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Line Defects in Single Crystal CeB₆ Electron Emitters

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Line Defects in Single Crystal CeB$_6$

Electron Emitters

Nicholas Fairhart

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of the requirements for the degree of

BACHELOR OF SCIENCE

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Abstract

Electron emitters are essential components in many microscopy systems, including scanning electron microscopes, transmission electron microscopes, and scanning Auger microprobes. One feature of good electron emitter materials is a low surface work function. CeB$_6$ is one such material. Line defects seen in CeB$_6$ affect the work function of the emitting surface, causing the emitted electrons to have a wider spread of energies. This causes chromatic aberration, reducing the resolution of the microscope systems. The purpose of this research is to find the source of these line defects in the CeB$_6$ emitter fabrication process. It was suspected that defects were in the form of oxides deposited from water contamination. This study confirms that the defects do contain more oxygen than other areas of the surface. The source of this oxygen has yet to be determined.
# Table of Contents

1. Introduction ................................................................................................................... 1

2. Background ................................................................................................................... 2

3. Electron Emitter Production ......................................................................................... 4

4. Theory ........................................................................................................................... 6
   4.1 Time of Flight Secondary Ion Mass Spectrometry .............................................. 6
   4.2 EDAX ..................................................................................................................... 8
   4.3 Possible Contaminates ....................................................................................... 10

5. Results and Analysis ................................................................................................... 11
   5.1 EDAX .................................................................................................................... 11
   5.2 Time of Flight Secondary Ion Mass Spectrometry ............................................. 12

6. Conclusions .................................................................................................................. 19

7. Acknowledgements. ..................................................................................................... 20

8. References .................................................................................................................... 21
List of Figures

Figures

2.1 Ray diagram illustrating chromatic aberration in an electron microscope ............... 3

3.1 Schematic of the zone refining process ........................................................................ 5

4.1 Basic scheme of TOF-SIMS ....................................................................................... 7

4.2 Schematic of the EDAX x-ray emission for the K_{\alpha} transition ............................ 9

5.1 EDAX energy spectrum .............................................................................................. 11

5.2 Optical microscope image of a line defect .................................................................. 13

5.3 Mass spectrum from TOF-SIMS ............................................................................... 14

5.4 TOF-SIMS images ..................................................................................................... 15

5.5 Definition of areas of interest. ..................................................................................16

5.6 Quantitative analysis of the sample ...........................................................................18
List of Tables

Table

4.1 Possible oxide contaminates of CeB$_6$ ................................................................. 10
1. Introduction

Electron emitters play a critical role in many different microscopy techniques and analysis. Scanning electron microscopes, transmission electron microscopes and scanning Auger microprobes all need reliable electron emitters to function properly.

The first electron emitters were simply tungsten hairpin filaments that relied on high temperature to pull electrons from the apex of the surface. Today, there are two primary types of electron emitters, Schottky sources and Thermal sources. The thermal emitters that are of particular interest are CeB$_6$ and LaB$_6$. These materials must be heated to high temperature, about 1800 degree Kelvin, to emit electrons effectively. There are a couple of advantages to using CeB$_6$ or LaB$_6$ as electron emitters. First and foremost both materials have a low work function of around 2.5-2.7 eV. This low work function allows the emitters to function with high brightness and high beam current. Generally CeB$_6$ has the lower work function allowing cooler operating temperatures that yield lower evaporation rates and a longer emitter lifetime. All of these factors combine to produce desirable qualities for use in microscopy applications as they reduce service and improve performance of the device.
2. **Background**

After the electrons leave the emitter, they pass through magnetic and electrostatic lenses which collimate and focus the beam. However, the magnetic lenses experience the same issues that affect performance as optical lenses. These issues include spherical aberration and chromatic aberration among other issues. Spherical aberration can be minimized with proper lens design and consistent source shaping. Chromatic aberration has two sources, the magnetic lenses, which can be minimized by design, and also the source itself. Figure 1 depicts chromatic aberration in an electron microscope system.

In order to minimize chromatic aberration the source should have a small energy spread of electrons leaving the surface. Some of this spread is inherent to the material but can be controlled by having a uniform crystal structure and few or no defects in the crystal face. These factors help ensure uniform work function over the surface of the electron emitter, minimizing the energy spread and chromatic aberration.

Recently, contamination has entered the electron emitter production process. The production process is discussed later in this paper. Defects have been found in the crystal faces that have a negative effect on the uniformity of the crystal structure and the composition of material itself leading to an unnecessarily large energy spread. These defects can be seen optically as a straight line.

