-definition scans, the quantification in XPS can be challenging due to the handling of samples and instrumental factors, such as variation in X-ray source intensity, detector efficiency, and signal attenuation. This condition can be exacerbated when samples have differences in height along with incomplete homogeneous mixing [135]. Secondly, using the smaller spot size can give a broader difference in peaks compared to an increased spot size that would have better peak averaging across a sample vs. taking multiple spot locations [133]. Additionally, more complex phenomena are possible when switching between samples and runs, such as differential charging and matrix effects, and the potential for variation from environmental influences that further complicate the quantitative analysis. Even with the challenges and variations, the calibration curve gave the confidence in the system to evaluate CLS solid solutions in powder and ceramic form.
CHAPTER 7: RESULTS –CALCIUM LANTHANUM SULFIDE 90:10

7.1 Background CALCIUM LANTHANUM SULFIDE 90:10

In this chapter, we will be discussing calcium, lanthanum, and sulfur as they relate to CLS a tertiary metal complex as CaLa$_2$S$_4$. While the major stoichiometry for this material is still based on $\gamma$-La$_2$S$_3$ lattice, with the addition of CaS, still holds the Th$_3$P$_4$ crystal structure the same as the gamma ($\gamma$) phase of La$_2$S$_3$. The Ca ions incorporated to stabilize $\gamma$-phase also increase the defects in the CLS system, and this is why on the phase diagram for CLS, we have chosen a 10% composition of CaS for a 90:10 composition. The solid solution of 90 mol% $\gamma$-La$_2$S$_3$ and 10 mol% CaS can generate high-quality infrared windows and thermoelectric generators [58]. The parameter for this composition can be identified from the following equations. [181]

$$(1 - x)La_2S_3 + xCaS \rightarrow Ca_xLa_{2(1-x)}S_{3-2x} \quad \text{Eq. 3}$$

Using a 90:10 composition (i.e., $x = 0.1$) will yield theoretical at% for each of the elements as following Table 12:

Table 12: Ideal Theoretical composition in at%

<table>
<thead>
<tr>
<th></th>
<th>at% Ca</th>
<th>at% La</th>
<th>at% S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Theoretical Composition (90:10)</td>
<td>2.13</td>
<td>38.30</td>
<td>59.57</td>
</tr>
</tbody>
</table>

XPS spectra of four specific samples will be considered given as, i) CLS powder, ii) CLS sintered ceramic coupon surface and, iii) CLS sintered ceramic coupon cross-section fracture in ambient conditions, and iv) CLS sintered ceramic coupon cross-section fracture in inert environment. Such an investigation will allow us to delineate the difference between surface oxidation effects and bulk ceramic quality unaffected by
moisture and oxygen. The data and analysis include scans for S 2p, La 3d, Ca 2p, O 1s, and C 1s surface photoelectron signals atomic ratio changes of experimental CLS 90:10 powders as it is converted into IR transparent ceramic window.

7.2 Results of CALCIUM LANTHANUM SULFIDE 90:10

7.2.1 XPS on Cold Isostatically Pressed CLS Powder Coupon

XPS was conducted on cold isostatically pressed (CIP’ed) powder samples attached to carbon tape, as shown in Figure 18 called ‘Green’, to indicate it has had no heat treatment. The samples were cleaned using Ar\(^+\) sputtering at 500 eV for 8 mins on powders and 20 mins on ceramics, and both the cross-section exposed to atmosphere and the cross-section in inert atmosphere, had a modified Ar\(^+\) sputtering for 2 mins at 4000 eV and processing before collecting spectra. A spot size of 650 \(\mu\)m was used.

Additional information on preparation and collection specifications are provided in Chapter 3 materials and methods.

Figure 18: CIP’ed samples of Calcium Lanthanum Sulfide 90:10

A survey spectrum was taken for the powder compact for elemental identification of the sample, as seen in Figure 19. The survey scan from 0 to 1300 eV. Because the \textit{in situ} process was done and carbon was
degraded, the survey spectrum was compared to the survey spectrum of the non-processed sample collected at the same time and compared for the peak shift of the processed sample, and with no peak shift, the samples were calibrated to the C 1s to 284.8 eV binding energy. As with previous chapters, high-resolution scans, the fine spectra of sulfur, calcium, and lanthanum can be seen as composites S 2p, Ca 2p, and La 3d, as well as O 1s and C 1s in Figure 20.

Figure 19: XPS Survey spectrums for Calcium Lanthanum Sulfide as CIP’ed coupon.
Figure 20: XPS fine spectrum of Calcium Lanthanum Sulfide 90:10 CIP’ed (A) S 2p fine spectra, (B) Ca 2p fine spectra, (C) La 3d fine spectra, (D) C 1s fine spectra, (E) O 1s fine spectra, (F) Peak Key Table

From Figure 19, we see that in the 90:10 CLS powder sample, the presence of the La 3d peaks along with a peak for sulfur S 2p, O1s, and Ca 2p, but as expected, we do not see a peak for C 1s as carbon is not a
major element present in the sample. Still, we can see the intensity differences between the calibration curve and the 90:10 CLS powder, as evidenced by the very weak intensity of the Ca 2p peak. Although we can see the changes in peak intensity, shape, and width, these changes do not have the resolution that can be seen in the fine spectra.

Because of spatial resolution in survey spectra, fine spectra are used to quantify the atomic percentage. Calculations are better done internally through the Thermo Scientific software, to the detriment of what the experimental calculations are as compared to the calibration data. The Thermo Scientific Advantage software internal library and sensitivity factors are used to accurately determine the atomic percentage of the major elements for analysis. From Figure 20, the fine spectra for sulfur, calcium, and lanthanum, we can see each element’s primary peak positions and shapes along with oxygen and carbon. From Figure 20 (A), we see sulfur fine spectra. We can deconvolute two sets of peaks the lower binding energy peaks I belonging to the metal sulfide and the higher binding energy peaks II belonging to the poly sulfur metal sulfide[167]. This poly sulfur metal sulfide can result from sulfurization and excess sulfur added into the powder production. Figure 20(B) shows the Ca 2p fine spectra from the low resolution. We can only deconvolute a single set of peaks identified as CaS bonding. Figure 20 (C) shows the La 3d peaks at high resolution. These peaks can be broken down into La 3d 5/2 and La 3d 3/2; for this analysis, we will focus on La 3d 5/2. The La 3d 5/2 has 3 components, the lower binding energy peak VI being the main La 5/2 peak, the middle deconvoluted peak VII the antibonding peak, and the higher binding energy peak V representing the bonding peak[168]. Figure 20 (D) shows the C 1s peak with the weakest intensity. Still, it can be seen as two peaks a low binding energy X representing carbon-carbon bonding and a higher binding energy peak XI representing the carbonate/ carboxyl bonding. Figure 20 (E) shows the O 1s peak with a relatively high intensity for an element that is not a major component of the material. The O 1s
have two peaks the lower binding energy peak XII representing the bonding with La, and the higher
binding energy peak XIII representing Hydroxide / Other Oxygen[106, 160, 176].

The fine spectra are used to calculate peak position and atomic parentage using Thermo Scientific
Advantage software for each spectrum collected. For the 90:10 CLS powder sample, all peaks shown
were used for atomic % calculation following methods shown in Chapter 3 material and methods. Table
13 is the deconvoluted spectral features table and details the peak energy at.% concentration and peak
assignments for all peaks in Figure 20 (A-F).

Table 13: Calcium Lanthanum Sulfide 90:10 CIP’ed Deconvoluted Spectrum ID, Peak Energy, Peak Width
FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor, Concentration (at.%), and Peak Assignment.

