

CHARACTERIZATION OF A BARIUM SURFACE BY AES, XPS AND SIMS

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Abstract

The surface of a solid barium sample has been studied by surface analysis techniques. The procedure to obtain a clean surface is discussed. In depth distribution of the sputtered ions during cleaning provides a good way to understand the evolution in the surface composition. Ion images show clear differences in the composition of the sputtered spot relatively to the adjacent area.

The acquisition of XPS and AES spectra showed that the surface is clean according to usual guidelines. However, positive and negative SIMS spectra gave insight in the identification of the low level contaminants. About 12 compounds have been identified in the 'clean' barium surface.

Introduction

Most of the surface studies, require the ability to characterize in detail the composition of the surface. The presence of unknown species in the surfaces may introduce uncontrollable variables and then the experimental results may become difficult to explain.

Very often, 1% is taken as the maximum allowed limit for contamination and this is checked by techniques such Auger Electron Spectroscopy— AES or X-ray Photoelectron Spectroscopy— XPS [1]. Besides this criterion, no surface can have a contamination level lower than the bulk, if the target is homogeneous and there is no diffusion. When the purity of the surface reaches the purity of the bulk, one can conclude that the surface is as clean as possible. However it is very important to know

the contamination left, since even at low concentrations it may have species chemically active.

In this work we describe the procedure to obtain a clean surface of solid barium. Furthermore, we discuss the evolution of the composition of the surface during the cleaning process and a detailed analysis of the remaining contaminants.

Experimental

The work has been performed in a multitechnique surface analysis apparatus using the analytical techniques SIMS— Secondary Ion Mass Spectrometry, AES and XPS. This system has been detailed elsewhere [2].

The sample was prepared from a 99% pure barium rod obtained from Goodfellow [3]. According to the supplier, it is produced by heating barium oxide BaO with aluminum. A slice with 6 mm long \times 10 mm in diameter was cut and clamped on a stub. It was mechanically clean with sandpaper under paraffin oil. Then it was carefully washed in dried hexane and introduced in the fast entry air lock under an argon jet to minimize atmosphere exposure. Although it was only for a few seconds that the barium could be exposed to air, a thin white hydroxide layer was formed.

To achieve a bulk like clean surface, further cleaning was done in fast entry air lock chamber with a sputter argon ion gun (40 hours of 5 μ A, 800 eV beam) followed by annealing at 870 K for 1 hour in the analysis chamber. Alternatively the sample was sputtered in small spots by the SIMS ion gun and the intensities of relevant ions were followed. To check the state of the surface XPS, AES and SIMS spectra could be acquired.

The working pressure during XPS or AES was in the 10^{-10} mbar range. The pressure raised to about 5×10^{-9} mbar when SIMS spectra were acquired due to some gas load from the ion source.

Results

Depth profiles were obtained from the ions emitted during the cleaning by sputtering. Fig. 1 shows two of these profiles normalized to the sum of both ions. In a) the two most abundant positive ions are represented. Although at start the emission of all positive ions is strongly enhanced due to the presence of oxygen, the relative intensity of BaO⁺ rapidly drops down and the relative intensity of barium increases. In graph b) the oxide and hydride negative ions are plotted. Again a similar behavior is observed indicating a more intense concentration of BaH₂⁻ in the bulk.

Figure 2 shows two ion images acquired over the previously sputtered spot and the adjacent area. Since the images look complementary, it seems evident that the barium oxide is a surface compound and the barium hydride is a bulk compound.

The XPS spectrum obtained from the clean barium surface is shown in Fig. 3. With this technique it is not easy to identify concentrations lower than 1%. Indeed, the spectrum only indicates the presence of oxygen as detectable contaminant.

In Fig. 4 the Auger spectrum is represented. This spectrum shows the presence of 9 Auger peaks attributed to barium transitions and two more peaks assigned to calcium and oxygen.

Positive and negative SIMS spectra are shown in Fig. 5 and 6. The positive spectrum was obtained with a 5 keV He⁺ beam of 180 nA. Helium was used instead of argon in order to be able to measure the ⁴⁰Ca⁺ peak. The negative spectrum was acquired under the bombardment of 4 keV Ar⁻ beam of 200 nA.

