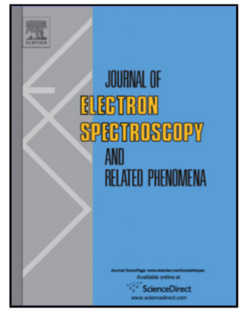

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X-ray Photoelectron Spectroscopy Study of $BaWO_4$ and Ba_2CaWO_6

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Highlights:

- XPS reference spectra for Ba_2CaWO_6 and $BaWO_4$ are presented
- Binding energies of Ba3d and W4f lines are 0.7 eV higher for $BaWO_4$ than Ba_2CaWO_6.
- Ca2p spectrum contains two sets of Ca2p doublets attributed to Ba_2CaWO_6 and $CaCO_3$.

Abstract

XPS reference spectra for Ba_2CaWO_6 and $BaWO_4$ are presented, including high resolution spectra of the Ba 3d, W 4f, C 1s, Ca 2p, and O 1s lines. The peak locations and full widths at half maximum are also given. The binding energies of the Ba 3d and W 4f lines are 0.7 eV higher for $BaWO_4$ than for Ba_2CaWO_6. The Ca 2p spectrum contains two sets of Ca 2p doublets that were attributed to Ba_2CaWO_6 and $CaCO_3$.

Keywords: XPS, barium, tungsten, calcium, tungstate

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1. Introduction

$BaWO_4$ is a candidate material for all-solid-state lasers and for use as a crystal in stimulated Raman spectroscopy as a result of its good mechanical and optical properties[1,2,3]. $BaWO_4$ and other scheelite ceramics are also promising microwave substrate materials for wireless communication applications because of their low permittivity and dielectric losses[4]. Ba_2CaWO_6 is used for activation of tungsten cathodes in high pressure discharge lamps, and Riedel et al. have studied these cathodes using scanning electron microscopy, electron microprobe, cathodoluminescence, and secondary ion mass spectrometry[5].

Both $BaWO_4$ and Ba_2CaWO_6 are also thought to form in porous tungsten cathodes impregnated with BaO and CaO after oxygen contamination[6,7,8]. Energy dispersive spectroscopy and scanning electron microscopy have been used in post-test analyses of these cathodes and have suggested the presence of $BaWO_4$ and Ba_2CaWO_6 on the emitter surface[9]. These thick solid tungstate layers have poor emission properties and may close off the tungsten pores to prevent the release of barium to the surface—a key component for achieving the low work function surface necessary for proper operation of these cathodes[9]. XPS data on these tungstates are limited, and therefore, the objective of this work is to obtain the reference binding energies. XPS spectra of both compounds are presented and discussed.

2. Experimental Setup

X-ray photoelectron spectra were obtained for $BaWO_4$ and Ba_2CaWO_6 using an M-Probe XPS system with monochromatic Al Kα X-rays at the Molecular Materials Research Center at the California Institute of Technology. The samples were analyzed under UHV at a base pressure less than 1×10^{-9} Torr. High resolutions scans, with a resolution of ~0.8 eV, were collected and the binding energies were measured for the most intense barium (Ba 3d), tungsten (W 4f), calcium (Ca 2p), and oxygen (O 1s) lines. Binding energies were calibrated by measuring the binding energy of a gold foil and setting the binding energy of the Au $4f_{7/2}$ line to 83.8 eV. The measured spectra for each tungstate sample were referenced to the adventitious C 1s line at 284.8 eV. The tungstate samples analyzed in this work are powders of $BaWO_4$ and Ba_2CaWO_6 (99.9% purity, Sigma-Aldrich) pressed into indium foil. The indium was etched in a solution of 10% HCl by volume for five minutes at room temperature in order to remove oxides from the surface. The indium was rinsed twice in 18 MΩ-cm deionized water and then rinsed with acetone. The samples were not electrically conductive, and therefore, charge compensation was necessary. Following the procedure presented by Vasquez[10], a low energy flood gun was used to eliminate charging effects, and a 90% transmitting mesh screen was mounted approximately 1.5 mm above the sample to improve electron optics. CasaXPS version 2.3.16 was used to calculate the peak locations, areas, and full widths at half maximum from the high-resolution data. All atomic ratios were calculated using the relative sensitivity factors listed in Ref. [11].