<table>
<thead>
<tr>
<th>Figure Label</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV x cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D)</td>
<td>C1s X</td>
<td>284.98</td>
<td>3.37</td>
<td>842.49</td>
<td>1</td>
<td>3.04</td>
<td>C-C</td>
</tr>
<tr>
<td>(D)</td>
<td>C1s XI</td>
<td>290.22</td>
<td>3.37</td>
<td>514.22</td>
<td>1</td>
<td>...</td>
<td>Carbonates/Carboxyl</td>
</tr>
<tr>
<td>(B)</td>
<td>Ca2p 3/2 III</td>
<td>346.69</td>
<td>2.15</td>
<td>1050.18</td>
<td>3.94</td>
<td>1.9</td>
<td>CaS</td>
</tr>
<tr>
<td>(B)</td>
<td>Ca2p 1/2 IV</td>
<td>350.29</td>
<td>2.15</td>
<td>539.2</td>
<td>2.02</td>
<td>...</td>
<td>CaS</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 3/2 V</td>
<td>838.12</td>
<td>1.68</td>
<td>56148.41</td>
<td>32.94</td>
<td>40.85</td>
<td>La2S4/ La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5/2 V</td>
<td>854.87</td>
<td>1.68</td>
<td>38936.49</td>
<td>22.58</td>
<td>...</td>
<td>La2S4/ La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5/2 VI</td>
<td>833.53</td>
<td>2.14</td>
<td>46716.61</td>
<td>32.94</td>
<td>...</td>
<td>La2S4/ La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5/2 VII</td>
<td>850.43</td>
<td>2.14</td>
<td>32395.94</td>
<td>22.58</td>
<td>...</td>
<td>La2S4/ La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5/2 VIII</td>
<td>835.92</td>
<td>3.37</td>
<td>53880.91</td>
<td>32.94</td>
<td>...</td>
<td>La2S4/ La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5/2 VII</td>
<td>852.52</td>
<td>3.37</td>
<td>37364.07</td>
<td>22.58</td>
<td>...</td>
<td>La2S4/ La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d VIII</td>
<td>847.39</td>
<td>4.96</td>
<td>28053.61</td>
<td>55.53</td>
<td>...</td>
<td>Plasmon</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d IX</td>
<td>862.7</td>
<td>14.06</td>
<td>90959.54</td>
<td>55.53</td>
<td>...</td>
<td>Plasmon</td>
</tr>
<tr>
<td>(E)</td>
<td>O1s XII</td>
<td>529.05</td>
<td>1.33</td>
<td>5989.06</td>
<td>2.88</td>
<td>15.23</td>
<td>La2O3</td>
</tr>
<tr>
<td>(E)</td>
<td>O1s XIII</td>
<td>531.01</td>
<td>1.93</td>
<td>5716.17</td>
<td>2.88</td>
<td>...</td>
<td>Hydroxide/ Other Oxygen</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p3/2 I</td>
<td>160.96</td>
<td>1.58</td>
<td>5217.74</td>
<td>1.24</td>
<td>38.98</td>
<td>Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p3/2 I</td>
<td>162.06</td>
<td>1.58</td>
<td>2665.28</td>
<td>0.63</td>
<td>...</td>
<td>Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p3/2 II</td>
<td>162.12</td>
<td>1.41</td>
<td>1882.29</td>
<td>1.24</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p3/2 II</td>
<td>163.26</td>
<td>1.42</td>
<td>961.5</td>
<td>0.63</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
</tbody>
</table>

7.2.2 Sintered coupon – Surface Analysis

Ceramic analysis by XPS was conducted on a sintered Ceramic 90:10 CLS sample attached to carbon tape
Figure 21. The ceramic surface top and bottom have been polished with alumina slurry, as illustrated in
Appendix D. The wet polishing leaves alumina oxide polishing media on the ceramic surfaces. The
surface contamination from the polishing media is one of the main needs for sonically cleaning the
ceramics before loading into the XPS. In the previous sample not sonically cleaned, the presence of aluminum can be seen in the spectra before Ar+ sputtering. The samples had *in situ* via Ar+ sputtering at 500 eV for 20 mins. A spot size of 650 μm was used for additional information on preparation and collection specifications in Chapter 3 materials and methods.

**Figure 21:** Sintered Hot Pressed Samples of Calcium Lanthanum Sulfide 90:10

A survey spectrum was taken for the sintered ceramic coupon for elemental identification of the sample, as seen in Figure 22. The survey scan from 0 to 1300 eV is shown in Figure 22. As with powder samples, because the in-situ process was done and carbon was degraded, the survey spectrum was compared to the survey spectrum of the non-processed sample collected at the same time and compared for the peak shift of the processed sample, and with no peak shift, the samples were calibrated to the C 1s to 284.8 eV binding energy. The survey was analyzed for the unique peaks because each element has a unique binding energy that can be identified. The survey found peaks that could be identified as lanthanum, calcium, sulfur, and oxygen. As with previous chapters, high-resolution scans, the fine
spectra of sulfur, calcium, lanthanum, carbon, and oxygen can be seen as composites S 2p, Ca 2p, and La 3d, C 1s, and O 1s in Figure 26.

Figure 22: XPS Survey Spectrum for Calcium Lanthanum Sulfide 90:10 Sintered Hot Pressed Coupon.
Figure 23: XPS fine spectrum of Calcium Lanthanum Sulfide 90:10 Hot Pressed Sintered Sample (A) S 2p fine spectra, (B) Ca 2p fine spectra, (C) La 3d fine spectra, (D) C 1s fine spectra, (E) O 1s fine spectra, (F) Peak Key Table

From Figure 22, we see that in the 90:10 CLS Sintered Ceramic sample, the presence of the La 3d peaks along with a peak for sulfur S 2p, O1s, and Ca 2p, but as expected, we do not see a peak for C 1s as
carbon is not a major element present in the sample. Still, we can see the intensities differences between the calibration curve and the 90:10 CLS powder and 90:10 CLS sintered ceramic, as evidenced by the slightly stronger intensity of the Ca 2p peak similar in intensity and size to the calibration curve 90:10 mixture.

From Figure 23, the fine spectra for sulfur, calcium, and lanthanum, we can see each element's primary peak positions and shapes along with carbon and oxygen. From Figure 23 (A), we see sulfur fine spectra with a significant peak shape changed compared to Figure 20 (A). We can deconvolute two sets of peaks, the lower binding energy peaks II belonging to the metal sulfide and the higher binding energy peaks I belonging to the poly sulfur metal sulfide, a flip from what was seen in the powder compact. Additionally, we see a more defined spin-orbit splitting (SOS) in the peak shape. This poly sulfur metal sulfide can result from a high heat process and the loss of sulfur along with the rearrangement of bonds resulting in more of the metal sulfide being closer to other sulfur bonds.

Figure 23(B) shows the Ca 2p fine spectra from the low resolution. We can only deconvolute a single set of peaks identified as CaS bonding. Unlike the powder, we have higher resolution and intensity, evident by the greater definition of the plasmon and the higher counts. Figure 23 (C) shows the La 3d peaks at high resolution. As with the powder, we will follow the same peak analysis tend. The La 3d 5/2 has 3 components, the lower binding energy peak VI being the main La 5/2 peak, the middle deconvoluted peak VII the antibonding peak, and the higher binding energy peak V representing the bonding peak [168]. Figure 26 (D) shows the C 1s peak with the weakest intensity. Still, it can be seen as two peaks a low binding energy X representing carbon-carbon bonding and a higher binding energy peak XI representing the carbonate/carboxyl bonding. Figure 23 (E) shows the O 1s peak with a relatively high intensity and a strong La-O bonding peak. The relative at.% of the La-O peak for the powder and ceramic showed 0.2% difference.
The fine spectra are used to calculate peak position and atomic parentage using Thermo Scientific Advantage software for each spectrum collected. For the 90:10 CLS ceramic, we followed the same protocol as the 90:10 CLS powder sample. Table 14 is the deconvoluted spectral features table and details the peak energy at.% concentration and peak assignments for all peaks in Figure 23 (A-F).