These SIMS spectra reach such large dynamic range and are so rich that each one is represented with two different scales to allow identification of low intensity ions. In the positive spectrum, the presence of BaO⁺, BaO₂⁺, BaOH⁺ and Ba(OH)₂⁺ indicate that the 'clean' surface still contains oxides and hydroxides. Ions from the same earth-alkali group Ca and Sr can also be easily identified. Alkali ions of Na⁺ and K⁺ also can be seen as well as H⁺. Combination of oxide ions were also emitted— BaCaO⁺, Ca₂O⁺ and SrCaO⁺.

In the negative spectrum of Fig.6 the O⁻ peak was clipped (the intensity is about 8×10⁷ counts). This is the most intense ion but C⁻, F⁻, C₂⁻, CN⁻ and Cl⁻ also present high intensities. The main barium anions are BaH₂⁻ and BaO₂⁻. Negative ions from calcium and strontium hydrides are also observed.

A few peaks remain to be identified mainly in the positive spectrum.

Discussion

The in-depth distribution of secondary ions during sputter cleaning, allows defining the conditions (in terms of sputtering time) when the barium surface could be considered clean. Further sputtering do not turn the surface cleaner. This demonstrates that a good criterion is ratio of the molecular ions BaH₂⁻ and BaO₂⁻. The surface is "clean" when this ratio reaches a maximum and constant value. Although the BaO⁺ is still present in a smaller amount in the clean surface, the relative intensity of Ba⁺ comes to a maximum. The ion images (Fig. 2) confirm that barium hydride is a bulk compound. The BaH₂⁻ is only seen in the cleaned area.

The spectra obtained by AES and XPS shows that oxygen and calcium are the main residual contaminants. All the many other elements detected by SIMS are low level contaminants (<1%). Quantification of the AES spectrum shows a slightly lower purity of the barium sample— 96.4% of barium, 2% of calcium and 1.6% of oxygen. Although the sensibility of the technique is about 1% for those acquisition techniques, this result suggests that the barium surface had a contamination level higher then the one indicated by the supplier.

The positive and negative SIMS spectra need a more detailed discussion. The total negative ion yield was found to be higher then the total positive ion yield. This is because barium has a low work function of 2.7 eV. Consequently, the neutralization probability is rather low for the sputtered negative ions but much higher for the positive ions.

In table 1 it is summarized the compounds that are identified in the SIMS spectra as the main barium contaminants. Most of them are barium based compounds or similar compounds of strontium and calcium.

Calcium and strontium are expectable impurities since they have a similar reactivity and thus they are more difficult to separate from barium. The presence of magnesium is not clear. The $^{24}\text{Mg}^+$ is adjacent to the intense $^{23}\text{Na}^+$ peak and therefore the detected counts can be attributed to the decay of the 23 peak. The presence of lithium and sodium are nor surprising since they are common metal contaminants. Moreover they are very well detectable in SIMS due to its low ionization potential [4].

The presence of oxygen is in the form of barium oxides BaO , BaO_2 and in the hydroxide $\text{Ba}(\text{OH})_2$. This is certainly due to some barium oxide that remained from the refining process. The detection of the oxide combinations referred does not inevitably indicate their presence on the sample since they can be formed out of the surface by recombination [5]. Barium oxide anions were present in the negative spectrum before the annealing of the sample or when the annealing temperatures were bellow 550°C . According to Hill et. al.[6] annealing at 870 K began to decompose the oxide. Unclean barium displayed very strong BaO_2^- and BaO^- peaks. These peaks could be one order of magnitude higher then the hydride peak.

The emission of the barium hydride anion BaH_3^- is due to the sputtering of BaH_2 . Apparently the BaH_2 molecule picks-up an H^- anion at the surface to form BaH_3^- . Since the electron affinity of barium is positive but rather low [7], $\text{EA}=0.145$ eV, we suppose that BaH_3^- is the most stable molecular anion due a large electron affinity of BaH_3^- [8]. The three electrons from the hydrogen plus the two valence electrons of barium, probably fill the 6p sub-shell, thus presenting a rare gas like configuration. Barium

hydride is a typical saline hydride with the outstanding characteristic of very large solubility in barium metal. Peterson et. al.[9] have shown that the solubility of BaH_2 is even higher in solid than in liquid barium at the same temperature. A consequence of the high solubility of BaH_2 in barium is that the hydride diffuses very easily, or in other words, diffusion coefficient of H_2 in barium is very high. This explains why others authors have found that even high purity barium appear to contain large amounts of hydrogen [6].