3. Results and Discussion

A survey scan of the Ba_2CaWO_6 sample is presented in Fig. 1, and the major lines are identified. Note the presence of the In 3d lines as a result of using In foil as a substrate material. The C 1s spectra for both tungstates are presented in Fig. 2. All spectra were adjusted so that the adventitious C 1s line occurred at 284.8 eV. Ba_2CaWO_6 also contains lines in the C 1s spectrum at 287.9 and 289.1 eV, and $BaWO_4$ contains lines at 285.8 and 288.5 eV. Both samples were exposed to atmosphere and were analyzed “as received.”' Therefore, the C 1s spectra show typical surface contamination in which oxygen is bonded to carbon contaminants, with the peaks at 287.9 and 285.8 eV likely referring to a C-O-C component and the peaks at 289.1 and 288.5 eV referring to a O-C=O component.

The Ba 3d, W 4f, O 1s, and Ca 2p spectra are presented in Figs. 3-6 and a summary of the binding energies and full widths at half maximum are given in Table 1. The Ba 3d spectra shown in Fig. 3 consist of two lines at 780 and 795 eV, corresponding to the Ba $3d_{5/2}$ and Ba $3d_{3/2}$ lines, respectively. The Ba 3d lines for $BaWO_4$ are approximately 0.7 eV higher in binding energy than those for Ba_2CaWO_6. The W 4f spectra shown in Fig. 4 consist of two lines at 35 and 37 eV, which correspond to the W $4f_{7/2}$ and W $4f_{5/2}$ lines, respectively. The W 4f lines for $BaWO_4$ are also shifted to higher binding energies than those for Ba_2CaWO_6 by 0.7 eV. The Ba/W atomic ratios are 0.82 and 1.93 for $BaWO_4$ and Ba_2CaWO_6, respectively.

The O 1s spectra are shown in Fig. 5. The component at 531.1 eV in both samples can be assigned to the oxygen in $BaWO_4$ and Ba_2CaWO_6. The Ba/O and W/O atomic ratios for the $BaWO_4$ sample were calculated to be 0.20 and 0.25, respectively. These values are consistent with the theoretical value of 0.25. The Ba/O and W/O atomic ratios for the Ba_2CaWO_6 sample were calculated to be 0.33 and 0.17, respectively, which also agree well with the theoretical values. The O 1s spectrum for Ba_2CaWO_6 contains a component at 529.3 eV that is not present for $BaWO_4$. Using this O 1s component and the C 1s component at 289.1 eV in the Ba_2CaWO_6 sample gives a C/O atomic ratio of 0.33, which may indicate the presence of a carbonate.

The Ca 2p spectrum shown in Fig. 6 contains four lines at 345.2, 347.0, 348.4, and 350.5 eV. Based on the area ratios and distances between peak locations, these lines are two sets of Ca 2p doublets spaced ~2 eV apart. The Ba/Ca, Ba/W, and Ba/O atomic ratios are 1.76, 1.93, and 0.33, respectively, using the low binding energy set of Ca 2p lines at 345.2 and 348.4 eV. This is in agreement with the chemical formula for Ba_2CaWO_6. The second set of Ca 2p peaks at higher binding energy may be attributed to $CaCO_3$. The ratio of Ca to CO_3 using the set of Ca 2p peaks at 347.0 and 350.5 eV is 0.75, which is 25% lower than the theoretical value of 1 expected for $CaCO_3$. The carbonate may not be completely in the form of $CaCO_3$, however, and some In_2CO_3 from the substrate may be present. A high resolution scan of the In 3d peak was not taken, but the peak heights in the Ba_2CaWO_6 survey scan can give some information on the relative quantity of In. Using the relative sensitivity factors based on height given in Ref. [11], the total amount of Ca present in the sample volume was about twice the amount of In. However, since half of the Ca was in the form of Ba_2CaWO_6, the ratio of In to $CaCO_3$ is approximately 1. Assuming In is present in the form of In_2CO_3, this suggests there is twice as much $CaCO_3$ as In_2CO_3. This lowers the ratio of Ca to CO_3 to 0.67, which is much closer to the measured value.