**Table 14: Calcium Lanthanum Sulfide 90:10 Sintered Ceramic Deconvoluted Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor, Concentration (at.%), and Peak Assignment.**

<table>
<thead>
<tr>
<th>Figure Label</th>
<th>Element/Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV x cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at.%)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D)</td>
<td>C1s X</td>
<td>284.93</td>
<td>3.37</td>
<td>1575.23</td>
<td>1</td>
<td>3.06</td>
<td>C-C</td>
</tr>
<tr>
<td>(D)</td>
<td>C1s XI</td>
<td>286.81</td>
<td>3.37</td>
<td>756.73</td>
<td>1</td>
<td>...</td>
<td>Carbonates/Carboxyl</td>
</tr>
<tr>
<td>(E)</td>
<td>Ca2p 3d III</td>
<td>346.68</td>
<td>2.02</td>
<td>2197.18</td>
<td>3.944</td>
<td>1.48</td>
<td>CaS</td>
</tr>
<tr>
<td>(E)</td>
<td>Ca2p 3d IV</td>
<td>350.16</td>
<td>2.02</td>
<td>1128.1</td>
<td>2.027</td>
<td>...</td>
<td>CaS</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d V</td>
<td>836.03</td>
<td>1.83</td>
<td>139786.83</td>
<td>32.944</td>
<td>41.42</td>
<td>La2O3/La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d V</td>
<td>854.70</td>
<td>1.83</td>
<td>96935.47</td>
<td>22.588</td>
<td>...</td>
<td>La2O3/La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d VI</td>
<td>833.5</td>
<td>2.17</td>
<td>144991.59</td>
<td>32.944</td>
<td>...</td>
<td>La2O3/La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d VI</td>
<td>850.30</td>
<td>2.17</td>
<td>106545.65</td>
<td>22.588</td>
<td>...</td>
<td>La2O3/La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d VII</td>
<td>836.04</td>
<td>3.37</td>
<td>139520.65</td>
<td>32.944</td>
<td>...</td>
<td>La2O3/La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d VII</td>
<td>852.64</td>
<td>3.37</td>
<td>96751.1</td>
<td>22.588</td>
<td>...</td>
<td>La2O3/La2O3</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d VIII</td>
<td>847.62</td>
<td>5.42</td>
<td>81038.66</td>
<td>55.532</td>
<td>...</td>
<td>Plasmon</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d IX</td>
<td>862.57</td>
<td>14.06</td>
<td>260244.87</td>
<td>55.532</td>
<td>...</td>
<td>Plasmon</td>
</tr>
<tr>
<td>(E)</td>
<td>O1s XII</td>
<td>528.53</td>
<td>1.33</td>
<td>164127.71</td>
<td>2.881</td>
<td>16.71</td>
<td>La2O3</td>
</tr>
<tr>
<td>(E)</td>
<td>O1s XIII</td>
<td>530.9</td>
<td>1.86</td>
<td>17910.95</td>
<td>2.881</td>
<td>...</td>
<td>Hydroxide/Other Oxygen</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p 3/2 I</td>
<td>161.57</td>
<td>1.06</td>
<td>12596.45</td>
<td>1.245</td>
<td>37.32</td>
<td>Poly Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p 3/2 I</td>
<td>162.82</td>
<td>1.06</td>
<td>6434.4</td>
<td>0.836</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p 3/2 II</td>
<td>180.53</td>
<td>1.06</td>
<td>6556.01</td>
<td>1.245</td>
<td>...</td>
<td>Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p 3/2 II</td>
<td>161.83</td>
<td>1.06</td>
<td>2838.53</td>
<td>0.638</td>
<td>...</td>
<td>Metal Sulfide</td>
</tr>
</tbody>
</table>

**7.2.4 XPS of sintered ceramic cross-section exposed to ambient**

Ceramic fracture in ambient analysis by XPS was conducted on a Sintered Ceramic 90:10 CLS Fractured in an Ambient sample attached to carbon tape Figure 24. The samples had in situ via Ar+ sputtering at 4000 eV for 2 minutes. A spot size of 650 µm was used for additional information on preparation and collection specifications in Chapter 3, materials and methods.
A survey spectrum was taken for the ambient fracture sintered ceramic coupon for elemental identification of the sample, as seen in Figure 24. The survey scan from 0 to 1300 eV is shown in Figure 24. Charge correction was done the same manner as with the previous ceramic sample because the in-situ process was done, and carbon was degraded. The sample was calibrated to the C 1s to 284.8 eV binding energy. The survey found peaks that could be identified as lanthanum, calcium, sulfur, and oxygen.

High-resolution scans, the fine spectra of sulfur, calcium, lanthanum, carbon, and oxygen can be seen as composites S 2p, Ca 2p, and La 3d, C 1s, and O 1s in Figure 25.
Figure 25: XPS Survey Spectrum for Ambient Fracture of Sintered Hot Pressed Sample of Calcium Lanthanum Sulfide 90:10
Figure 26: XPS fine spectrum of Calcium Lanthanum Sulfide 90:10 Hot Pressed Sintered Fractured in Ambient Conditions Sample (A) S 2p fine spectra, (B) Ca 2p fine spectra, (C) La 3d fine spectra, (D) C 1s fine spectra, (E) O 1s fine spectra, (F) Peak Key Table

From Figure 24, we see that in the ambient fracture of a sintered sample of CLS 90:10, the presence of the La 3d peaks along with a peak for sulfur S 2p, O1s, and Ca 2p, but as expected, we do not see a peak for C 1s. Compared to the 90:10 CLS Ceramic, the fracture sample has a less intense O 1s peak in the survey.

Figure 26 (A) shows sulfur fine spectra with a significant peak shape change compared to Figure 23 (A). We can deconvolute three sets of peaks, the lower binding energy peaks II belonging to the poly sulfur metal sulfide and the higher binding energy peaks I belonging to the poly sulfur metal sulfide, along with a third set of peaks higher on the binding energy than in the previous scans also belong to a third type of poly sulfur metal sulfide bond[167]. These poly sulfur metal sulfides can result from a thermal process resulting in loss of sulfur along with the rearrangement of bonds, causing more of the cations being closer to other sulfur bonds.

Figure 26 (B) Ca 2p shows little change compared to previous ceramic spectra. Figure 26 (C) shows the La 3d peaks at high resolution. We will follow the same peak analysis trend as the previous ceramic spectra.

<table>
<thead>
<tr>
<th>Peak Key</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Poly Metal Sulfide</td>
</tr>
<tr>
<td>II Poly Metal Sulfide</td>
</tr>
<tr>
<td>III Poly Metal Sulfide</td>
</tr>
<tr>
<td>IV CaS</td>
</tr>
<tr>
<td>V CaS</td>
</tr>
<tr>
<td>VI La2S5/ La2O3</td>
</tr>
<tr>
<td>VII La2S5/ La2O3</td>
</tr>
<tr>
<td>VIII La2S5/ La2O3</td>
</tr>
<tr>
<td>IX Plasmons</td>
</tr>
<tr>
<td>X Plasmons</td>
</tr>
<tr>
<td>XI Carbon-Carbon</td>
</tr>
<tr>
<td>XII Carbonate/Carboxyl</td>
</tr>
<tr>
<td>XIII La2O3</td>
</tr>
<tr>
<td>XIV Hydroxide / Other Oxygen</td>
</tr>
</tbody>
</table>
The La 3d 5/2 has 3 components, the lower binding energy peak VII being the main La 5/2 peak, the middle deconvoluted peak VIII the antibonding peak, and the higher binding energy peak VI representing the bonding peak [168, 169]. We see some slight visual changes to the peak morphology compared to the 90:10 powder and ceramic. This set of La 3d 5/2 peaks has a noticeable height difference in the lower binding energy peak compared to the higher binding energy peak. Figure 26 (D) shows the C 1s as the weakest peak, two peaks with lower binding energy XI for carbon-carbon bonding, and the higher binding energy peak XII for carbonates/ carboxyl. Figure 26 (E) shows the O 1s peak is visibly less intense than the previous ceramic sample and has the lower contribution of other oxygen peaks XIII and La-O bonding peak XIII representing a total oxygen concentration lower than in previous samples.