The presence of carbon, fluorine and chlorine can be attributed to the producing process of barium. These elements are common in washing liquids and they remain in the recipient walls. Due to the high reactivity of these elements and barium, fast reactions can easily take place and very stable compounds be formed.

Conclusions

Depth profiles were very useful to define when to stop the sputtering in a cleaning process of the barium surface. A constant maximum intensity in the BaH_2^- peak is reached when the surface is clean.

XPS and AES spectra have shown that the amount of impurities in barium was low. Only calcium and oxygen were detected by these techniques. Consequently, they can be recognized as the main impurities.

However the ‘clean’ surface analyzed by SIMS displayed many low level contaminants. SIMS spectrum let conclude that oxygen is bounded to barium as BaO and BaO_2 . SIMS also identified others contaminants such as strontium, sodium and hydrogen (not detected by other techniques). The negative SIMS spectrum showed that hydrogen is bounded to barium as BaH_2^- .

The spectra obtained by SIMS allowed the identification of many elementary contaminants combined in more than 16 compounds. Although quantification of these spectra were not possible, SIMS made possible a deep understanding of the surface composition.

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Table 1 — Main contaminants identified in the ‘clean’ barium surface

Chemical formula	Compound	Main detected ions
BaO	Barium oxide	BaO ⁺ , BaO ⁻ , O ⁺ , O ⁻
BaO ₂	Barium peroxide	BaO ₂ ⁺ , BaO ₂ ⁻
Ba(OH) ₂	Barium hydroxide	BaOH ⁺ , BaOH ⁻ , Ba(OH) ₂ ⁻
BaH ₂	Barium hydride	BaH ₃ ⁻ , H ⁺ , H ⁻
Ba(CN) ₂	Barium cyanide	CN ⁻ , BaCN ⁺ , Ba(CN) ₂ ⁺
BaCO ₃	Barium carbonate	CO ₃ ⁻
BaCl ₂	Barium chloride	Cl ⁻ , BaCl ⁺
BaF ₂	Barium fluoride	F ⁻ , BaF ⁺
CaH ₂	Calcium hydride	CaH ₃ ⁻ , H ⁺ , H ⁻
CaO	Calcium oxide	CaO ⁺ , CaO ⁻ , O ⁺ , O ⁻
Ca(OH) ₂	Calcium hydroxide	CaOH ⁺
CaF ₂	Calcium fluoride	F ⁻ , CaF ⁺
CaCl ₂	Calcium chloride	Cl ⁻ , CaCl ⁺
Ca(CN) ₂	Calcium cyanide	CN ⁻ , CaCN ⁺
SrH ₂	Strontium hydride	SrH ₃ ⁻ , H ⁺ , H ⁻
SrO	Strontium oxide	SrO ⁺
SrF ₂	Strontium fluoride	F ⁻ , SrF ⁺
SrCl ₂	Strontium chloride	Cl ⁻ , SrCl ⁺

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Figure Captions

Figure 1— In depth relative distribution of the unclean layer. The profile of the main positive ions are represented in a) and in b) the main negative anions. A clean surface is reached only when the ion intensities are kept constants. The intensities have been normalized to the sum of both peaks. The two graphs were obtained from different measurements and thus the sputtering time is not comparable. The total area is about $4 \times 4 \text{ mm}^2$.

Figure 2— Ion images obtained by SIMS of BaO^+ and BaH_3^- . The color scale is from yellow for maximum intensity to dark brown for minimum. The darkest spot in the BaO^+ image is the sputtered area. The bright spot in the BaH_3^- image show the barium hydride is only a bulk compound.

Figure 3— XPS spectrum of cleaned barium. Only oxygen are detected as contaminant.

Figure 4— AES spectrum of cleaned barium. 9 Ba transitions were identified. The presence of oxygen and calcium were also identified.

Figure 5— Positive SIMS spectrum acquired under the bombardment of a cleaned barium surface by a 5 keV, 180 nA He^+ beam. In most cases, only the most abundant isotope is identified.

