LBNL-39731
UC-410
Preprint

ERNEST ORLANDO LAWRENCE
BERKELEY NATIONAL LABORATORY

Resonant Inelastic Scattering at the L Edge of Ti in Barium Strontium Titanate by Soft X-ray Fluorescence Spectroscopy

Y. Uehara, D.W. Lindle, T.A. Callcott,
L.T. Terminello, F.J. Himpsel, D.L. Ederer,
J.H. Underwood, E.M. Gullikson, and
R.C.C. Perera
Accelerator and Fusion Research Division

December 1996
Submitted to
Applied Physics A

REFERENCE COPY
Does Not
Circulate
Bldg. 50 Library - Ref.
Lawrence Berkeley National Laboratory
Copy 1
LBNL-39731

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBNL-39731
LSBL-254

RESONANT INELASTIC SCATTERING AT THE L EDGE OF TI IN BARIUM STRONTIUM TITANATE BY SOFT X-RAY FLUORESCENCE SPECTROSCOPY

Y. Uehara, D.W. Lindle
Department of Chemistry, University of Nevada, Las Vegas, NV 89154

T.A. Callcott
Department of Physics, University of Tennessee, Knoxville, TN 37996

L.T. Terminello
Lawrence Livermore National Laboratory, Livermore, CA 94551

F.J. Himpsel
Synchrotron Radiation Center, University of Wisconsin, Stoughton, WI 53589

D.L. Ederer
Department of Physics, Tulane University, New Orleans, LA 70118

J.H. Underwood, E.M. Gullikson, and R.C.C. Perera
Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, California 94720

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

Light Source Note:
Author(s) Initials 12/2/96 Date
Group Leader's initials 12/11/96 Date

Resonant Inelastic Scattering at the L Edge of Ti in Barium Strontium Titanate by Soft X-ray Fluorescence Spectroscopy

Y. Uehara*, D.W. Lindle
Department of Chemistry, University of Nevada, Las Vegas, NV 89154
** on leave from Mitsubishi Electric Co., Amagasaki, Hyogo 661, Japan*
(Fax: +81-6/497-7602, E-mail: uehara@ana.edl.melco.co.jp)

T.A. Callcott
Department of Physics, University of Tennessee, Knoxville, TN 37996

L.T. Terminello
Lawrence Livermore National Laboratory, Livermore, CA 94551

F.J. Himpsel
Synchrotron Radiation Center, University of Wisconsin, Stoughton, WI 53589

D.L. Ederer
Department of Physics, Tulane University, New Orleans, LA 70118

J.H. Underwood, E.M. Gullikson, and R.C.C. Perera
Lawrence Berkeley National Laboratory, Berkeley, CA 94720
(Fax: +1-510/486-7696, E-mail:rupert@Csa2.lbl.gov)

Abstract.

Photon-excited Ti L fluorescence spectra were measured for cubic barium strontium titanate (BST) using tunable synchrotron radiation around the Ti L-edge. Elastic (recombination) peaks were observed around Ti L_3 and L_2 resonances, especially strong at the L_3 resonance, while inelastic peaks were observed from well below the resonance and showed complex features at the excitation energies between the Ti L_3 and L_2 resonances. The calculated band structures of STO and BTO indicate electron transition channels which may be related to the inelastic features in the emission spectra of BST.

PACS: 73; 77; 78.70

Perovskite-type titanates, such as Strontium Titanate (STO), Barium Titanate (BTO), and Lead Titanate (PTO) have been widely studied because they show good electric and optical properties. In recent years, thin films of Barium Strontium Titanate (BST) have been paid much attention as dielectrics of dynamic random access memory (DRAM) capacitors [1]. BST is a better insulator with a higher dielectric constant than STO and can be controlled in a paraelectric phase with an appropriate ratio of Ba/Sr composition, however, few studies have been done on the electronic structure of the material. Studies of the electronic structure of such materials can be beneficial, both for fundamental physics research and for improving technological applications.

Soft x-ray emission spectroscopy using photon excitation, i.e., soft x-ray fluorescence (SXF), has a lot of unique advantages [2]. Both excitation and emission are selective chemically and in terms of angular momentum, thus one can obtain information about partial density of states. Photon penetrates many atomic layers into the matter, not as affected by surface contamination as electron spectroscopy, making it a true bulk probe of the electronic structure. Furthermore, the tunability of the synchrotron radiation has stimulated interests in the problem of understanding of the coupling of excitation and emission processes for excitation near threshold. Traditionally, SXF spectroscopy has been severely limited by weak excitation sources and low radiative yields of the emission process. However, with the development of intense undulator-based synchrotron radiation sources and improved spectrometers, many new experiments are now feasible [3,4].