4. Conclusions

The reference spectra presented here may be useful for identification of these tungstates. Both samples showed contamination as indicated by the presence of C-O-C and O-C=O components in the C 1s and O 1s spectra. The binding energies of both the Ba 3d and W 4f lines were 0.7 eV higher for $BaWO_4$ than for Ba_2CaWO_6. The O 1s spectrum for Ba_2CaWO_6 contained a low binding energy component not present in the $BaWO_4$ spectrum that has been attributed to $CaCO_3$ and In_2CO_3. Additionally, the Ca 2p spectrum for Ba_2CaWO_6 contained two sets of Ca 2p doublets spaced 2 eV apart. The set of Ca 2p peaks at lower binding energy was attributed to Ba_2CaWO_6 and the set at higher binding energy was attributed to $CaCO_3$.

Acknowledgements

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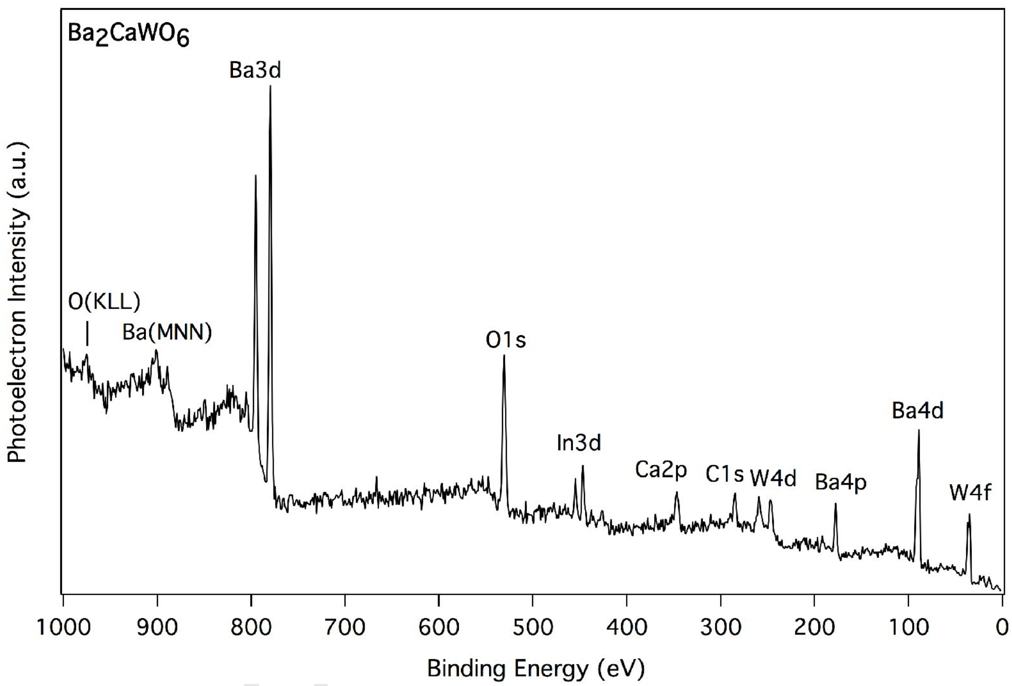

Figure 1: XPS survey scan of Ba_2CaWO_6.

