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ABSTRACT

Potassium Dihydrogen Phosphate (KDP) is a non-linear optical material used for laser frequency conversion and optical switches. Unfortunately, when KDP crystals are coated with a porous silica anti-reflection coating [1] and then exposed to ambient humidity, they develop dissolution pits [2,3]. Previous investigations [2] have shown that thermal annealing renders KDP optics less susceptible to pitting suggesting that a modification of surface chemistry has occurred. X-ray absorption and fluorescence were used to characterize changes in the composition and structure of KDP optics as a function of process parameters. KDP native crystals were also analyzed to provide a standard basis for interpretation. Surface sensitive total electron yield and bulk sensitive fluorescence yield from the K 2p, P 2p ($L_{2,3}$-edge) and O 1s (K-edge) absorption edges were measured at each process step. Soft X-ray fluorescence was also used to observe changes associated with spectral differences noted in the absorption measurements. Results indicate that annealing at 160°C dehydrates the surface of KDP resulting in a metaphosphate surface composition with K:P:O = 1:1:3.

INTRODUCTION

Potassium dihydrogen phosphate [KH_2PO_4 (KDP)] is a transparent dielectric material best known for its nonlinear optical and electro-optical properties. Because of its nonlinear optical properties, it has been incorporated into various laser systems for harmonic generation and optoelectrical switching. In addition, KDP is particularly suitable for use in large-aperture laser systems such as that located at the National Ignition Facility (NIF) because it can be grown as a single crystal to large size. For NIF, the KDP optical components are single-point diamond machined, solvent cleaned, and then coated with a porous silica sol-gel anti-reflection layer [1]. Unfortunately, when the KDP crystals are subsequently exposed to ambient humidity, the porous sol-gel coating provides a reservoir of water adsorbed from the air which can then wick up dissolved KDP and form etch pits [2,3]. Previous investigations [2] have shown that thermal annealing at 160°C renders KDP optics less susceptible to pitting, suggesting that a modification of surface chemistry has occurred. Thermal annealing KDP optics for 1 -2 weeks at 160°C has proven an effective technique for improving the bulk laser damage threshold [4]. The effect of this process on the surface chemistry of KDP, however, has not been previously reported.

Thermal decomposition of alkali metal dihydrogen phosphates, has been reported to proceed through various polymeric intermediates during the course of dehydration to eventually form KPO_3 [5]. In our laboratory, we have followed the dehydration of KDP and consequent formation of metaphosphate by infrared spectroscopy. Using a Bomem MB-104 Fourier-transform infrared spectrometer (FTIR) operating in reflectance mode, KDP optical components were analyzed before and after annealing at 160 °C for 84 days.

The resulting spectra are shown in Figure 1. Dehydration is indicated by the complete loss of P-O-H bands 2420 cm^{-1} (not shown). Formation of a metaphosphate is indicated by the appearance of P-O-P bands at 1150 cm^{-1} and 680 cm^{-1}, and by the "splitting" of P-O and PO_4^{-3} bands at 1300 cm^{-1}, 1095 cm^{-1}, and 550 cm^{-1}.

This paper uses x-ray absorption and x-ray fluorescence to characterize changes in the composition and structure of KDP optics as a function of process parameters. Surface sensitive total electron yield and bulk sensitive fluorescence yield from the K 2p, P 2p ($L_{2,3}$-edge) and O 1s (K-edge) absorption edges were measured at each process step. Soft X-ray fluorescence was also used to observe changes associated with spectral differences noted in the absorption measurements.

EXPERIMENTAL

X-ray absorption spectroscopy (XAS) probes empty or unfilled electronic states and provides information on the local chemical environment. This analysis was performed at beamline 8.2 at the Stanford Synchrotron Radiation Laboratory (SSRL) and at beamline 8.0.1 at the Advanced Light Source (ALS) by scanning the photon energy of the incoming monochromatic synchrotron radiation through the K 2p, P 2p ($L_{2,3}$-edge) and O 1s (K-edge) core-level edges while monitoring the total electron yield (TEY, surface sensitive, 50-100Å). At ALS, we were also able to monitor the fluorescence yield (FY, bulk sensitive, 0.1–1.0 µm).