Figure 6— Negative SIMS spectrum acquired by the bombardment of a cleaned barium surface by a 4 keV, 200 nA Ar^- beam. In most cases, only the most abundant isotope is identified.

Figure 1 a) and b)

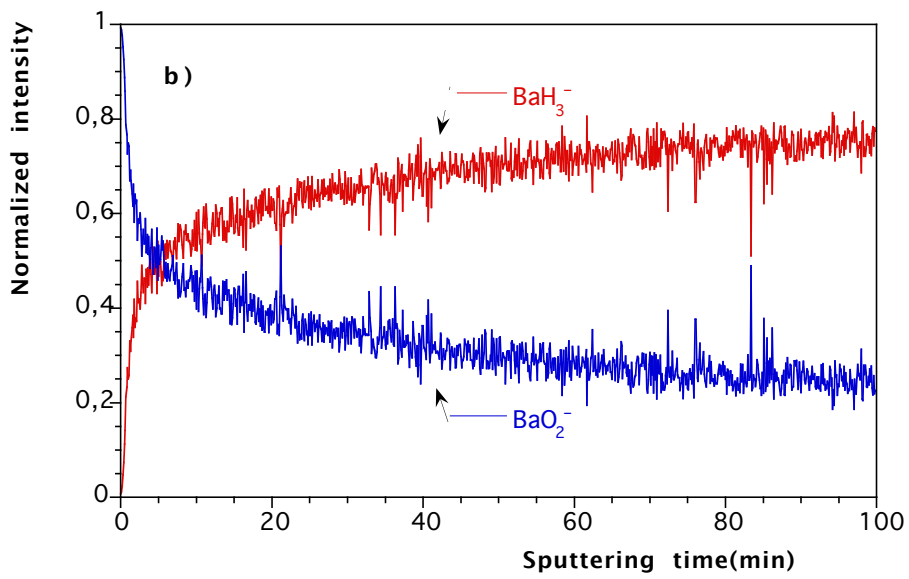
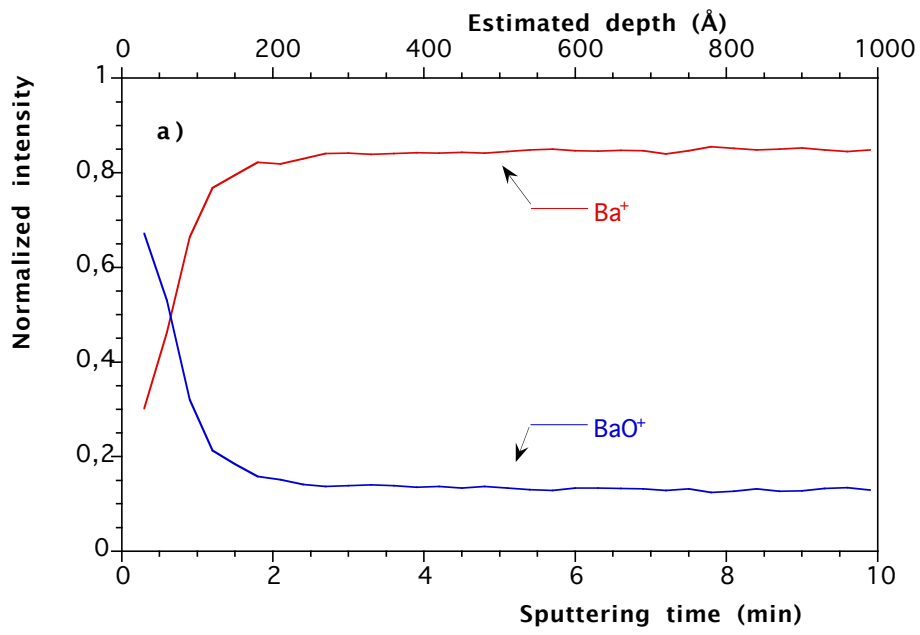