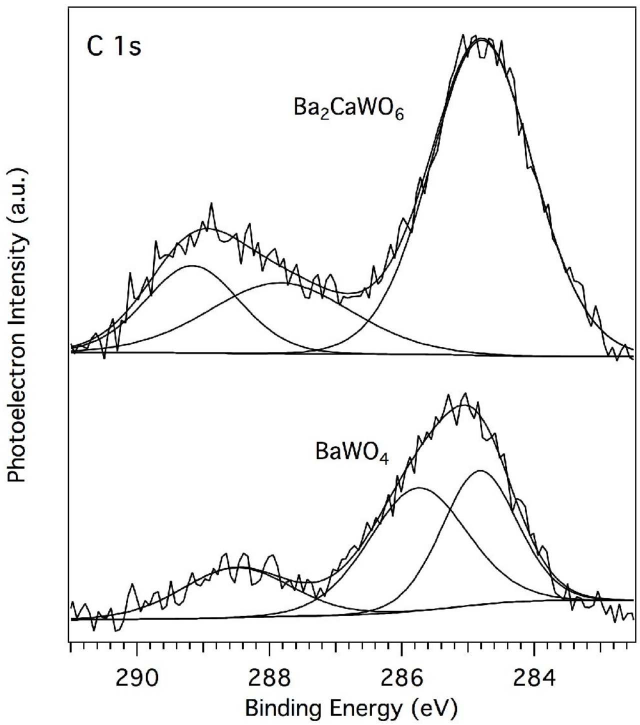

Figure 2: High resolution scans of the C 1s peaks for $BaWO_4$ and Ba_2CaWO_6.

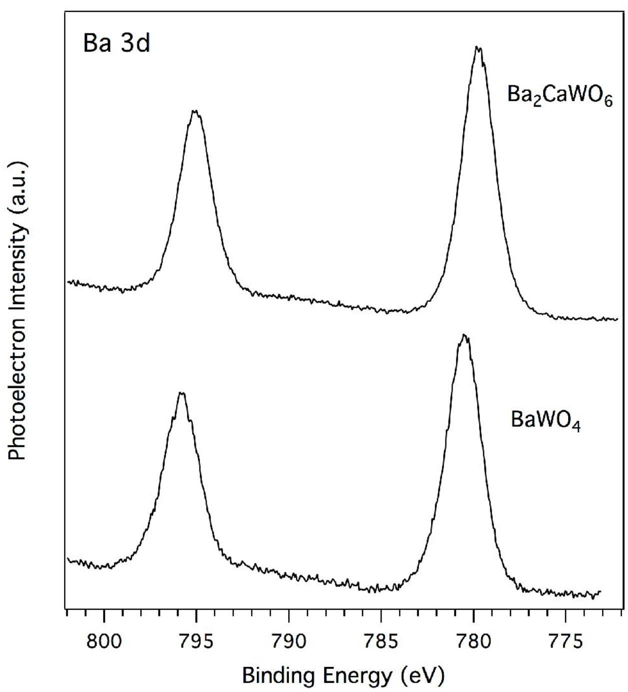

Figure 3: High resolution scans of the Ba 3d peaks for $BaWO_4$ and Ba_2CaWO_6.

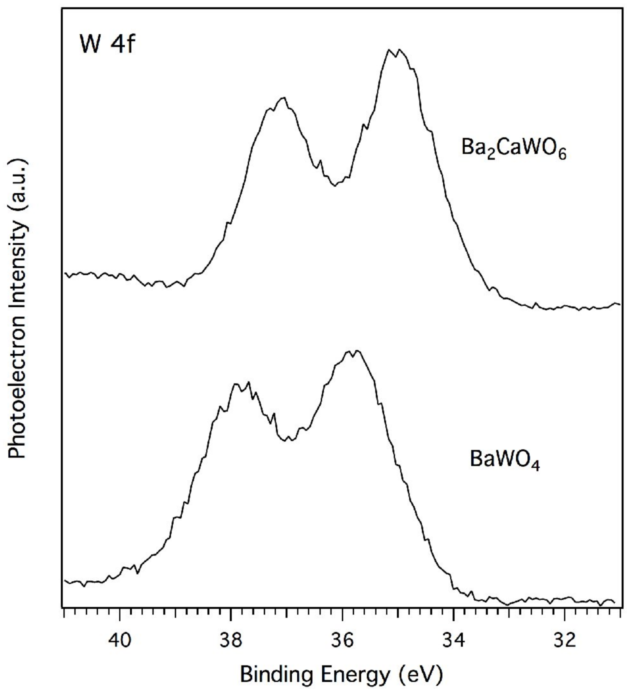

Figure 4: High resolution scans of the W 4f peaks for $BaWO_4$ and Ba_2CaWO_6.