Recently, J. Jimenez-Mier et al.[5] reported interesting results on Ti L x-ray emission spectra of several Ti compounds, including BTO. Details on the energy dependence of the spectra of BTO has not been shown yet, however, the spectrum of BTO in the report shows

several inelastic scattering peaks when excited with photons of 461.0 eV. BTO is a famous ferroelectric material with a tetragonal structure, in which Ti and Ba atoms are slightly displaced from the lattice points. On the other hand, BST keeps a paraelectric phase, which means that the atoms are still at the cubic lattice points. It should be of great interests to see how this difference of the local structure around Ti atoms between BTO and BST has effects on the emission spectra, i.e. the electronic structure of the matters.

In this paper, we present the Ti $L_{2,3}$ fluorescence spectra of BST excited with photon energies near the Ti $L_{2,3}$ absorption edges, as well as the Ti $L_{2,3}$ absorption spectra of STO, BTO, and BST measured with very high accuracy in energy of the absorption features. A speculation about the origin of inelastic peaks seen in the Ti $L_{2,3}$ fluorescence spectra of BST is also presented partially based on calculated band structures of STO and BTO.

1 Experimental

STO and BTO powders were commercially available ones with over 99.9% purity. BST powder was obtained from a commercially available sputtering target ceramic, which was purchased from Mitsubishi Materials Co. Ba/Sr molar ratio of the powder was analytically determined to be 1, and x-ray powder diffraction revealed that the material remains a cubic structure.

The x-ray absorption measurements were carried out on Beamline 6.3.2 at the Advanced Light Source (ALS), an entrance slitless bend magnet beamline equipped with a Hettrick-Underwood type varied line space (VLS) grating monochromator [6]. The energy resolution of the monochromated photons was set at $E / \Delta E = 3000$ around the Ti L-edge energy region. The powder samples were spread onto an indium foil, and the absorption

spectra presented in this work were obtained in step scanning the monochromator and measuring the total electron yield (photoelectron, Auger and secondary) from the sample (foil). The monochromator in BL6.3.2 was constructed and assembled in a manner that provides absolute energy measurements [6,7]. The photo-currents from the third mirror was monitored as the incident photon flux monitor.

The SXF experiments were performed at Beamline 8.0 at the ALS. Monochromatized photons from the 5.0 cm period undulator (U5.0) were focused onto the sample, and emitted radiation was measured with a Rowland-circle-type spectrometer [8] utilizing 5m radius spherical gratings and a photon counting area detector. The energy band-pass of the photons from the monochromator was set at 0.5 eV, while the spectrometer was operated at a resolution of around 1 eV for the Ti L-edge. The BST powder was pressed into a pellet for the SXF measurements. Incident photon flux was monitored by measuring photo-currents from a gold-coated screen inserted in the beam just upstream from the sample.

2 Results and Discussions

Figure 1 shows the x-ray absorption spectra around Ti $L_{2,3}$ edge of STO, BST, and BTO. The three spectra are quite similar to each other, and show four distinct peaks which correspond to the transition of Ti $2p_{3/2}$ - Ti 3d and Ti $2p_{1/2}$ - Ti 3d. Energy shifts of as much as 0.3 eV are observed between the peaks of STO and those of BTO, and the peaks of BST resemble the middle energy. From these results, it can be predicted that the distortion of TiO_6 clusters due to the tetragonal crystal structure in BTO does not affect the fine structure of Ti 3d levels. However, the Ti - O bond length has some effects on the energy levels of those states. Besides those eminent peaks, two weak pre-edge peaks are observed on all three

spectra. According to the band structure calculations [9], the lowest unoccupied molecular orbital (LUMO) is mainly formed by Ti 3d orbital in these materials. However, O 2p orbital, which is just few eV below the Ti 3d orbital, may perform as transition states for the excited Ti 2p electrons.

Figure 2 shows the SXF spectra of BST excited with photon energies near the Ti L-edge. All spectra are normalized to the incident photon flux, and labeled by the excitation energy. For display purposes, the spectra excited at 459 - 463 eV are shown in Fig. 3. Self-absorption may distort the emission spectra when absorption and emission spectra overlap. As for titanium, the L_2 emission lays above the L_3 absorption. Since our discussion in this report is qualitative in nature, no attempt was made to correct the data presented in this work for self absorption.