The fine spectra are used to calculate peak position and atomic parentage using Thermo Scientific Advantage software for each spectrum collected. For the Ambient Fracture 90:10 CLS ceramic, we followed the same protocol as the 90:10 CLS sintered ceramic sample. Table 15 is the deconvoluted spectral features table and details the peak energy at.% concentration and peak assignments for all peaks in Figure 26 (A-F)
Table 15: Ambient Fracture Calcium Lanthanum Sulfide 90:10 Sintered Ceramic Deconvoluted Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor, Concentration (at.%), and Peak Assignment

<table>
<thead>
<tr>
<th>Figure Label</th>
<th>Element/ Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV x cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D)</td>
<td>C1s XI</td>
<td>285.1</td>
<td>3.34</td>
<td>2169.97</td>
<td>1</td>
<td>6.71</td>
<td>C-C</td>
</tr>
<tr>
<td>(D)</td>
<td>C1s XII</td>
<td>290.91</td>
<td>3.37</td>
<td>831.93</td>
<td>1</td>
<td>...</td>
<td>Carbonates/Carboxyl</td>
</tr>
<tr>
<td>(E)</td>
<td>Ca2p 3/2 IV</td>
<td>347.26</td>
<td>2.46</td>
<td>1538.94</td>
<td>3.944</td>
<td>1.78</td>
<td>CaS</td>
</tr>
<tr>
<td>(E)</td>
<td>Ca2p 1/2 V</td>
<td>350.66</td>
<td>2.46</td>
<td>790.15</td>
<td>2.027</td>
<td>...</td>
<td>CaS</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 3/2 VI</td>
<td>838.57</td>
<td>2.21</td>
<td>96234.64</td>
<td>32.944</td>
<td>41.8</td>
<td>La₂S₂/La₂O₃</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 1/2 VII</td>
<td>834.35</td>
<td>2.53</td>
<td>102084.5</td>
<td>32.944</td>
<td>...</td>
<td>La₂S₂/La₂O₃</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 3/2 VII</td>
<td>851.23</td>
<td>2.53</td>
<td>701079.21</td>
<td>22.588</td>
<td>...</td>
<td>La₂S₂/La₂O₃</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 1/2 VIII</td>
<td>836.69</td>
<td>2.47</td>
<td>52959.34</td>
<td>32.944</td>
<td>...</td>
<td>La₂S₂/La₂O₃</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 3/2 VIII</td>
<td>853.43</td>
<td>2.47</td>
<td>36725.01</td>
<td>22.588</td>
<td>...</td>
<td>La₂S₂/La₂O₃</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 1/2 IX</td>
<td>846.48</td>
<td>6.35</td>
<td>52896.41</td>
<td>55.532</td>
<td>...</td>
<td>Plasmon</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d X</td>
<td>882.09</td>
<td>14.62</td>
<td>147880.5</td>
<td>55.532</td>
<td>...</td>
<td>Plasmon</td>
</tr>
<tr>
<td>(E)</td>
<td>O1s XII</td>
<td>526.66</td>
<td>1.21</td>
<td>7527.19</td>
<td>2.831</td>
<td>12.84</td>
<td>La₂O₃</td>
</tr>
<tr>
<td>(E)</td>
<td>O1s XIV</td>
<td>531.74</td>
<td>1.77</td>
<td>7947.05</td>
<td>2.831</td>
<td>...</td>
<td>Hydroxide/ Other Oxygen</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p1/2 I</td>
<td>161.51</td>
<td>0.54</td>
<td>1016.19</td>
<td>1.245</td>
<td>36.88</td>
<td>Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p3/2 I</td>
<td>163.1</td>
<td>0.54</td>
<td>519.08</td>
<td>0.836</td>
<td>...</td>
<td>Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p5/2 II</td>
<td>151.63</td>
<td>1.39</td>
<td>6028.52</td>
<td>1.245</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p3/2 II</td>
<td>152.74</td>
<td>1.39</td>
<td>4101.06</td>
<td>0.636</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p5/2 III</td>
<td>163.35</td>
<td>1.37</td>
<td>1484.12</td>
<td>1.245</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p1/2 III</td>
<td>164.65</td>
<td>1.37</td>
<td>758.11</td>
<td>0.636</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
</tbody>
</table>

7.2.4 XPS of sintered ceramic cross-section inert atmosphere

XPS was conducted on a sintered ceramic 90:10 CLS fractured in an inert atmosphere sample attached to carbon tape. For this sample, the fracture was conducted in an inert atmosphere glove box that was then transferred in an inert atmosphere transfer chamber and finally transferred into the antechamber of the ESCALAB Xi⁺ XPS, as seen in Figure 7. The samples had in situ via Ar+ sputtering at 4000 eV for 2mins. A spot size of 650 µm was used for additional information on preparation and collection specifications in Chapter 3, materials and methods.

A survey spectrum was taken for the ambient fracture long-hold hot-pressed ceramic coupon for elemental identification of the sample, as seen in Figure 27. The survey scan from 0 to 1300 eV is shown
in Figure 27. Charge correction was done in the same manner as with the previous ceramic sample because the in-situ process was done, and carbon was degraded. The sample was calibrated to the C 1s to 284.8 eV binding energy. The survey was analyzed for the unique peaks because each element has a unique binding energy that can be identified. The survey found peaks that could be identified as lanthanum, calcium, sulfur, and oxygen. As with previous chapters, high-resolution scans show the fine spectra of sulfur, calcium, lanthanum, carbon, and oxygen in S 2p, Ca 2p, and La 3d, C 1s, and O 1s in Figure 28.
Figure 27: XPS Survey Spectrum for Inert Atmosphere Fracture of Sintered Hot-Pressed Sample of Calcium Lanthanum Sulfide 90:10
Figure 28: XPS fine spectrum of Calcium Lanthanum Sulfide 90:10 Hot Pressed Sintered Fractured in Inert Atmosphere Conditions Sample (A) S 2p fine spectra, (B) Ca 2p fine spectra, (C) La 3d fine spectra, (D) C 1s fine spectra, (E) O 1s fine spectra, (F) Peak Key Table

From Figure 27, we see inside the bulk of the sample that has never been exposed to ambient oxygen or moisture, the presence of the La 3d peaks along with a peak for sulfur S 2p, O 1s, and Ca 2p, but like with other samples we still do not see the C 1s peak in the survey spectra. This sample has the least intense O 1s peak in the survey spectrum.

From Figure 28, the fine spectra show visual peak shape changes for sulfur and oxygen BE shifts, while calcium and lanthanum look like previous scans. The peak for oxygen and carbon also has visual peak changes. Figure 28 (A) shows sulfur fine spectra with no significant peak shape change compared to Figure 26 (A), yet deconvolution shows the II peak moving back to metal sulfide. This shift could be regionally specific as the coupons are not homogeneous. We can deconvolute three sets of peaks, the lower binding energy peaks II belonging to the metal sulfide and the higher binding energy peaks I belonging to the poly sulfur metal sulfide, along with a third set of peaks higher on the binding energy than in the previous scans also belong to a third type of poly sulfur metal sulfide bond. Figure 28(B) Ca 2p shows little change compared to previous ceramic spectra. Figure 28 (C) shows the La 3d peaks at high resolution. We will follow the same peak analysis trend as the previous ceramic spectra. The La 3d
5/2 has 3 components, the lower binding energy peak VII being the main La 5/2 peak, the middle deconvoluted peak VIII the antibonding peak, and the higher binding energy peak VI representing the bonding peak[168, 176]. We see larger visual changes to the peak morphology compared to the 90:10 powder and ceramic. This set of La 3d 5/2 peaks has a noticeable height difference in the lower binding energy peak compared to the higher binding energy peak.