Since emitter production is a delicate, labor and time intensive process it is of great importance to eliminate the source of the contamination. Often times defects cannot be recognized until near end of the production process, after much time and care has been spent working on the defective emitter.
This research focuses on finding the form of the contamination using surface analytical technique of time of flight-secondary ion mass spectroscopy and energy dispersive x-ray spectrometry and locating the source of this contaminate in the production process.

**Figure 2.1** Ray diagram illustrating chromatic aberration in an electron microscope. The red line depicts the path of electrons with energy 1 while the red path depicts the path for electrons with energy 2.
3. **Electron Emitter Production**

Electron emitters originate as bulk material in the form of a 5.00 by 5.00 by 0.375 inch sintered block. From there the block is cut into the proper length and width for zone refining using a diamond saw and water for cooling and lubrication. A diamond saw must be used to cut the material because the sintered block is very hard and dense and cannot be cut using other methods. At this point in the production process the sintered block is porous and has an opportunity to absorb water. It is suspected that the source of the line defects in the electron emitters originate as this water contamination. After the stock is cut it is baked overnight at 150 °Celsius under atmospheric pressure.

Zone refining is the act of creating a single crystal material from bulk stock. The zone refining occurs in a chamber that has been pumped to vacuum and backfilled with argon. This zone refined crystal will have a specific orientation chosen based on the use of the crystal. In this case <100> orientated crystals are used as electron emitters. To create a single crystal an arc of plasma is used to heat up the top of the material until it is at its melting point. This melted region is then joined with a seed crystal, where the molten zone is held by surface tension. The melted region then matches crystal orientation of the seed crystal and when it cools becomes a single crystal. Next the arc welders are slowly advanced to move the melting region as more and more material is made single crystal. When the refining process has finished all of the sintered material has been transformed into a single crystal of CeB₆. This process is illustrated in Figure 2.1.
After the stock has been zone refined into a single crystal, it is centerless ground to 0.030 inches in diameter using diamond paste. The stock is cleaned again, this time in a sonic cleaner and solution and rinsed with isopropyl alcohol. Then the single crystal reaches final shaping where one end is ground to a point using diamond grit sandpaper and water for lubricant and polished smooth.

Figure 3.1 Schematic of the zone refining process. Bulk material is melted and joined to a seed crystal. At this point the stock material starts becoming single crystal and the melting “zone” is passed from one end of the crystal to the other. When complete, the stock material is single crystalline.
4. **Theory**

4.1. **Time of Flight-Secondary Mass Spectrometry**

Data was collected using the Time of Flight- Secondary Ion Mass Spectrometer (TOF-SIMS). TOF-SIMS, seen in figure 3.1, uses a pulsed ion beam to pulverize the surface of the sample. This is a very surface sensitive technique since only the first few atom layers are removed and detected. The primary ions in the beam eject secondary ions from the surface of the sample. Using the time it takes the secondary ions to reach the detector one may identify the composition of the pulverized area to a very high degree of accuracy.

Products of the incident ion’s interaction with the surface include secondary electrons, secondary positive ions, neutral atoms and secondary negative ions. Secondary electrons may be used to create an image of the sample in the exact same way a scanning electron microscope creates an image. However, the primary use of the TOF-SIMS is the detection of either the positive or negative ions.

The method of detection utilizes the time of flight of the ions to find their mass. In order to do this all ions ejected from the surface are accelerated through a voltage, $V$. Usually ions are only singly ionized, they either have charge of plus or minus $q$. One may find the time of the ions after traveling through this potential as,

$$qV = \frac{1}{2}mv^2$$

where $q$ is the charge of an electron, $V$ is the potential, $m$ is the mass of the atom and $v$ is velocity.
Then,

\[ v = \frac{d}{t} \]

where \( d \) is distance and \( t \) is time. Plugging equation 2 into equation 1 we now can find a relation between \( t \) and the ratio of \( m/q \),

\[ t = \sqrt[2]{\frac{md^2}{2qV}} \]

Again, since most atoms entering the detector are singly ionized we find that the time of flight is proportional to the mass.

Because the mass is proportional to the time of flight TOF-SIMS is incredibly sensitive and can distinguish molecules down to parts of an AMU. A typical mass spectrum can be seen in figure 4.2.