At higher energy, well above the Ti $L_{2,3}$ edges region, the normal Ti L fluorescence peaks, generated by the radiative recombination of Ti valence states with the core holes, are observed at about 450 eV ($L\alpha_{1,2}$) and 457 eV ($L\beta_1$), with a satellite peak at about 463 eV. The peaks, labeled E, appear when the excitation energy is above 456 eV, and disappear completely above 466 eV. The energy positions of those peaks coincide with the excitation energy of each spectrum, thus those emissions should attribute to the resonant elastic peaks (the recombination peaks), a phenomena in which the electron is excited to a well-localized unoccupied state, and if the core hole lives long enough for the excited electron to relax directly into the initial state. It should be noted that these elastic peaks are not so prominent at the L_2 resonance region as at the L_3 resonance, even when considering the self absorption. A weak emission peak appears when the excitation energy is 454 eV, more than 3 eV below the first resonance peak, but on the pre-edge peak. This symmetric peak increases in intensity and

shifts toward higher energy as the excitation energy increases, and becomes unsymmetrical when the excitation energy is 460 eV, the energy just above the second resonance peak. Besides the main peak (labeled A in Fig. 3) at about 450 eV, the spectrum at 460 eV has another peak (labeled B) which overlaps the main peak but clearly has a maximum about a few eV higher than the main peak, and also has a humped tail at the low energy side (labeled C & D). When excited at 461 eV, the spectral features clearly separate into three peaks labeled A, B, and C, with the low energy tail labeled D. The peak B tracks the excitation energy, has the maximum when excited at around 456 eV, on the fourth resonance, then decreases into the satellite peak mentioned above. The peak C maintains the energy and becomes the normal fluorescence, as the excitation energy increases. On the other hand, the peak A seems to disappear when the excitation energy is above 463 eV.

The changes in the emission spectra are so complex, it is not easy to understand the whole processes occurring in the BST based on calculated band structures of STO and BTO. The existence of the elastic recombination peaks suggests that the Ti 3d states in BST are localized. When explaining the inelastic features, peak B in Fig.3 and the symmetric peaks in Fig.2 for the excitation energies from 454 eV to 459 eV, we have to consider relaxation passes of the electron excited to the valence band or to an excitonic state. Figure 4 shows the band structures of STO (a) and BTO (b), obtained using an *ab-initio* cluster calculation [9]. Comparing the two materials, while energy levels in BTO split due to tetragonal symmetry and direct and indirect band gaps are smaller than those of STO, the shape of the band structure of BTO is similar to that of STO. From this similarity, we can assume that the shape of the band structure of BST is also similar to those of BTO and STO. The shape and the energy levels of the band structure indicate that the inelastic features are related to electron transition channels

of Ti (3d) -> O (2p) and Ti (3d) -> Ti (3d). Further experimental studies on related materials and theoretical works are expected to reveal the whole features of the emission spectra.

3 Conclusions

We have presented the Ti $L_{2,3}$ fluorescence spectra of a cubic BST excited with photon energies around the Ti $L_{2,3}$ absorption edges, as well as the precisely measured Ti $L_{2,3}$ absorption spectra of STO, BTO, and BST. The absorption spectra of the three materials are quite similar to each other, while energy shifts of as much as 0.3 eV were observed between the resonance peaks of STO and BTO. In the Ti $L_{2,3}$ emission spectra of BST, the resonant elastic (recombination) peaks and complex resonant inelastic peaks were observed. The calculated band structures of STO and BTO indicate electron transition channels which may be related to the inelastic features in the emission spectra.

Acknowledgments.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract Nos. DE-AC03-76SF00098 and W-7405-ENG-48, and National Science Foundation Grant No. DMR-9017996 to the University of Tennessee.