Figure 28 (D) shows the C 1s as the weakest peak, a single peak XI at the lower binding energy for carbon-carbon bonding. Figure 28 (E) shows that the O 1s peak is less intense than the previous ceramic sample. The O 1s has three distinct peaks. A peak labeled XIII shows a lower contribution of other oxygen. While the third peak at the higher binding energy XIV at 532.47 eV can be identified as hydroxide bonding. Also, peak XII the peak with the lowest binding energy peak, is attributed to the La-O bonding peak and is at a lower concentration than in previous samples. While looking at the O 1s, the three peaks represent a total oxygen concentration lower than in previous samples totaling 7.74 at.%

As with the previous Chapter, the fine spectra are used to calculate peak position and atomic parentage using Thermo Scientific Advantage software for each spectrum collected. For the Inert Atmosphere Fracture 90:10 CLS ceramic, we followed the same protocol as the 90:10 CLS sintered ceramic sample. Table 16 is the deconvoluted spectral features table and details the peak energy at% concentration and peak assignments for all peaks in Figure 28 (A-F)
Table 16: Inert Atmosphere Fracture Calcium Lanthanum Sulfide 90:10 Sintered Ceramic Deconvoluted Spectrum ID, Peak Energy, Peak Width FWHM (eV), Peak Area (eV x cts/s), Sensitivity Factor, Concentration (at.%), and Peak Assignment

<table>
<thead>
<tr>
<th>Figure Label</th>
<th>Element/ Transition</th>
<th>Peak Energy (eV)</th>
<th>Peak Width FWHM (eV)</th>
<th>Peak Area (eV x cts/s)</th>
<th>Sensitivity Factor</th>
<th>Concentration (at. %)</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D)</td>
<td>C1s XI</td>
<td>284.78</td>
<td>2.88</td>
<td>1161.66</td>
<td>1</td>
<td>2.49</td>
<td>C-C</td>
</tr>
<tr>
<td>(B)</td>
<td>Ca2p 3d IV</td>
<td>346.59</td>
<td>2.46</td>
<td>1509.51</td>
<td>3.94</td>
<td>1.66</td>
<td>CaS</td>
</tr>
<tr>
<td>(B)</td>
<td>Ca2p 3d V</td>
<td>350.19</td>
<td>2.46</td>
<td>775.03</td>
<td>2.02</td>
<td>...</td>
<td>CaS</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d VI</td>
<td>837.57</td>
<td>2.24</td>
<td>10785.16</td>
<td>32.94</td>
<td>40.17</td>
<td>La₄S/ La₂O₃</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d VI</td>
<td>854.41</td>
<td>2.24</td>
<td>74790.41</td>
<td>22.58</td>
<td>...</td>
<td>La₄S/ La₂O₃</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d VII</td>
<td>833.49</td>
<td>2.54</td>
<td>98213.37</td>
<td>32.94</td>
<td>...</td>
<td>La₄S/ La₂O₃</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d VII</td>
<td>850.42</td>
<td>2.54</td>
<td>68106.71</td>
<td>22.58</td>
<td>...</td>
<td>La₄S/ La₂O₃</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 5d VIII</td>
<td>835.73</td>
<td>2.27</td>
<td>46517.11</td>
<td>32.94</td>
<td>...</td>
<td>La₄S/ La₂O₃</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 3d VIII</td>
<td>852.62</td>
<td>2.27</td>
<td>32257.6</td>
<td>22.58</td>
<td>...</td>
<td>La₄S/ La₂O₃</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d 3d IX</td>
<td>847.89</td>
<td>6.73</td>
<td>57731.03</td>
<td>55.32</td>
<td>...</td>
<td>Plasmon</td>
</tr>
<tr>
<td>(C)</td>
<td>La3d X</td>
<td>862.19</td>
<td>13.79</td>
<td>142669.6</td>
<td>55.32</td>
<td>...</td>
<td>Plasmon</td>
</tr>
<tr>
<td>(E)</td>
<td>O1s XII</td>
<td>528.74</td>
<td>1.08</td>
<td>3573.85</td>
<td>2.88</td>
<td>7.74</td>
<td>La₂O₃</td>
</tr>
<tr>
<td>(E)</td>
<td>O1s XIII</td>
<td>530.75</td>
<td>1.34</td>
<td>5622.04</td>
<td>2.88</td>
<td>...</td>
<td>Hydroxide/ Other Oxygen</td>
</tr>
<tr>
<td>(E)</td>
<td>O1s XIV</td>
<td>532.47</td>
<td>1.65</td>
<td>5715.54</td>
<td>2.88</td>
<td>...</td>
<td>Hydroxide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p 3d II</td>
<td>160.44</td>
<td>0.93</td>
<td>3076.55</td>
<td>1.24</td>
<td>47.94</td>
<td>Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p 1s II</td>
<td>161.54</td>
<td>0.93</td>
<td>1571.53</td>
<td>0.63</td>
<td>...</td>
<td>Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p 3d I</td>
<td>161.1</td>
<td>0.94</td>
<td>8829.96</td>
<td>1.24</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p 1s I</td>
<td>162.2</td>
<td>0.94</td>
<td>4510.44</td>
<td>0.63</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p 3d III</td>
<td>162.57</td>
<td>1.34</td>
<td>2404.82</td>
<td>1.24</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
<tr>
<td>(A)</td>
<td>S2p 1s III</td>
<td>163.67</td>
<td>1.34</td>
<td>1228.41</td>
<td>0.63</td>
<td>...</td>
<td>Poly Metal Sulfide</td>
</tr>
</tbody>
</table>

7.2.5 XPS of sintered ceramic cross-section in the atmosphere and inert atmosphere depth profile

In the previous section, the study focused on a single center point from each cross-section. For each cross-section, we collected points from the top to the bottom. The data consists of a depth profile for each sample. The details of the depth profiles have been collated in Table 17 and presented in Figure 29.

The trend is that there is a greater concentration of oxygen and carbon on the ceramic surfaces exposed to ambient conditions. Because carbon can be seen as more of an elemental contaminant not participating in the matrix, it has also been removed from both data sets. The oxygen concentration in
the samples increases from the initial powder sample to the surface of the ceramic. The trend in the oxygen concentration also shows that as depth increases in the ceramic, the oxygen concentration lowers, as seen in Figure 29.

Table 17: Ambient Atmosphere & Inert Atmosphere Fracture Calcium Lanthanum Sulfide 90:10 Sintered Ceramic atomic % table based on the spot in the cross-section with and without carbon quantification, (A) Ambient Atmosphere Fracture Sintered CLS 90:10 Cross-section at. % table (B) Inert Atmosphere Fracture Sintered CLS 90:10 Cross-section at. % table

(A)

<table>
<thead>
<tr>
<th>Sample</th>
<th>at.% Ca</th>
<th>at.% La</th>
<th>at.% S</th>
<th>at.% O</th>
<th>at.% C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long Hold Bottom Inert</td>
<td>1.7</td>
<td>43.69</td>
<td>32.72</td>
<td>18.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Long Hold Middle Bottom Inert</td>
<td>1.58</td>
<td>42.66</td>
<td>40.2</td>
<td>12.21</td>
<td>3.36</td>
</tr>
<tr>
<td>Long Hold Center Inert</td>
<td>1.78</td>
<td>41.85</td>
<td>36.84</td>
<td>12.82</td>
<td>6.71</td>
</tr>
<tr>
<td>Long Hold Middle Top Inert</td>
<td>1.7</td>
<td>39.85</td>
<td>43.35</td>
<td>8.52</td>
<td>6.57</td>
</tr>
<tr>
<td>Long Hold Top Inert</td>
<td>1.88</td>
<td>35.97</td>
<td>40.02</td>
<td>9.18</td>
<td>12.96</td>
</tr>
<tr>
<td>Long Hold Surface Ambient</td>
<td>1.48</td>
<td>41.42</td>
<td>37.32</td>
<td>16.71</td>
<td>3.06</td>
</tr>
<tr>
<td>Green Powder Ambient</td>
<td>1.9</td>
<td>40.85</td>
<td>38.98</td>
<td>15.23</td>
<td>3.04</td>
</tr>
<tr>
<td>Theoretical (90:10)</td>
<td>2.13</td>
<td>38.3</td>
<td>59.57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(B)