Soft x-ray fluorescence spectroscopy (SXRF) was performed at beamline 8.0.1 of ALS. It is a bulk-sensitive probe due to the long mean free path of photons in solids (0.1–

1.0 μm). Since core levels are involved in absorption and emission, SXRF is both element- and angular-momentum-selective. SXRF measures the local element specific partial density of states (DOS).

In SXRF, a valence emission spectrum results from transitions from valence band states to the core hole produced by the incident photons. In the non-resonant energy regime, the excitation energy is far above the core binding energy, and the absorption and emission events are uncoupled. The fluorescence spectrum resembles emission spectra acquired using energetic electrons and is insensitive to the incident photon's energy. In the resonant excitation energy regime, core electrons are excited by photons to unoccupied states just above the Fermi level. The absorption and emission events are coupled and this coupling manifests itself in several ways depending in part on the localization of the empty electronic states in the material.

RESULTS

XAS

The K L -edge, P $L_{2.3}$–edge and O K-edge absorption spectra for the native crystals are presented in Figures 2-4, respectively. The spectra have been normalized to the same edge-jump. [6] Native samples provide XAS baseline standards for interpretation of processed diamond turned KDP optics. These native crystals exist as a tetragonal prism consisting of four faces of the form {100} terminated by two opposing tetragonal pyramids consisting of {101} faces. Theory predicts that prismatic {100} faces should have exactly one surface termination. However, for the pyramidal {101} faces, two alternative terminations are theoretically possible. One has the negative $H_2PO_4^-$

groups on the outside, and the other the positive K^+ ions. The surface atomic structure of both the prismatic (100) and pyramidal (101) faces has been determined by surface x-ray diffraction.[7] These results do indeed show that the (100) surface is neutral, terminated by both K^+ and $H_2PO_4^-$ groups. However, the (101) surface was shown to be terminated by K^+. Our XAS results clearly show that the (101) surface is K-rich relative to the (100) surface, in concurrence with the surface x-ray diffraction results.

Figure 5 shows the C K-edge and K L-edge spectra for the series of processed KDP optics. Again, all spectra have been normalized to the same edge-jump by equalizing baselines below the edge, then equalizing intensities well above the edge by a multiplicative factor. [6] The prominent features in these spectra are the series of C 1s peaks around 285.0 eV and the K 2p peaks at 295.0 and 297.6 eV. The peak at 285.0 eV is usually assigned to excitations into C=C molecular orbitals, and is strongest for the toluene cleaned diamond turned KDP. This indicates that toluene cleaning leaves residual carbonaceous contamination on the KDP surface. However, the UV Ozone treatment breaks the C=C bond as indicated by the decreasing peak intensity, leaving features at 286 eV and 288 eV representative of C–H and C–O, respectively. Thus UV ozone treatment successfully removes some of the residual surface contamination. In addition, the surface becomes progressively cleaner with annealing as evidenced by the increased K 2p peak intensities and diminished C peak intensities.

Figure 6 shows the O K-edge spectra for the series of processed KDP optics. The presence of the π^* feature at ~530 eV indicates residual carbonaceous contamination due to toluene cleaning. The intensity of this feature is diminished following the longer anneals. The major peak at 535.2 eV is assigned to a transition from the O 1s core level to an unoccupied σ^* orbital of the O–P bond. After anneal, additional peak structure is observed due to changes in local chemical environment. A compositional and structural change of the $–PO_4$ tetrahedra on the surface to another form of phosphate (e.g. $–P_2O_7$ with one bridging O or $–P_3O_9$ with three bridging O's) would introduce additional bonding orbitals and thus additional transitions, or peaks, as we observe.

Other differences observed between the unannealed and the annealed diamond turned KDP surfaces are seen in the P L-edge spectra presented in Figure 7. Once again, the diminished peak intensities indicate residual surface contamination due to toluene. Of special interest is the change in peak structure indicating a change in surface chemistry after annealing. Formation of $–P_2O_7$ or $–P_3O_9$ complexes at the surface, due to annealing and consequent dehydration, are structurally different from the $–PO_4$ tetrahedra, thus resulting in changes in the electronic structure. Changes in the surface electronic structure would manifest themselves as additional occupied valence band states and unoccupied conduction band states. Comparison of the P 2p peak structure of the annealed KDP with phosphate standards [8,9] indicates that the surface has dehydrated and converted to a metaphosphate with K:P:O = 1:1:3.