Figure 4.1 Basic scheme of TOF-SIMS. Pulsed Ions bombard the sample ejecting secondary ions which are detected in a time of flight detector.
4.2. EDAX

Energy dispersive x-ray spectrometry, EDAX, is a surface analysis technique used

to characterize surface composition. In EDAX, a beam of electrons excites the surface of
the sample causing it to emit x-rays. These x-rays have an energy characteristic of the
atom from which they originated, which then identifies the atom.

The emission of x-rays is a multistep process. The first step is the ejection of an
electron from an inner electron orbital shell, such as the K orbital, by an incident electron
beam, leaving a hole in that shell. Typical energies for the incident electron beam range
from 2-30 keV for EDAX. Next an electron from a higher energy electron orbital, such
as the L orbital, relaxes into the empty hole. In the process of relaxing, the electron from
the higher orbital shell either emits an x-ray photon or gives its energy to an Auger
electron in the same or nearby orbital shell. The energy of the photon is equal to the
change in potential energy of the electron dropping between shells. The transition from
the L orbital to K orbital is known as the Kα transition. Since the energy of the photon is
unique to each atom the surface composition can be found by measuring the x-ray
energy. It is important to note that other transitions are possible such as the Kβ transition,
which is the transition from the M orbital to the K orbital, or the Lγ transition which is
the transition from the O orbital to the L orbital. Figure 4.2 depicts the emission of an x-
ray through electron bombardment.
Figure 4.2 Schematic of the EDAX x-ray emission for the $K\alpha$ transition. An incident electron (red) ejects an orbital electron (green) which leaves a hole in the $K^{th}$ orbital shell. This hole is filled by the blue electron, while emitting an x-ray photon seen as a blue arrow. This photon is detected and its wavelength characterized to determine the atom from which it originated.
4.3. Possible Contaminants

The samples discussed here are single crystal CeB₆ prepared as described in the methods section. As stated before it is suspected that water is the main contaminant that has entered the stock before the zone refining process. It is expected that the water has produced oxides that have contaminated the crystals. Through the use of TOF-SIMS and EDAX, the contamination itself and source of the contamination are investigated. Possible oxides of Cerium and Boron are listed in table 3.1. These oxides may also break into components of each molecule in TOF-SIMS. For example CeO₂ may ionize into Ce⁺ and O₂⁻ but there are other combinations and ionizations. EDAX can only detect atoms so any contamination by oxides would be seen as a spike in the oxygen peak in comparison to surrounding areas.

Table 4.1 Possible oxide contaminates of CeB₆.

<table>
<thead>
<tr>
<th>Cerium</th>
<th>Boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>B₂O₃</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>B₆O</td>
</tr>
<tr>
<td></td>
<td>B₂O</td>
</tr>
</tbody>
</table>
5. Results and Analysis

5.1. EDAX

EDAX data was taken using the Philips XL 40 SEM. Figure 3.1 shows the x-ray energy spectrum taken from the line defect. The most prominent peak heights were cerium, fluorine and boron. Oxygen did not have a significant peak height. No red flags immediately arise from this data. Fluorine is a typical surface contaminates and the surface was not able to be sputtered with an ion beam to clean it surface contamination. That coupled with the fact that EDAX only has a spatial resolution of about 100 nm means that these results were not unexpected.iii In order to get higher spatial and mass resolution TOF-SIMS will be the primary tool for analysis.

![EDAX energy spectrum](image.png)

**Figure 5.1** EDAX energy spectrum. The most prominent peaks and their transitions are displayed. i.e. the transition for cerium was L\textsubscript{α1}. 

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iii In this context, the number "iii" is likely a reference to some earlier content or footnote, indicating that the cited point is the third in a sequential list. However, without additional context from the surrounding text, it's difficult to determine its exact relevance or meaning. The text continues: "In order to get higher spatial and mass resolution TOF-SIMS will be the primary tool for analysis."
5.2. **TOF-SIMS**

Data was collected using the ION-TOF Model IV SIMS. Samples had been prepared as described in the experiment section and had defects that were visible under an optical microscope. These areas can be seen as highly reflective lines on the surface as seen in Figure 5.2. Ions sputtered from a liquid metal ion source, in this case Cesium, cleaned the area of the surface of interest for a total of seven minutes before imaging. This was done to ensure that all contaminants from the atmosphere did not interfere with our measurements, especially since oxygen was suspected as the main source of contamination. The sputter rate of this particular apparatus was about one angstrom a second which corresponds with a sputter depth of less than 0.05 micrometers. By comparing the area and features being analyzed, it was evident that the sputter had little to no effect on the sample other than the intended removal of surface contaminants.