Figure 2

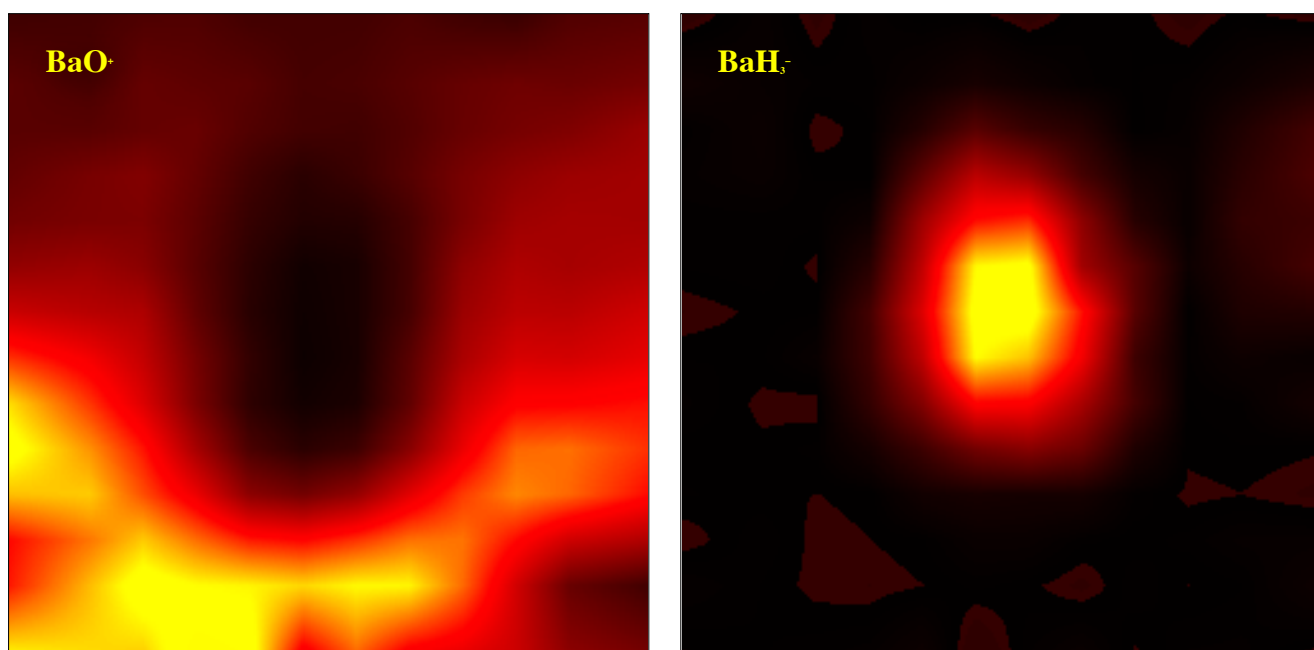


Figure 3