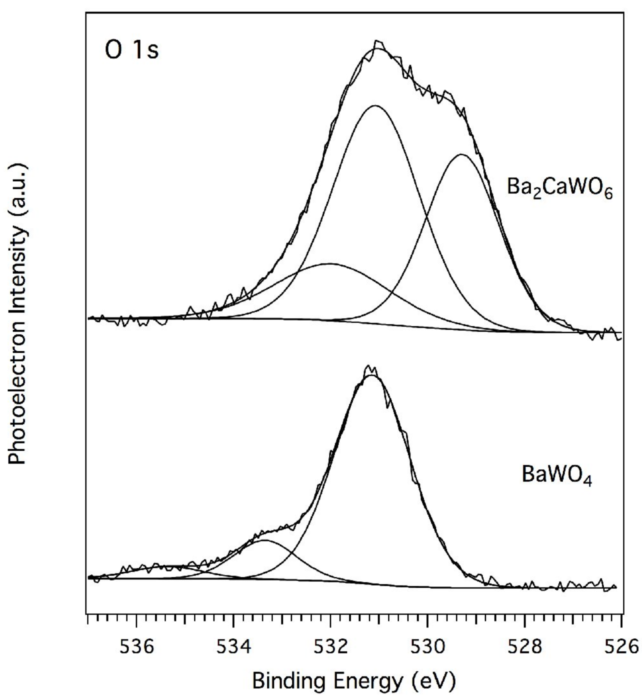

Figure 5: High resolution scans of the O 1s peaks for $BaWO_4$ and Ba_2CaWO_6.

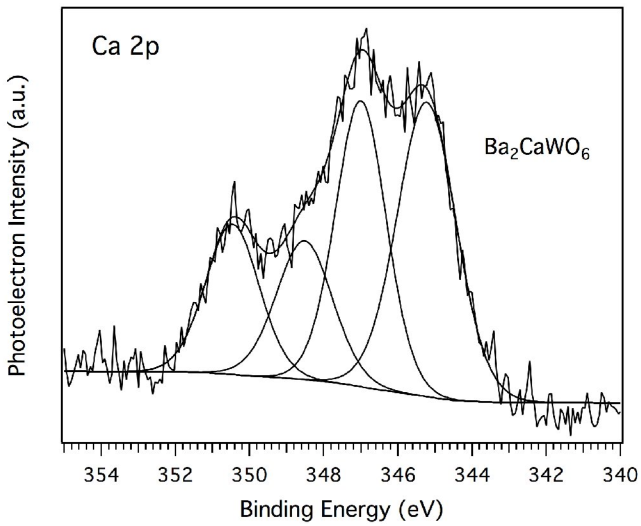

Figure 6: High resolution scan of the Ca 2p peaks for Ba_2CaWO_6.

Table 1: Values of the peak positions and full widths at half maximum for $BaWO_4$ and Ba_2CaWO_6.

Line	$BaWO_4$ BE (fwhm), eV	Ba_2CaWO_6 BE (fwhm), eV
W $4f_{7/2}$	35.7 (1.72)	35.0 (1.57)
W $4f_{5/2}$	37.8 (1.75)	37.1 (1.45)
Ca $2p_{3/2}$	---	345.2 (1.87)
Ca $2p_{1/2}$	---	348.4 (1.78)
Ca $2p_{3/2}$	---	347.0 (1.61)
Ca $2p_{1/2}$	---	350.5 (1.70)
O 1s	531.1 (1.87)	529.3 (1.81)
O 1s	533.4 (1.53)	531.1 (2.12)
O 1s	535.4 (1.72)	532.0 (2.79)
Ba $3d_{5/2}$	780.5 (2.32)	779.7 (2.19)
Ba $3d_{3/2}$	795.8 (2.42)	795.1 (2.19)