<table>
<thead>
<tr>
<th>Sample</th>
<th>at.% Ca</th>
<th>at.% La</th>
<th>at.% S</th>
<th>at.% O</th>
<th>at.% C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long Hold Bottom Inert</td>
<td>1.78</td>
<td>40.89</td>
<td>48.32</td>
<td>7.76</td>
<td>1.26</td>
</tr>
<tr>
<td>Long Hold Middle Bottom Inert</td>
<td>1.72</td>
<td>41.69</td>
<td>47.11</td>
<td>7.68</td>
<td>1.8</td>
</tr>
<tr>
<td>Long Hold Center Inert</td>
<td>1.66</td>
<td>40.17</td>
<td>47.94</td>
<td>7.74</td>
<td>2.49</td>
</tr>
<tr>
<td>Long Hold Middle Top Inert</td>
<td>1.9</td>
<td>41.32</td>
<td>46.48</td>
<td>8.55</td>
<td>1.75</td>
</tr>
<tr>
<td>Long Hold Top Inert</td>
<td>2.1</td>
<td>40.28</td>
<td>45.4</td>
<td>8.53</td>
<td>3.68</td>
</tr>
<tr>
<td>Long Hold Surface Ambient</td>
<td>1.48</td>
<td>41.42</td>
<td>37.32</td>
<td>16.71</td>
<td>3.06</td>
</tr>
<tr>
<td>Green Powder Ambient</td>
<td>1.9</td>
<td>40.85</td>
<td>38.98</td>
<td>15.23</td>
<td>3.04</td>
</tr>
<tr>
<td>Theoretical (90:10)</td>
<td>2.13</td>
<td>38.3</td>
<td>59.57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Theoretical (90:10)
The depth profile also shows the inverse correlation of sulfur and oxygen. As oxygen increases in the system, sulfur is depleted, and as oxygen decreases in the system, sulfur increases in concentration. Looking back at fine spectra for the CLS CIP’ed and CLS ceramic in this chapter, these conclusions are also corroborated as we see that in lanthanum fine spectra, the La 3d 5/2 lower BE ~838 eV indicates bonding with oxygen along with in O1s BE peak at ~529 eV are indicative of binding with lanthanum\[168-170, 176, 182\].

### 7.2.6 Summary of results of fine spectra results

The XPS results presented in this chapter demonstrate the chemical composition and bonding state of CLS 90:10, a comparison of CIP’ed powder sample, sintered Ceramic, ambient fractured ceramic, and inert atmospheres fracture ceramic. We also present the results of depth profiles for ambient fractured ceramic and inert atmospheres fracture ceramic. The XPS spectra showed the presence of CLS as the main component of the powder and the presence of lanthanum oxide as more than trace amounts, even though an Ar⁺ sputter was done per the protocols listed in Chapter 3 for powder, ceramics, and fractures.
In the La peak La 3d 5/2 higher binding energy peak of ~838.00 eV, which is associated with sulfide, and the lower binding energy peak at 833.50 eV corresponds to lanthanum oxide in literature[108, 110, 169, 170, 172-176]. The main line peak at ~838.00 eV indicates an oxide bond consistent with the mixed phase of lanthanum bound to sulfur and oxygen[108, 110]. While looking at the La 3d 5/2, we have a distance of ~ 4.50 eV between the mainline peak and the satellite peak, consistent with the literature on the separation identified in lanthanum oxysulfide [108, 110, 169, 170, 172-176].

We looked at the S 2p 3/2 spectra for the CLS powders, and ceramics showed peaks at ~160.50 eV, ~161.50 eV, and a third set of peaks for the fractures in the ~162.60 eV range, indicating both metal sulfide and poly sulfur metal sulfides[111]. These peak BE at ~160.50 eV indicate metal sulfide, with the higher BE peak at ~161.50 eV and ~162.60 eV indicating a more sulfur-rich metal sulfide, that is referred to as poly sulfur metal sulfide. These BE energies are not yet in the range for sulfite (165.75-167.5 eV), or sulfate (168.75-171.50 eV) as predicted in other papers on CLS[37, 93, 102, 104, 110].

Thirdly, looking at the O 1s spectra, we see three peaks—the lower binding peak of ~528.00 eV, assigned to oxygen-lanthanum bonding. A second peak at ~530.00 eV can be attributed to other oxygen or a hydroxide-boding environment, and the highest of the binding energy peaks at ~532.00 eV as carboxyl/carbonate surface contamination[108, 110, 169, 170, 172-176]. Furthermore, C 1s spectra confirm the presence of carbonate, carboxyl, and adventitious carbons, as seen in Chapter 5.

7.3 Discussion CALCIUM LANTHANUM SULFIDE 90:10

Throughout this chapter, we have reviewed CLS 90:10 samples in several forms and collected data on the at% of each element Ca, La, S, O, and C. With the data collected from the fine spectra different trends can be seen by compiling the data into plots. The elemental information for the CIP’ed,
Sintered Surface, Sintered cross-section ambient, and Sintered cross-section inert atmosphere can be seen in Figure 30.

![Graph of atomic percent by element for CLS 90:10 Green, Sintered, Ambient Fracture, and Inert Fracture.]

**Figure 30:** Atomic Percent by Element for CLS 90:10 Green, Sintered, Ambient Fracture, and Inert Fracture

From Figure 30, it is evident that three trends can be seen from C, O and Ca, La. The green CIP’ed powder has a higher concentration of carbon than that of the sintered ceramics and that the carbon concentration may be a function of exposure to the atmosphere. Oxygen concentration is at a baseline from the powder and shows a linear decrease as you compare its exposure to the atmosphere and an inert atmosphere. We have the lowest oxygen concentration in the inert fracture samples. From comparison Ca and La have very little change, however La, the S concentration in depleted La concentration is increased. Another trend that can be seen from Figure 30, is in S and O a clear trend that when S concentration increases, the O concentration decreases.
Earlier in Chapter 5, we discussed the significance of the oxide presence in the $\gamma$-La$_2$S$_3$ powder: simple handling and cleaning protocols cannot manage contamination because the oxide is a more significant majority of the atomic percentage of the material. As we analyze the information from powder to ceramic and from ceramic through cross-section, we evolve as a story that oxygen may readily form an oxide layer with CLS with exposure to ambient conditions and that this layer might be thicker than what XPS is capable of penetrating in the 1-12 nanometers of the surface detection.

7.4 Conclusions

In Chapter 7, we studied CLS 90:10, investigating its chemical structure through XPS analysis and comparison to $\gamma$-La$_2$S$_3$ and CaS powders. We examined CLS 90:10 in various forms, including CIP’ed powder samples and sintered ceramic. XPS analysis revealed the presence of calcium, lanthanum, sulfur, and oxygen, with carbon being more prominent in the sintered surface ceramic samples.

Fine spectra analysis shows the existence of metal sulfide and poly-sulfide bonds and does not show any evidence of sulfites or sulfates. This result indicates that S may be labile and perhaps, not only form bonds with La and Ca but, may form oligomeric chains of closely linked S. This result suggests that S may have some tendency to occupy lanthanum vacancies. Furthermore, and most surprisingly, we find a very high at% O content in the CLS analyzed on the surface even after Ar sputtering at 500 eV for 20 minutes. The fine spectra can be deconvoluted into adsorbed O species at ~ 531 eV – to be expected on any surface, and a clear signature of the O-La bond at 528 eV.

Finally, to understand the origin of the high at% O found on sintered samples, we analyzed cross-sections of both the sintered ceramic samples in ambient and inert atmospheres. This critical experiment revealed that at% O varied significantly between the cross-sections of a CLS which was fractured in ambient vs. one that was fractured and transferred in an inert atmosphere. The implications
of this experiment being that surface oxidation contributed to a fair amount of O in the sample’s XPS analysis. Despite this conclusion, the “center” region of a sample never exposed to ambient showed 7.74 at% O with 2.56 at% O attributed to the O-La bond. This result suggests that CLS (either via powder processing or sintering) has affinity to dissolve O in its lattice, substituting the S in the process and resulting in a stable O-La bond detected via XPS.
CHAPTER 8: CONCLUSION & FUTURE WORK

8.1 Recap of Research Objectives

Through this thesis, we showed XPS to be a technique that can be used to understand the complex bonding environment in CLS. This includes oxygen dissolution and the loss of sulfur. These conclusions are drawn by studying and analyzing elemental fine spectra for Ca, La, C, O and S. The fine spectra analysis is also used to determine the samples' stoichiometry. Initially, we hypothesize that contamination in starting material and material processing results in ceramics that are not fully densified and have inclusions or characteristics that may fall short of meeting optical standards.