Thermodynamically, the most probable phosphate that will form is $–P_3O_9$, which has an estimated heat of formation ΔH_f of –720 kcal/mole. [11] The other possibility, $–P_2O_7$, has an estimated heat of formation ΔH_f of –543 kcal/mole. [11] Therefore, based on thermodynamic considerations, annealing of the KDP converts the surface composition to a trimetaphosphate.

SXRF

The resonant P 2p SXRF spectra associated with the P $L_{2,3}$-edge XANES for the unannealed and annealed diamond turned KDP optic are shown in Figures 8 and 9, respectively. The SXRF spectra were acquired at the energy positions indicated on the XANES spectra. The SXRF has three peaks that are non-dispersive as the excitation energy is varied across the P $L_{2,3}$–edge of the unannealed KDP optic. In the case of the annealed KDP optic, the structure of the emission peaks has changed. In addition, as the excitation energy is varied across the P $L_{2,3}$–edge, the lower energy emission features shift indicating a change in electronic structure. These changes in electronic structure coincide with the XAS measurements that indicate the formation of a metaphosphate.

The resonant O 1s SXRF spectra associated with the O K-edge XANES also reveal compositional differences between the bulk unannealed and annealed KDP (Figures 10 and 11). As before, the SXRF spectra were acquired at the energy positions indicated on the XANES spectra. Momentum conservation and selectivity are very much in force for all the excitation energies above, equal to, and below the π^* energy at ≈ 530 eV. Below this feature, three peaks are observed in the SXRF spectra for the unannealed material. The same three peaks are shifted to lower energy and have different intensity ratios in the SXRF spectra for the annealed material, again indicating a change in composition and structure due to annealing in air. In addition, the peak at $h\nu' \approx 528$ eV decreases in intensity as we move through the π^* energy and then reappears and slightly shifted to higher energy. At the σ^* edge, the feature located at $h\nu' \approx 531$ eV does not move with excitation energy. Note that its increased intensity corresponds with the σ^*

absorption edge energy ($h\nu = 535.0$ eV). The other dispersive feature at higher energy may also be associated with valence band electronic structure.

CONCLUSIONS

X-ray photoabsorption (XAS) and soft x-ray fluorescence (SXRF) spectroscopies were used to examine the composition and chemical bonding on various potassium dihydrogen phosphate (KDP) surfaces of a series of KDP Optics. Results show that the solvent cleaned KDP surface has residual carbonaceous contamination and that UV ozone cleaning removes this residual carbonaceous contamination Other distinct spectroscopic differences in the P and O spectra were observed between the unannealed and annealed KDP. These results indicate that annealing at 160°C dehydrates the surface of KDP resulting in a metaphosphate surface composition with K:P:O = 1:1:3. In addition, the surface becomes progressively cleaner following longer duration annealing. Results of this experimental investigation have provided a scientific basis for process engineering of KDP optics for NIF.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. Infrared spectrum of the surface of a KDP optical component before (A) and after (B) annealing at 160°C.

Figure 2. XAS K $L_{2.3}$–edge spectra for the native KDP crystals.

Figure 3. XAS P $L_{2.3}$–edge spectra for the native KDP crystals.

Figure 4. XAS O K–edge spectra for the native KDP crystals.

Figure 5. XAS C K–edge and K L–edge spectra for the series of processed KDP optics.

Figure 6. XAS O K–edge spectra for the series of processed KDP optics.

Figure 7. XAS P $L_{2.3}$–edge spectra for the series of processed KDP optics.

Figure 8. Resonant P 2p SXRF spectra and the associated P $L_{2,3}$–edge XANES for unannealed diamond turned KDP optic.

Figure 9. Resonant P 2p SXRF spectra and the associated P $L_{2,3}$–edge XANES for annealed diamond turned KDP optic.

Figure 10. Resonant O 1s SXRF spectra and the associated O K–edge XANES for unannealed diamond turned KDP optic.