References

[1] T. Horikawa, N. Mikami, T. Makita, J. Tanimura, M. Kataoka, K. Sato, M. Nunoshita: Jap. J. Appl. Phys. **32**, 4126 (1993)

[2] D.L. Ederer, T.A. Callcott, R.C.C. Perera: Synchrotron Radiation News **7**, 29 (1994)

[3] J.A. Carlisle, L.J. Terminello, E.A. Hudson, R.C.C. Perera, J.H. Underwood, T.A. Callcott, J.J. Jia, D.L. Ederer, F.J. Himpsel, M.G. Samant: Appl. Phys. Lett. **67**, 34 (1995)

[4] J.J. Jia, T.A. Callcott, A. Asfaw, J.A. Carlisle, L.J. Terminello, D.L. Ederer, F.J. Himpsel, R.C.C. Perera: Phys. Rev. **B52**, 4904 (1995)

[5] J. Jimenez-Mier, D.L. Ederer, U. Diebold, A. Moewes, T.A. Callcott, L. Zhou, J.J. Jia, J.A. Carlisle, E.A. Hudson, L.J. Terminello, A. Asfaw, F.J. Himpsel, R.C.C. Perera: Proc. of REX Conference, New Orleans, LA (Dec. 8-9, 1995)

[6] J.H. Underwood, E.M. Gullikson, M. Koike, P.J. Batson, P.E. Denham, K.D. Franck, R.E. Tackaberry, W.F. Steele: Rev. Sci. Instrum. (in press).

[7] J.J. Jia, J.H. Underwood, E.M. Gullikson, T.A. Callcott, R.C.C. Perera: J. Electron Spectrosc. and Relat. Phenom. **80**, 509 (1996)

[8] J.J. Jia, T.A. Callcott, J. Yurkas, A.W. Ellis, F.J. Himpsel, M.G. Samant, J. Stohr, D.L. Ederer, J.A. Carlisle, E.A. Hudson, L.J. Terminello, D.K. Shuh, R.C.C. Perera: Rev. Sci. Instrum.: **66**, 1394 (1995)

[9] T. Kamiya, T. Tanaka, T. Tsurimi, M. Daimon: Jap. J. Appl. Phys. **33**, 3965 (1994)

Figure captions

Fig. 1 The Ti L-edge absorption spectra of $SrTiO_3$ (STO), $Ba_{0.5}Sr_{0.5}TiO_3$ (BST), and $BaTiO_3$ (BTO) powders. The peak energies are indicated on each peak.

Fig. 2 The Ti $L_{2,3}$ emission spectra of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) powder. The numbers labeling the curves are the excitation energies. All spectra are normalized to the incident photon fluxes.

Fig. 3 The Ti $L_{2,3}$ emission spectra of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) powder excited with the photon energies of 459 to 463 eV.

Fig. 4 Calculated band structures of $SrTiO_3$ and $BaTiO_3$, taken from Ref. 8.