One advantage of the TOF-SIMS analysis is the high mass resolution. This is evident in the typical TOF-SIMS mass spectrum shown in Figure 5.3. The ION-TOF Model IV SIMS raster scans the sample and obtains a mass spectrum over an array of points on the sample surface. These mass spectra are stored, along with their position, and can then be analyzed and displayed as TOF-SIMS images. The images are made by associating peak height of a single mass peak or the total ion count for that pixel with a color. One may generate many different images of the sample using the information gathered. Figure 5.4 depicts the TOF-SIMS images for the defect area on our sample. The images selected were generated from the most prominent peak heights in the mass spectra.
Figure 5.2 Optical microscope image of a line defect, visible as a white line, in a CeB₆ electron emitter. (a) Line defect visible at 50x zoom. (b) Line defect visible at 100x zoom.
As seen in Figure 5.4(a), the line defect is especially visible in the oxygen spectrum, qualitatively confirming our hypothesis that the lines defects are in the form of oxides. However, the defect is also visible in maps corresponding to other parts of the spectrum, including the map of the total ion count. This indicates that the secondary ion sputter yield in the defect was higher than the surrounding regions. To take into account the variation in sputter yield across the surface the data was normalized to give a quantitative confirmation to the qualitative results.

**Figure 5.3** Mass spectrum from TOF-SIMS. This data only limited to a short mass range to better illustrate the high mass resolution. TOF-SIMS can extends past 1000 amu.³
Figure 5.4  (a) TOF-SIMS images images for each of the most proment mass peaks. (b) Defect profile in the oxygen image. Note the defect width is about 1 micron and the overall ion signal is stronger on the line defect.
Sputter yield is a function of topology and surface composition. The goal of normalization is to remove the effect of sputter yield from the results. The first step in normalization was to divide the TOF-SIMS images into four subsections indicated by red, green, blue and yellow in Figure 5.5. The red region is the line defect, which had a considerably more sputter yield than the rest of the surface. The second step in normalization is to add all the spectra in each subsection and then dividing summed spectrum by the total number of ions in that respective subsection. This gives the normalized average spectrum in each subsection and the data can now be directly compared.

Figure 5.5 Definition of areas of interest. The red line is the line defect and the regions also seemed to have distinct ion yields.
The results of this analysis, after normalization, can be seen in Figure 5.6. There is still an excess amount of oxygen in the defect region that still cannot be accounted for. This evidence supports our hypothesis that the defects may be in the form of oxides. Also noteworthy is the fact that BO₂ and BO are the second and third most prevalent molecules on the surface in all areas. This suggests that the surface, as a whole, oxidizes when exposed to atmosphere. There is also more CeO in the defect (Figure 5.6(b)), but the total yield of these molecules is very small compared to the other molecules and atoms, so more statistics would be needed to determine if this result is significant. It is also interesting to reexamine Figure 5.2. Cleave marks on the face of the crystal appear slightly rotated from one side of the defect to the other. This suggests that the line defect is actually a grain boundary in the crystal.
Figure 5.6 Quantitative analysis of the sample. (a) A comparison of relative molecule intensity in the four regions of interest seen in Figure 5.5. (b) A zoomed in view of the relative molecule intensity of CeO in each region of interest.
6. Conclusions

After examining the sample with EDAX the composition of the defect region was still inconclusive. As a result the method of TOF-SIMS was employed to examine the defect region in greater detail. The results of this analysis showed more oxygen was located in defect area.

Although there was excess oxygen located in the defect, it cannot determined from these results whether the grain boundary allows more oxygen to deposit in the defect or whether oxide contamination is responsible for the grain boundary.

There could be a couple different causes of a grain boundary in these electron emitters. Possible causes include temperature gradients in the zone refining process, causing non-uniform crystal growth, water contamination, leading to oxide growth, or other contamination or physical factors that have not been suspected yet.

Future plans are to explore this causality by baking the bulk material under vacuum and monitoring the vacuum composition via a residual gas analyzer. If water excess water vapor is detected the sample with be baked until most of the water is driven away. Then the sample with go through the production process and it will be determined whether or not this resolves the problem or if other factors are to blame.
7. Acknowledgements

I would like to personally thank Dr. Bill Mackie, without whom this project would not be possible, Dr. Jennifer Heath for driving down to Eugene and taking data with me and Dr. Steve Golledge at the Center for Advanced Materials Characterization in Oregon for assistance with the TOF-SIMS measurements.
8. References