Figure 11. Resonant O 1s SXRF spectra and the associated O K–edge XANES for annealed diamond turned KDP optic.

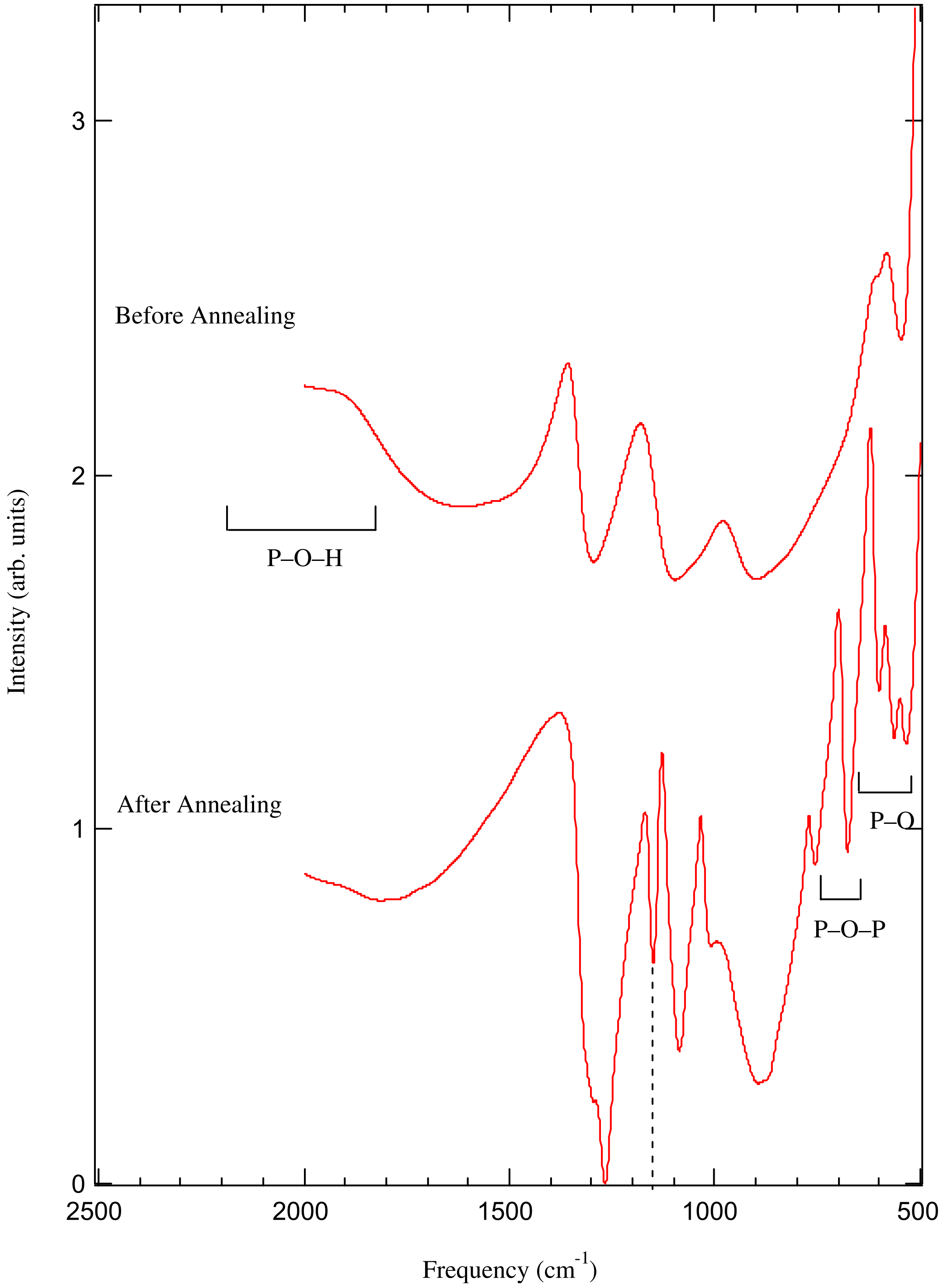

Figure 1. Infrared spectrum of the surface of a KDP optical component before (A) and after (B) annealing at 160°C.