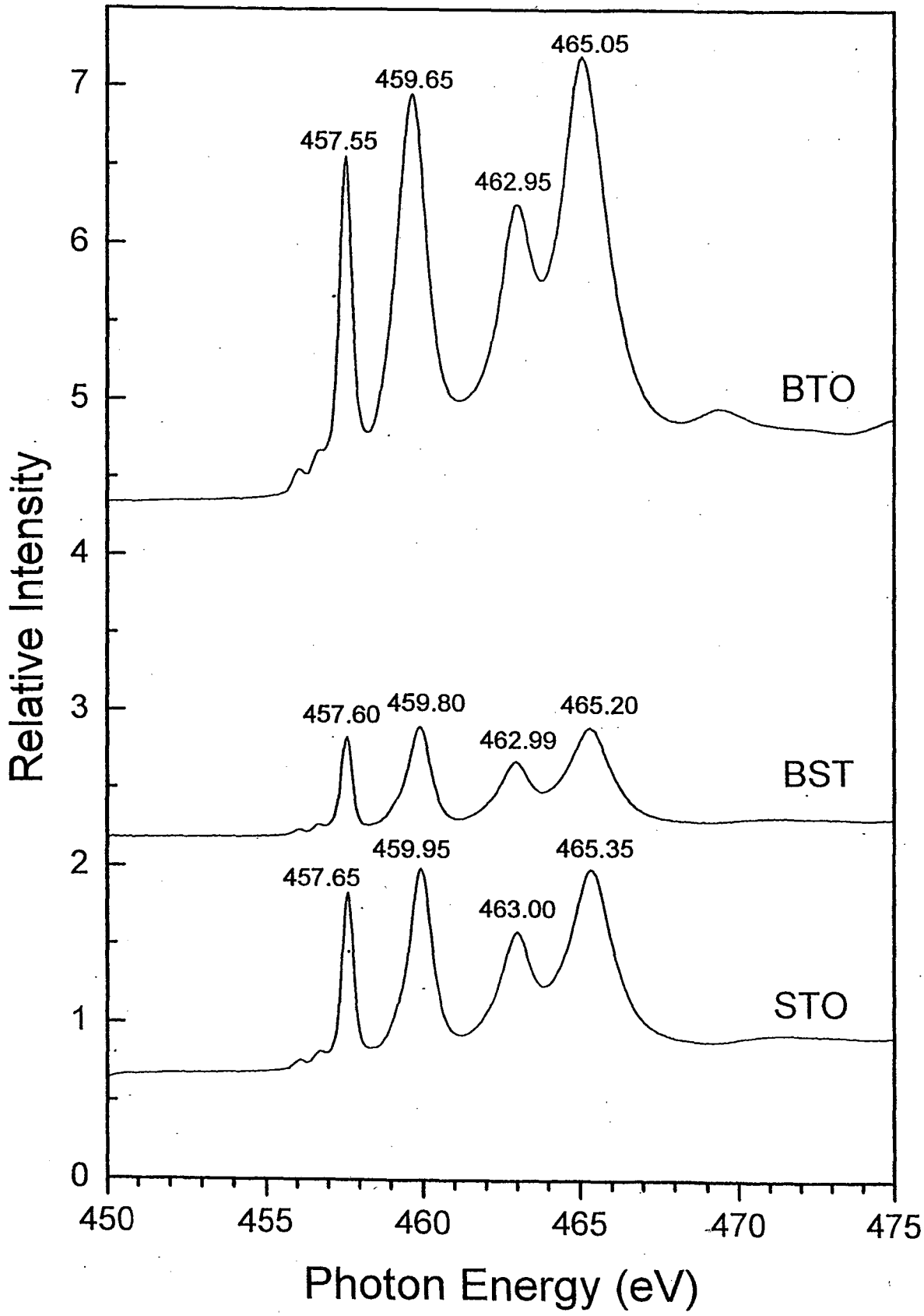

465.05
459.65
457.55
462.95
BTO
457.60
459.80
465.20
462.99
BST
459.95
465.35
457.65
463.00
STO
Relative Intensity
0
1
2
3
4
5
6
7
450
455
460
465
470
475
Photon Energy (eV)