However, in the previous chapter, we went through CLS from a starting powder to a finished ceramic. The investigation continued through the cross-section of the ceramic to investigate the changes that arise from the sintering process. From our investigation the question of is the impurities part of the starting material and are they brought through the process. The results of this investigation clearly show that several bonding states exist in the CLS 90:10 not previously identified. The presence of higher concentration of metal sulfide bonds vs poly sulfide bonds along with lower O content in the starting powder may result in material that produce higher-quality ceramic. We propose a set of experiments to qualify XPS as an additional characterization technique.

8.2 Summary of Findings

CLS is an IR optical material of great potential for use in broad-band IR applications and the up-and-coming hypersonic field. The properties that make CLS a material of great interest is its high thermal stability with its melting point at 1810°C, its thermal conductivity at 1.70 W/m-k, and its hardness with Knoop values of 570- 736. CLS is also more chemically resistant than current materials and can be a wide
bandgap semiconductor with a bandgap between 2.5 - 2.7 eV. CLS chemical bonding information is limited, and previous XPS characterization needs to be more extensive.

Chapter 4, the analysis identified the dominant presence of CaS, with a Ca:S atomic ratio of approximately 25.29:32.7. The Ca 2p3/2 and S 2p3/2 spectra provided clear evidence of the Ca-S bond. The analysis of the survey and fine spectra showed that contaminants in the form of oxygen and carbon are at levels higher than adsorbed surface molecules.

In Chapter 5, the major components identified were $\gamma$-La$_2$S$_3$, identified by sulfur (S 2s) at a binding energy of 224.62 eV, and lanthanum oxide (La 3d), with its 5/2 peak at 837.37 eV, indicating that both sulfide and oxide bonding existing in the same sample. Along with the existence of oxides, we find that sulfur-rich metal sulfides were detected, evident in the S 2p fine spectra, displaying two sets of peaks at 160.23 eV and 161.18 eV; these peaks show the diverse bonding environments of sulfur within the matrix.

Chapter 6, the mixtures were made in 10% changes to the molar percentage of the mixes from 100%-50% on both sides of the curve and then CIP'ed into coupons. The XPS system states an accuracy of ±2 at.% consistent with experimental data. The analysis done on fine spectra fell within the 95% confidence interval. The 90:10 concentration was observed with lower percentages of Ca in the fine spectra; for Ca 2p, there was a need to increase the number of accumulations during aquations to get sharper peak definitions and counts.

In Chapter 7, The investigation encompassed several samples in various forms of powder and ceramic. XPS analysis revealed the presence of Ca, La, S, O, and C. The C was more prominent on the surface of the sintered ceramic samples than the powder or fracture samples. Fine spectra analysis unveiled the existence of metal sulfide and poly-metal sulfide bonds. Furthermore, the analysis of fractured samples
showed variations in oxygen concentration, with an inverse correlation between sulfur and oxygen. Oxygen content increased closer to the surface exposed to the atmosphere, while sulfur concentration increased with depth into the ceramic's true center. In conclusion, this chapter's findings demonstrate that CLS 90:10 shifts elemental composition, particularly in terms of oxygen and sulfur, in response to processing and exposure to oxygen.

8.3 Conclusions

This research contributes significantly to understanding CLS's chemical composition on the surface chemistry and stoichiometry. Addressing gaps in previous knowledge and introducing novel insights and methods builds upon existing research in the field. These findings can positively impact future production, particularly in optical ceramics and their production processing and characterization.

8.4 Future Work

To carry on with this work in the future, there are several other experiments that would be beneficial to gain more insights into the CLS system. A series of experiments should consist of *in situ* heating of the samples in chamber both of powders and ceramics to look for effect of temperature on peaks that are attributed to Other oxygen. Additional XPS functions that had not been investigated in this research, sample area mapping for in sample homogeneity. One other challenging investigation would be Ar⁺ sputtering rate calibration study. This study would help with quantifying the depth from the surface that is eroded way during sputtering. Knowing the rate at which the materials is sputtered would help to determine how far into the sample the spectra has penetrated and if the O contamination is part of a thick Oxide coating in part due diffusion as part of the hot pressing process or exposure to ambient conditions. While this work focused on CLS 90:10 more variations of CLS should be investigated, for example, 70:30 and 50:50. The work should also be done on powders and ceramics from different
manufacturers. More in-depth studies and repetition should be done on fractured samples. A depth profiling study should determine if the oxide layer is just a thick shell outside the CLS or if the oxygen is truly found throughout the matrix. Along with the data collected from all samples should be placed in a matrix with data acquired through other techniques. Ultra-violet photoelectron spectroscopy (UPS) should also be exploited to study the valence band edge of CLS. Comparison with ab initio calculations should help further elucidate the critical role of stoichiometry and oxygen in determining the properties of CLS.

From data analysis perspective, a multi-variant analysis should look for trends to identify better what in processing can improve the CLS quality and reduce absorbent bands to increase transmission percentage. A study of lanthanum oxide, sulfide, and oxysulfide should be conducted separately to understand the variation in concentration of oxygen and sulfur and its effect on the highly complex La 3d 5/2 main peak. It is possible that there exists a correlation between the O/S ratio and the nature of the La 3d 5/2 peak which could provide additional understanding of CLS ceramics.
APPENDIX A: ATOMIC QUANTIFICATION
Quantitative Analysis: Atomic quantification

Atomic % of the elements can be calculated by

\[ n_i = \frac{n_i}{\sum n_i} \]

Each element and instrument has defined sensitivity factors

\[ S_i = \sigma_{ij} \lambda(KE) \]

One peak from each element gained from collected spectra can be used to calculate \( n_i \)

\[ n_i = \frac{I_{ij}/S_i}{\sum I_{ij}/S_i} \]

**Definitions:**
- \( n_i \) = Atomic %
- \( S_i \) = Sensitivity factors
- \( \sigma_{ij} \) = Photoionization cross-section
- \( j \) = Peak
- \( i \) = Element
- \( \lambda(KE) \) = Inelastic mean free path length
- \( I_{ij} \) = peak area

Thermo Scientific Avantage™ Software is used for atomic calculations. The background type used for atomic calculations was Shirley-type peak background.
APPENDIX B: Ar+ SPUTTERING
Ar+ Sputtering timed study for optimizing sputtering time for removal of advantages carbon-oxygen and residual polishing compound.

Adventitious C is reduced after >2 minutes of etching, and carbon reductions continue green until 8 minutes and 20 minutes for ceramics. Ceramics were not sonically cleaned before the study.
Thermo Scientific Avantage™ Software is used for atomic calculations. The background type used for atomic calculations was Shirley-type peak background.
APPENDIX C: FINE SPECTRA DECONVOLUTION
Fine spectra deconvolution is also known as peak fitting—the peak fitting starts with two main characteristics: the background and the peak shape. The background used for peak fitting is a Shirley background, and the peak shape used is a mixture of Gaussian and Lorentzian. The peak fitting is done because the visual peak shape cannot always determine the separation of the peaks into individual compounds. The peak compounds are then used to identify changes in chemistries and shift to the spectra.