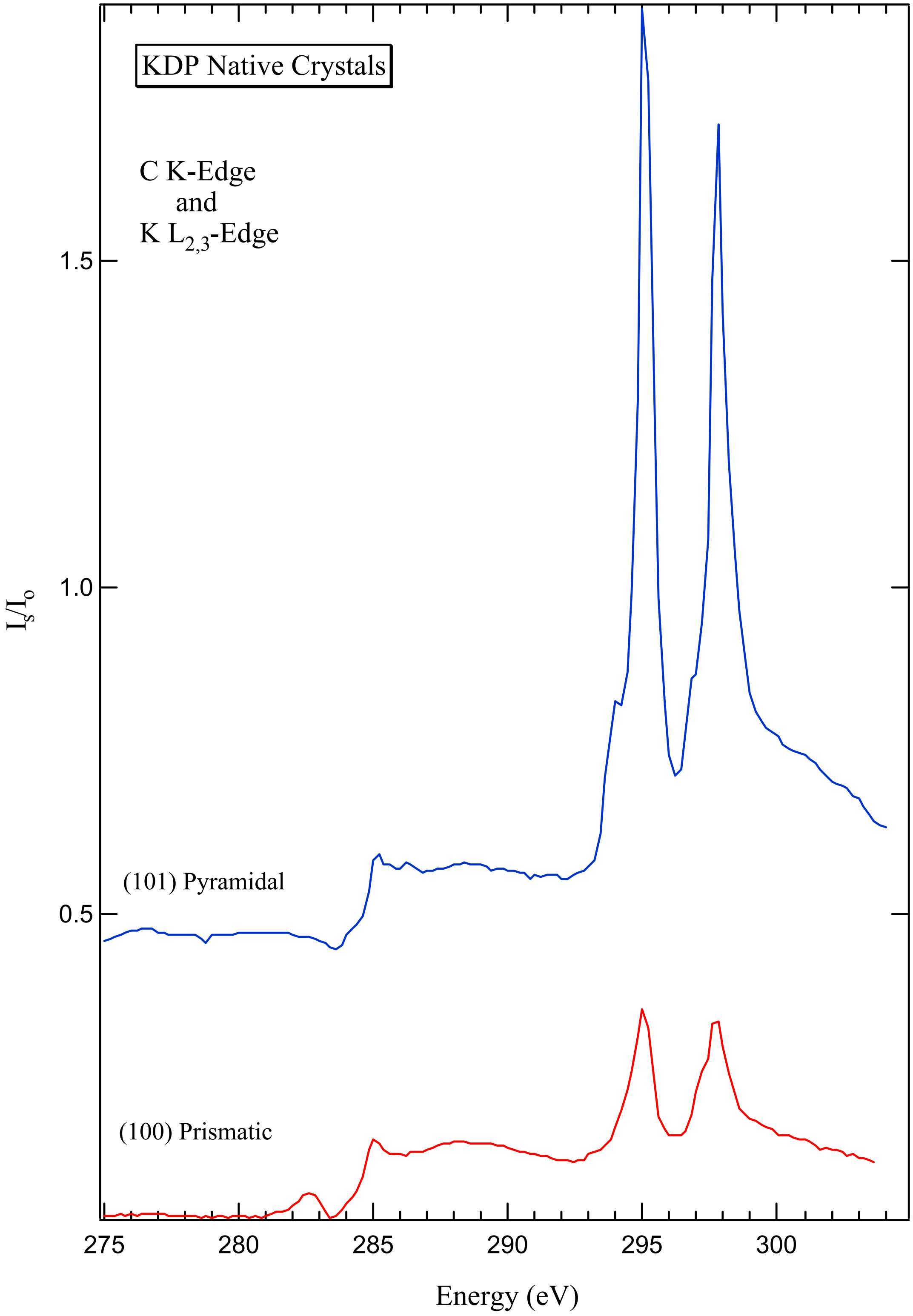
KDP Native Crystals
C K-Edge
and
K $L_{2,3}$-Edge
(101) Pyramidal
(100) Prismatic
I_s/I_o
1.5
1.0
0.5
275
280
285
290
295
300
Energy (eV)

Figure 2.