Figure 1

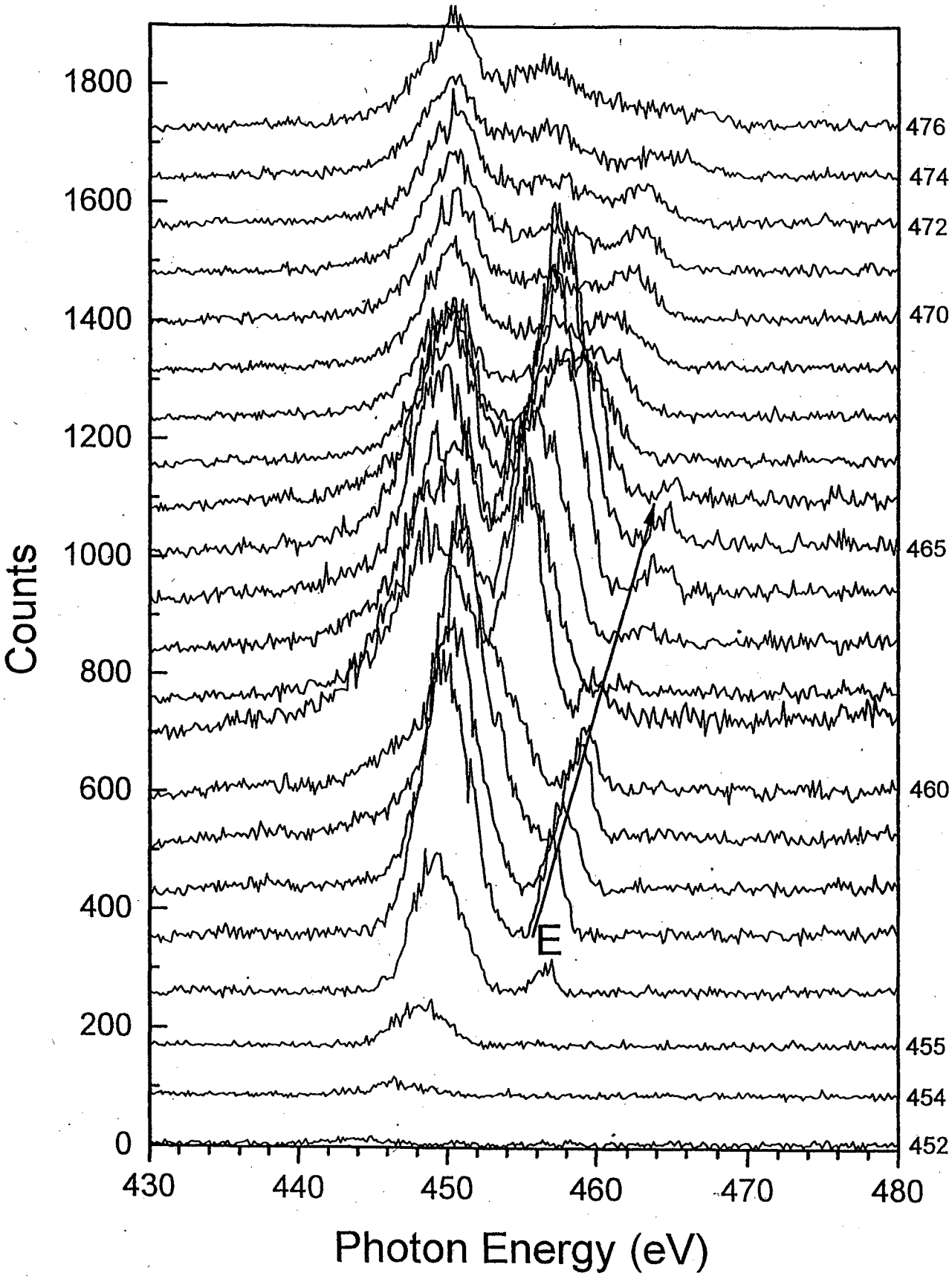

Counts
1800
1600
1400
1200
1000
800
600
400
200
0
430
440
450
460
470
480
Photon Energy (eV)
476
474
472
470
465
460
455
454
452
E