The peak fitting in this research used an approach based on peak fitting workflow that emphasizes qualitative and quantitative consistency between the different core level spectra for all elements. As a rule, literature and the XPS handbook [136] were used as spectral references for element and general peak trends. The Thermo Scientific Avantage™ Software was used for all peak fitting. The table of spin-orbit-splitting was used as part of the constraints for the full width half maximum (FWHM). The software would give the mean squared error (MSE) value for each fit as it applied to the constraints from the maintained database. Fitting aimed to maintain the best fit with the least amount of peaks. At the same time, many peaks can be added. The addition of additional peaks does not always greatly improve the fit. The core level spectrum peaks and all elements and levels were also fitted for comparisons and constraint reasoning. Any element with multiple spectra collected would be fitted and compared to identify if adding peaks matches each spectrum. This is a second layer of redundancy to check for properly fitted peaks.

For example, we will look at the fitting of S 2p with one set of peaks, two peaks, and three sets of peaks as an example of the results of the MSE and the difference between under-fitting and overfitting. As seen in the three figures, as you move between the fit, the first graph shows an MSE with some strong deviations in fit, while the second shows a good fit. The third shows a slightly better MSE, but the peaks are now overcrowded, have a larger spread, and do not provide as significant improvement to the MSE.

104
This is just an example of the fitting process, and information is compared with additional peaks of other elements and other core lines to confirm peak fitting.

Figure: S 2p fine spectra with one set of peaks for SOS

Figure: S 2p fine spectra with two set of peaks for SOS

Figure: S 2p fine spectra with Three set of peaks for SOS
MicroPolish alumina suspensions contain agglomerated alumina particles that offer high removal rates and are good for use on magnesium, lead, and alloys.

ABRASIVE MATERIAL: Alumina

CONTAINER SIZE: 32 oz

MICRON SIZE: 0.05 µm

PRODUCT FAMILY: MicroPolish

QTY/EA: 1

TYPE: Aqueous Suspension
APPENDIX E: RESUME
BRIAN E. BUTKUS

“Accomplished materials scientists specializing in advanced materials synthesis, characterization, and metrology looking to be a team player in the Aerospace and Defense industry.”

EDUCATION

University of Central Florida
Bachelor of Science in Biological Sciences and Chemistry
Orlando, Florida
December 2005

Illinois State University
Master of Science in Materials Science and Engineering
Normal, Illinois
August 2019

Master of Science in Nanotechnology

Skills

Software: Microsoft Office Suite: Word, Excel, PowerPoint; Origin
Language: Fluent in English (reading, writing, and speaking),
Business Skills: Laboratory safety program development and implementation, Industrial hygiene oversight and ergonomic analysis, Regulatory compliance and reporting, Effective communication with colleagues, clients, and technicians, Laboratory operations management, Assembly and installation of scientific instrumentation, Operational efficiency optimization, Proven leadership and team management, Hazardous material handling and shipping compliance, Project management for hazardous waste collection events, Waste management and wastewater treatment oversight, Strong focus on safety and security, Material estimation and procurement expertise, Biohazard cleanup and emergency response, Hazardous waste container handling and labeling, Manifest documentation and waste reporting

PUBLICATIONS


4. Brian Butkus, Matthew Havel, Alexandros Kostiogiannites, Andrew Howe, Myungkoo Kang, Romain Gaume, Kathleen A. Richardson, Parag Banerjee; Lanthanum sulfide powder analyzed by XPS. Surface Science Spectra 1 June 2023; 30 (1): 014001. https://doi.org/10.1116/6.0002252 Published

5. Brian Butkus, Matthew Havel, Alexandros Kostiogiannites, Andrew Howe, Myungkoo Kang, Romain Gaume, Kathleen A. Richardson, Parag Banerjee; Calcium sulfide powder analyzed by XPS. Surface Science Spectra 1 June 2023; 30 (1): 014005. https://doi.org/10.1116/6.0002304


CONFERENCES

1. STEMS 2023 (Orlando, Florida): Anatase Crystalline Phase Discovery on Ultra-Thin Layer TiO2 Films During Low-Temperature ALD on Fluorine-Rich Carbon Substrates” presented by Butkus, B


4. CSHEMA Spring Symposium 2022 (Orlando, Florida): “The Humble Lab Coat: A Case Study on Developing Lab Coat Program at UCF,” presented by Butkus, B.


8. ASSE 2015 (Dallas, Texas): Mixed Mode Learning in Academics,” presented by Butkus, B.
9. CSHEMA 2013 (Orlando, Florida): “Transitioning from Safety Lecture to Practical “presented by Butkus, B.

WORK EXPERIENCE

Graduate Research Assistant
University of Central Florida, Dr. Parag Banerjee’s Lab
May 2017- May 2019/ October 2020-present
Orlando, Florida

Laboratory Safety Manager & Chemical Hygiene Officer
University of Central Florida, EHS Office
June 2011-January 2022
Orlando, Florida

Account Specialist/ Project Manager
Clean Harbors Environmental Services, Inc
February 2009-June 2011
Bartow, Florida

Onsite Services Supervisor Continental Airlines project
Clean Harbors Environmental Services, Inc
Orlando, Florida
January 2008-February 2009

Senior Lead Chemist
Clean Harbors Environmental Services, Inc
November 2006-January 2009

ACCOUNTS AND TRAINING

- Awarded 2015 “Complete Environmental Health and Safety Program Award” (CSHEMA)
- Awarded 2014 “Solutions at Work Award Recipient Laboratory Safety Training Program” (CSHEMA)

CERTIFICATIONS AND TRAINING

- AAUS Scientific Diver registration and certification
- First Aid/ CPR / AED Training
- 40-Hour OSHA Certification
- 24-Hour RCRA Training
- 40-Hour Lab Pack Training
- 16-Hour Unknown Chemical Identification Training
- 8 Hr. Reactive Material Recognition & Awareness Training
- Household Hazardous Waste Event Supervisor Training
- DEA Controlled Substances Shipper Training
- BCSP- Certified Safety Management Specialist (SMS)
- IATA/ DOT hazmat and dangerous goods shipper training
- FEMA IS-100.HE, 200. b, 700. a, 800. b, 810
- American Biological Safety Association the Role of Threat Assessment in Biosecurity Programs
- Emergency Response Educators Clandestine Lab Awareness Training
- UCF Train the Trainer
- OSHERC UNC Biosafety Officer Training Course
- OSHERC UNC Chemical Hygiene Officer Training Course
- FBI Academic Biosecurity Workshop
- Laser Safety Officer Training- Laser Safety Institute

VOLUNTEER EXPERIENCE

Campus Safety Health & Environmental Management Association (CSHEMA)
Bloomington, Indiana
Chair for the Spring 2022 Symposium Committee
- Planned Symposium.

CSHEMA
Bloomington, Indiana
Chair for the Education Committee 2018-2020
- Planned Annual Conferences
- Found Keynote Speakers
- Planned Educational Tracks
- Chaired committee for technical presentation
- Designed pre and post-conference educational offerings.

CSHEMA
Bloomington, Indiana
Education Committee member
- Evaluate abstract submissions and provide feedback.
- Moderated Technical Sessions at conferences and symposium

110
LIST OF REFERENCES


7. Jiang, Z., et al., Robust Li6PS5I Interlayer to Stabilize the Tailored Electrolyte Li9.95SnP2S11.95F0.05/Li Metal Interface. Acs Applied Materials & Interfaces, 2021. 13(26): p. 30739-30745.


57. Harris, D.C. *Development of hot-pressed and chemical-vapor-deposited zinc sulfide and zinc selenide for optical windows*. SPIE.


80. Choidoohyun, W.K. Jung, and H. Won, Manufacturing infrared-transmitting zinc sulfide (ZnS) sintered body by seating ZnS plastic body on lower portion of the energization pressurization sintering device, applying current to upper and lower portions, and heat treating body. Agency Defense Dev.


114. Dianov, E.M., et al., *Crystallization kinetics of praseodymium-doped (Ga2S3)0.7(La2S3)0.3 glass*. Inorganic materials, 1997. 33(9): p. 975-977.


177. Mairaj, A.K. and D. Hewak, Optical channel waveguides in a chalcogenide (Ga:La:S) glass fabricated through short wavelength (lambda=244nm) illumination. 2002.