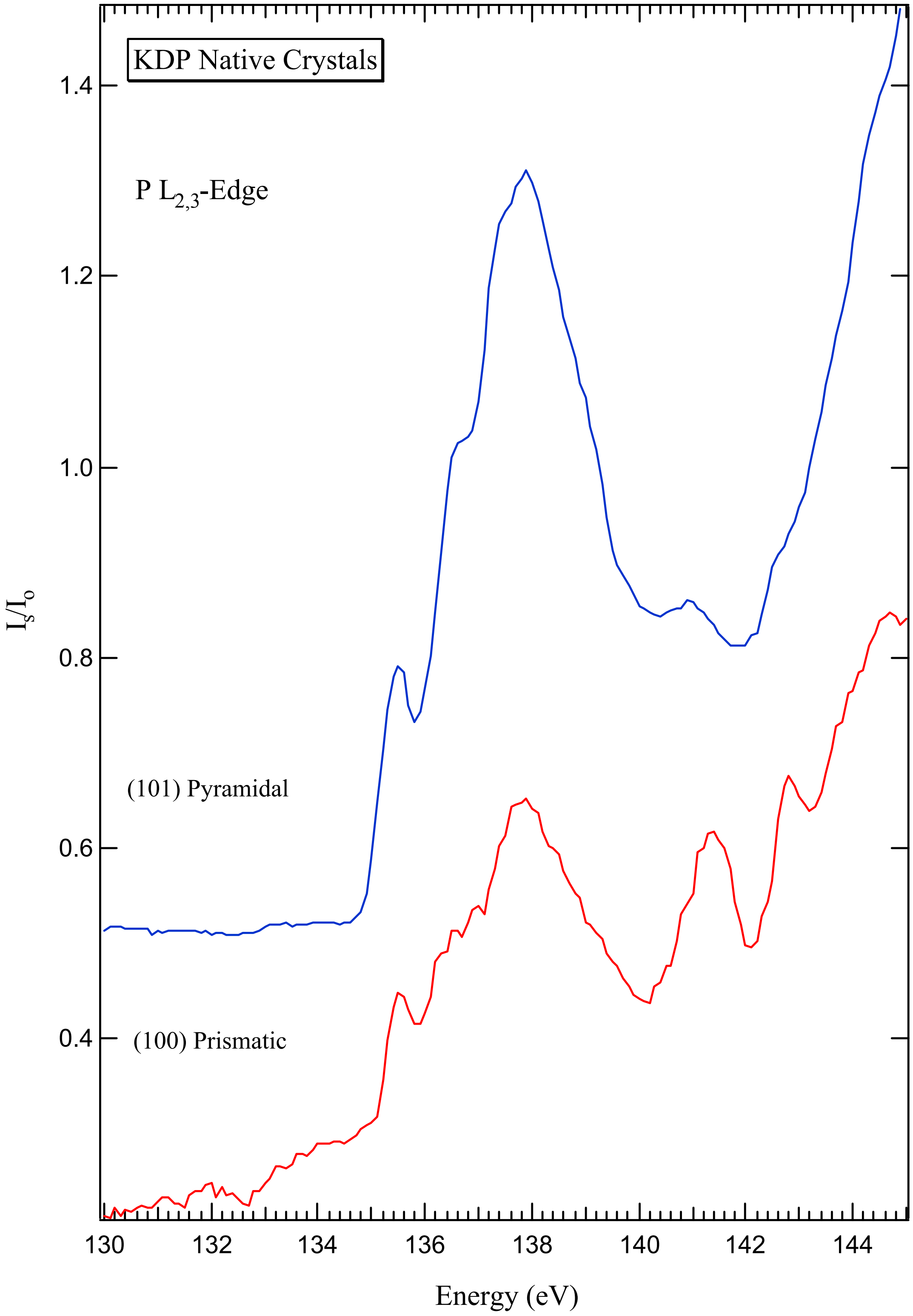
KDP Native Crystals
P $L_{2,3}$-Edge
(101) Pyramidal
(100) Prismatic
I_s/I_o
1.4
1.2
1.0
0.8
0.6
0.4
130
132
134
136
138
140
142
144
Energy (eV)

Figure 3.