Figure 2

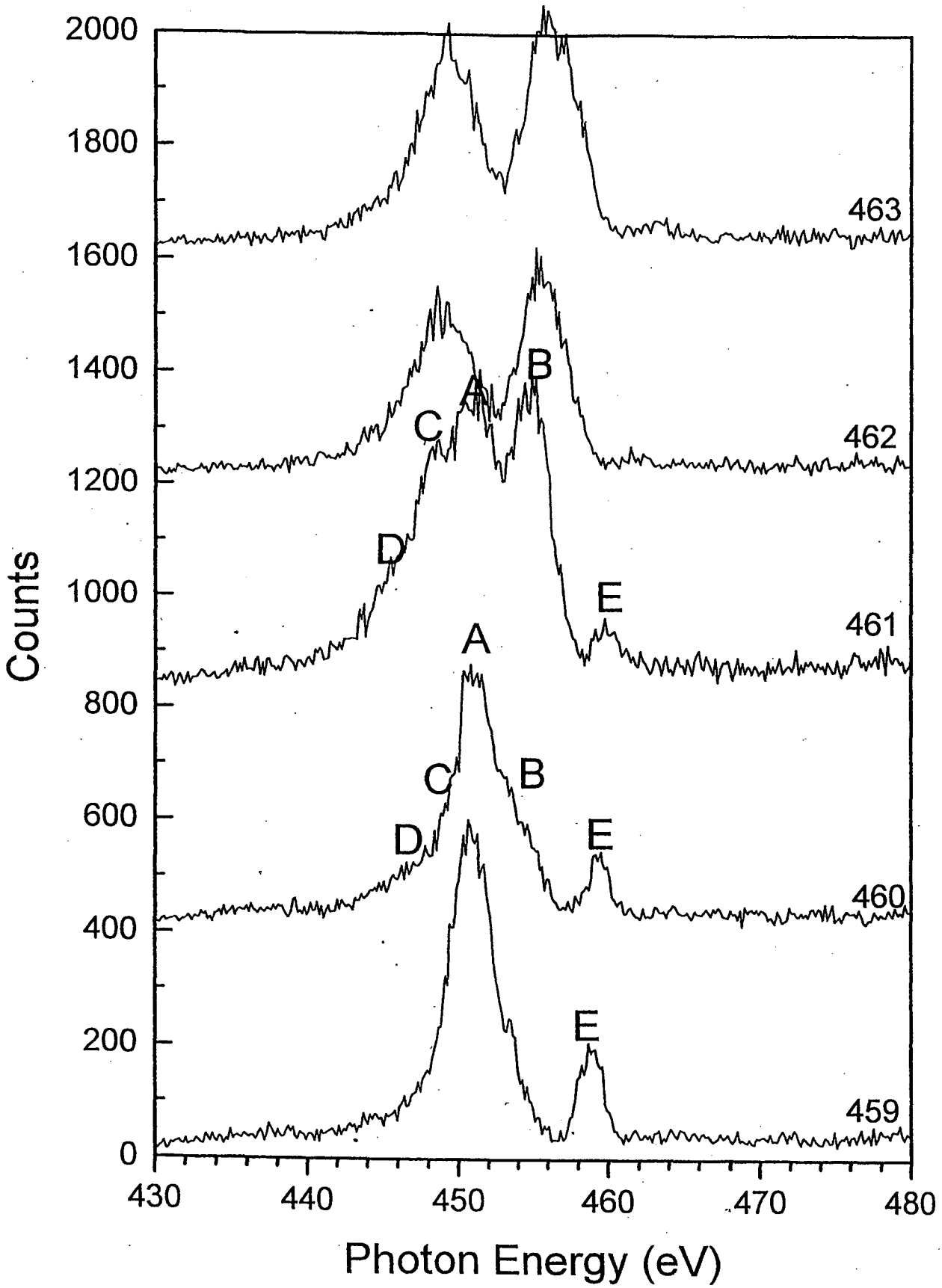
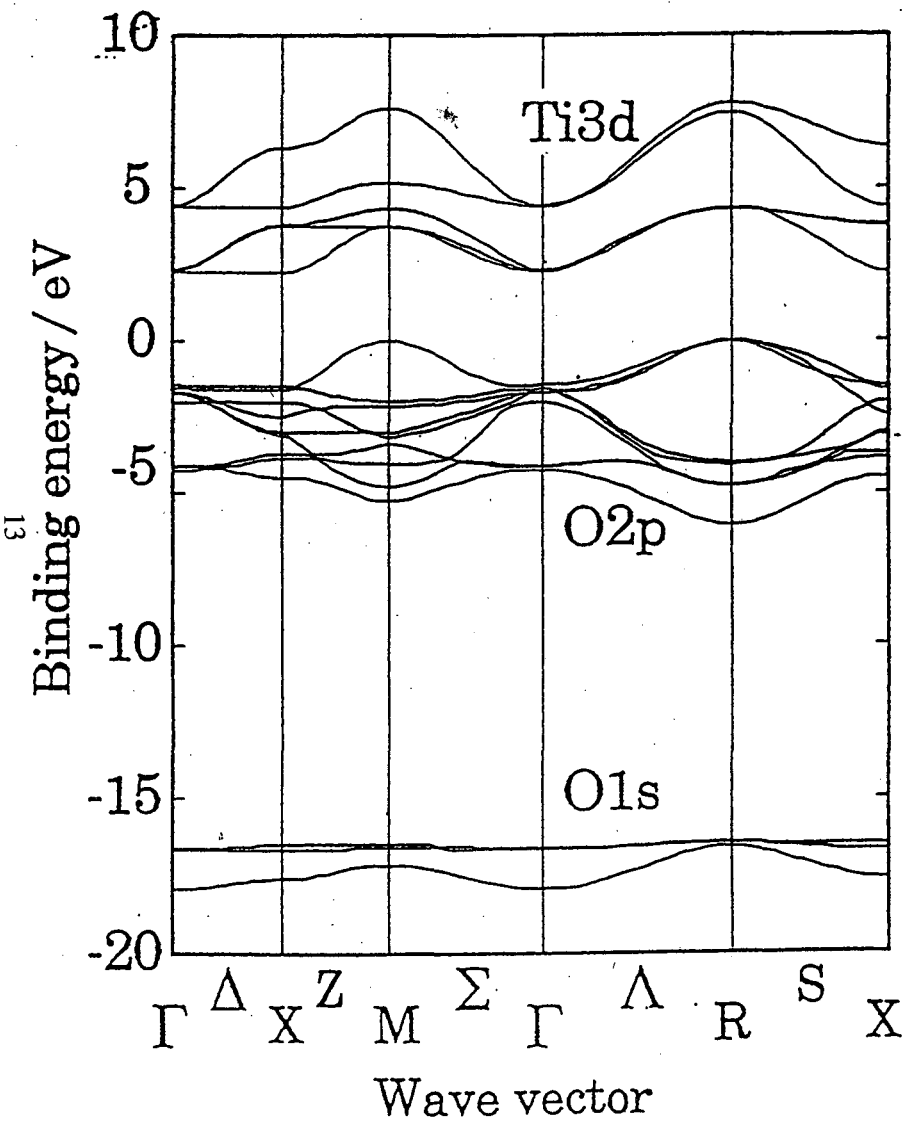