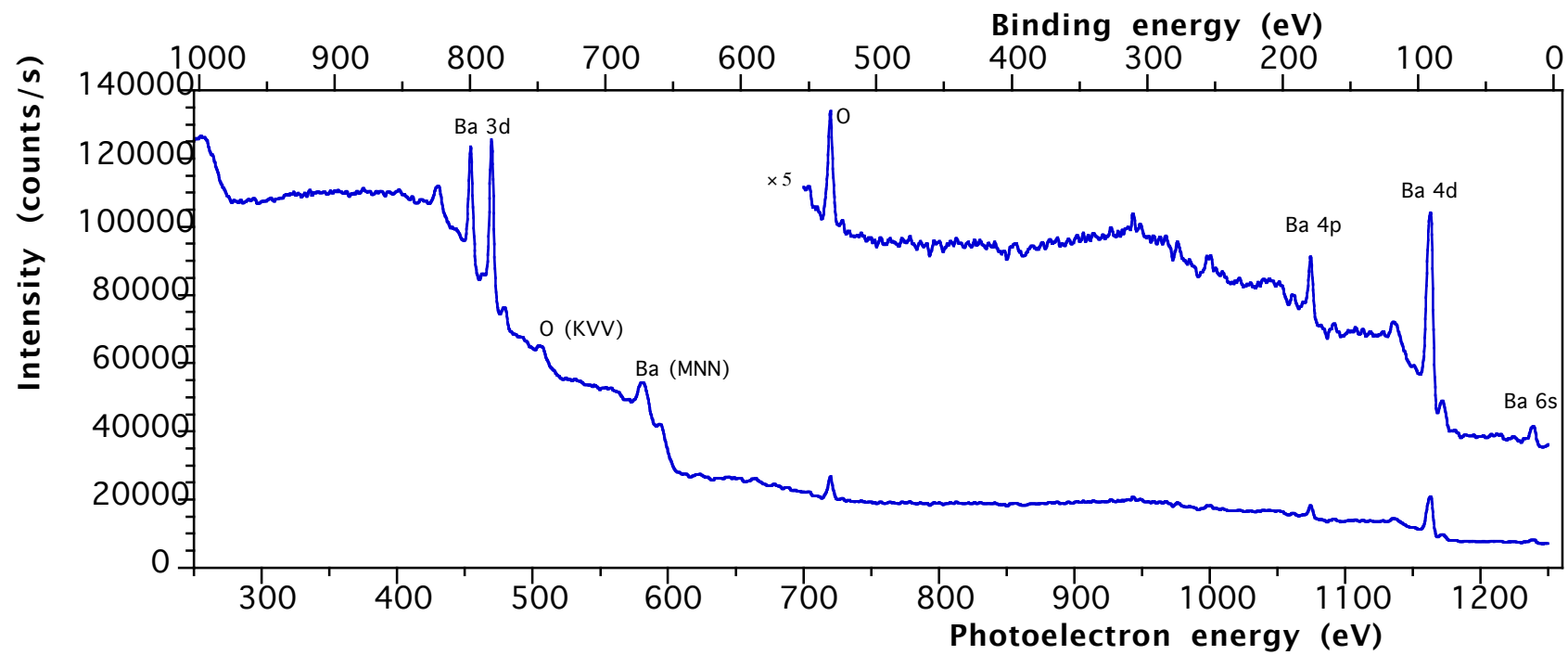


Figure 4

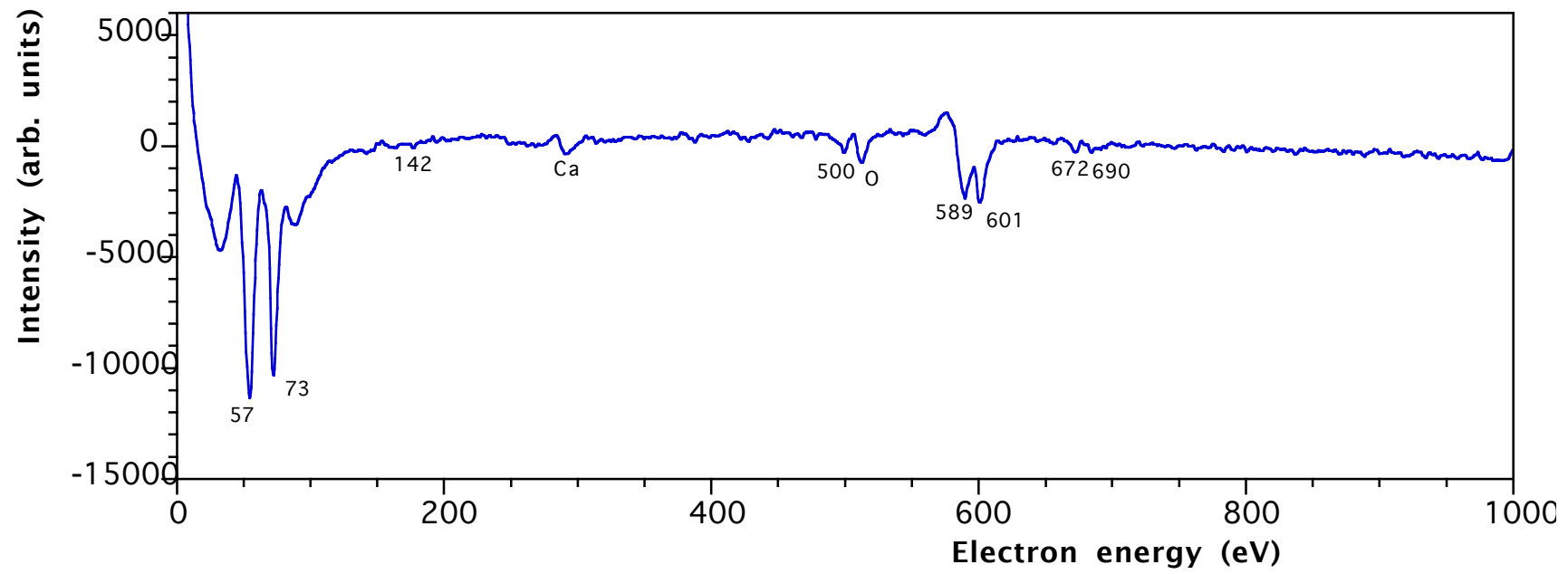