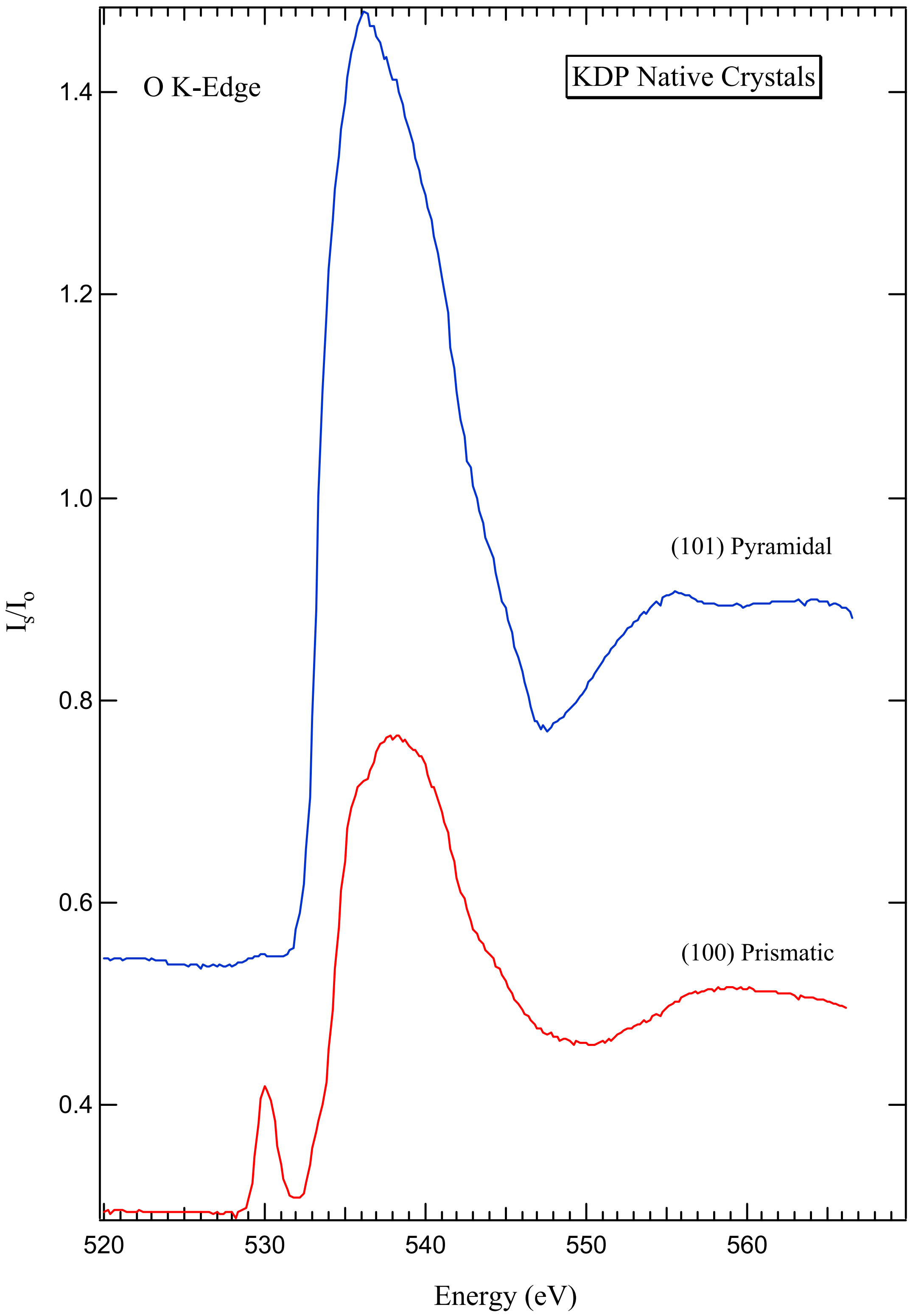
O K-Edge
KDP Native Crystals
(101) Pyramidal
(100) Prismatic
I_s/I_o
1.4
1.2
1.0
0.8
0.6
0.4
520
530
540
550
560
Energy (eV)

Figure 4.