2000
1800
1600
1400
1200
1000
800
600
400
200
0
Counts
430
440
450
460
470
480
Photon Energy (eV)
463
462
461
460
459
A
B
C
D
E

Figure 3


10
5
0
-5
-10
-15
-20
Binding energy / eV
Ti3d
O2p
O1s
Γ Δ X Z M Σ Γ Λ R S X
Wave vector

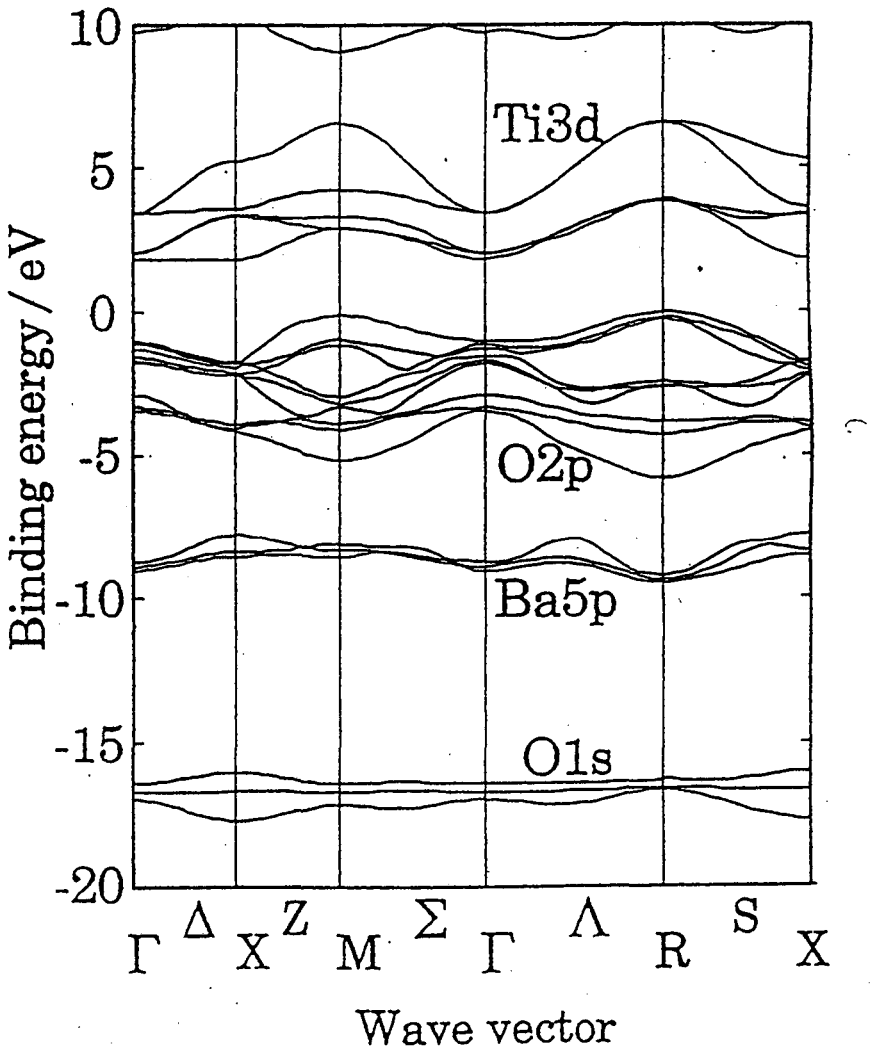

10
5
0
-5
-10
-15
-20
Binding energy / eV
Ti3d
O2p
Ba5p
O1s
Γ Δ X Z M Σ Γ Λ R S X
Wave vector

Figure 4

ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY
ONE CYCLOTRON ROAD | BERKELEY, CALIFORNIA 94720

Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098