Figure 5

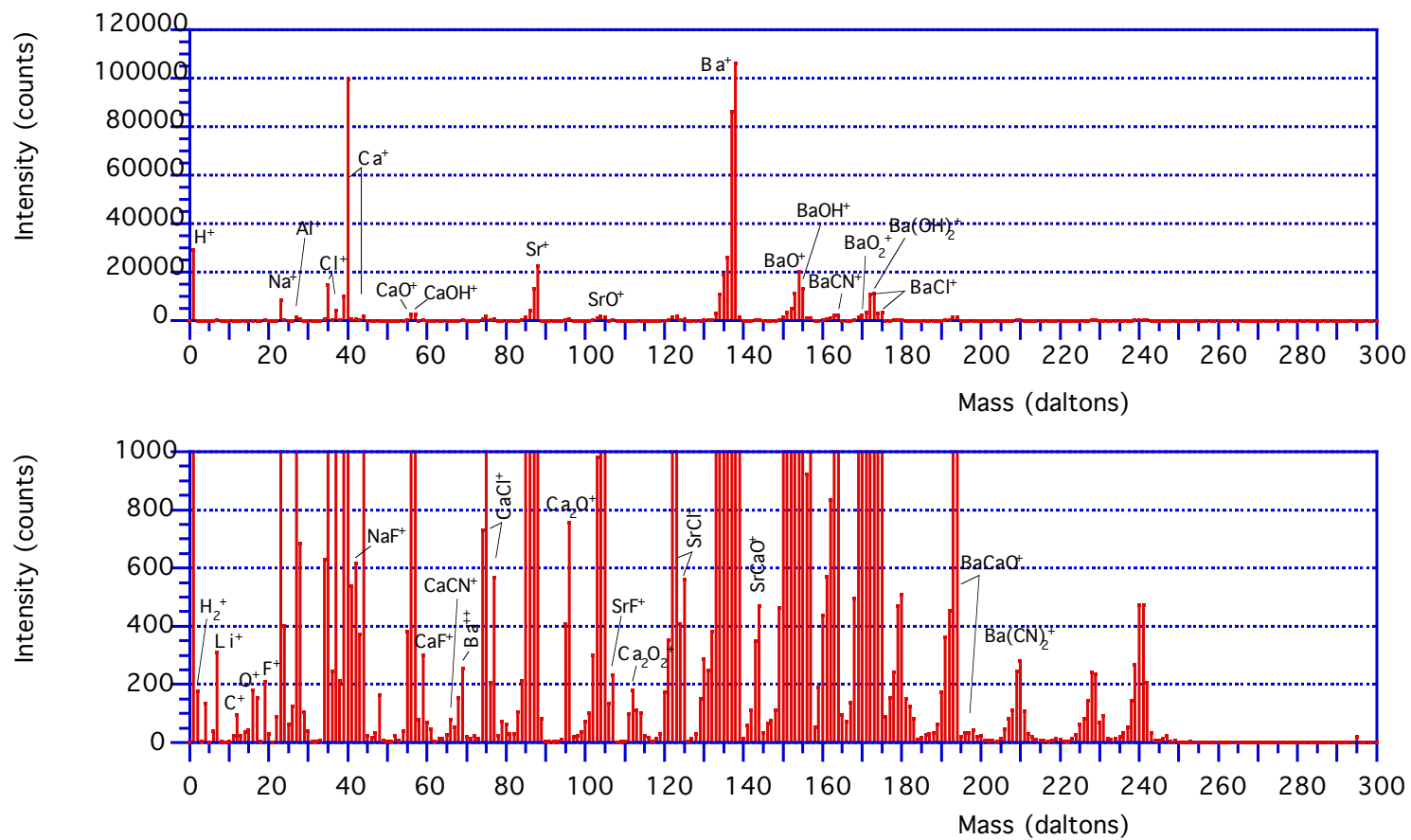


Figure 6