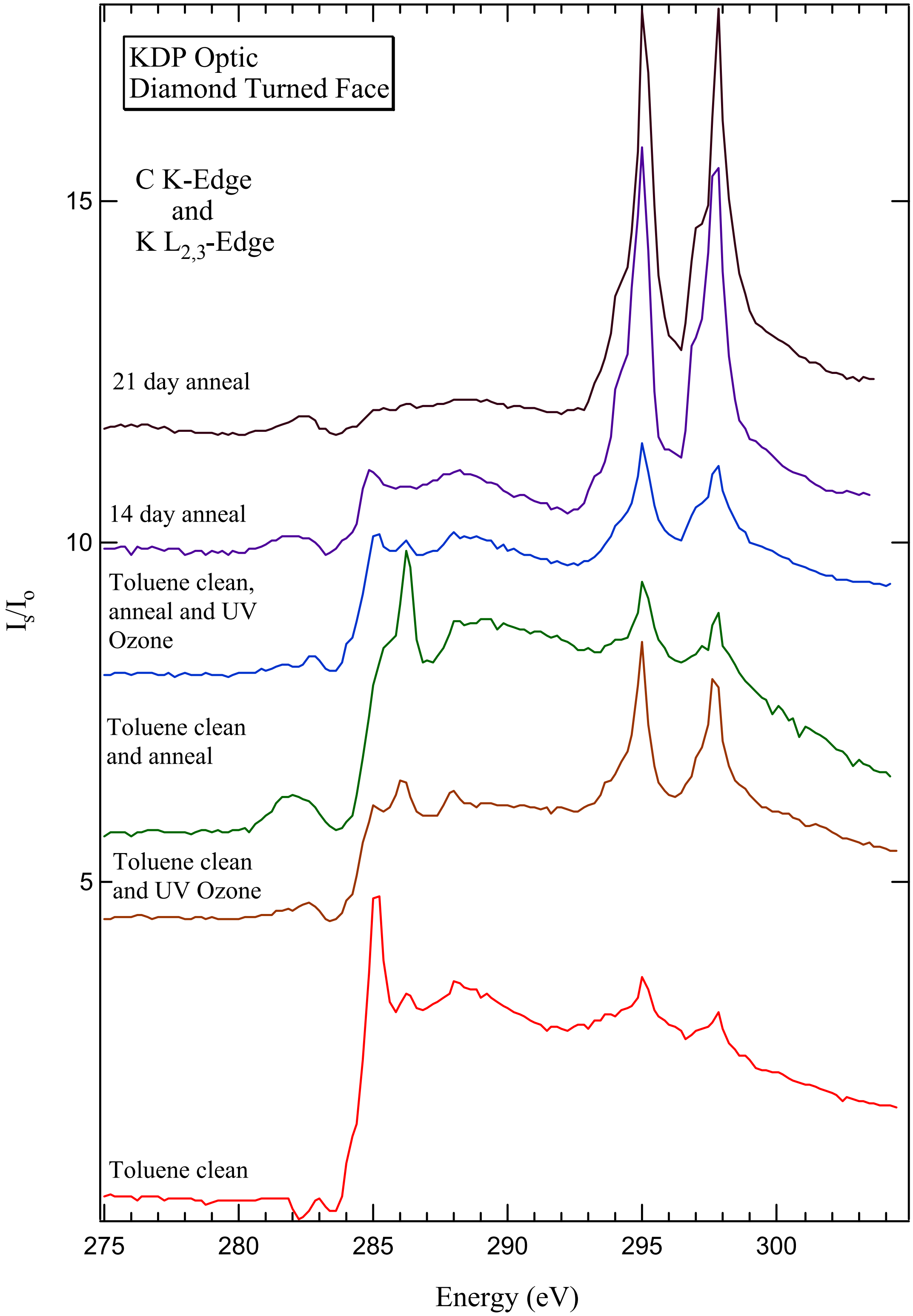
KDP Optic
Diamond Turned Face
C K-Edge
and
K $L_{2,3}$-Edge
21 day anneal
14 day anneal
Toluene clean, anneal and UV Ozone
Toluene clean and anneal
Toluene clean and UV Ozone
Toluene clean
I_s/I_o
15
10
5
275
280
285
290
295
300
Energy (eV)

Figure 5.

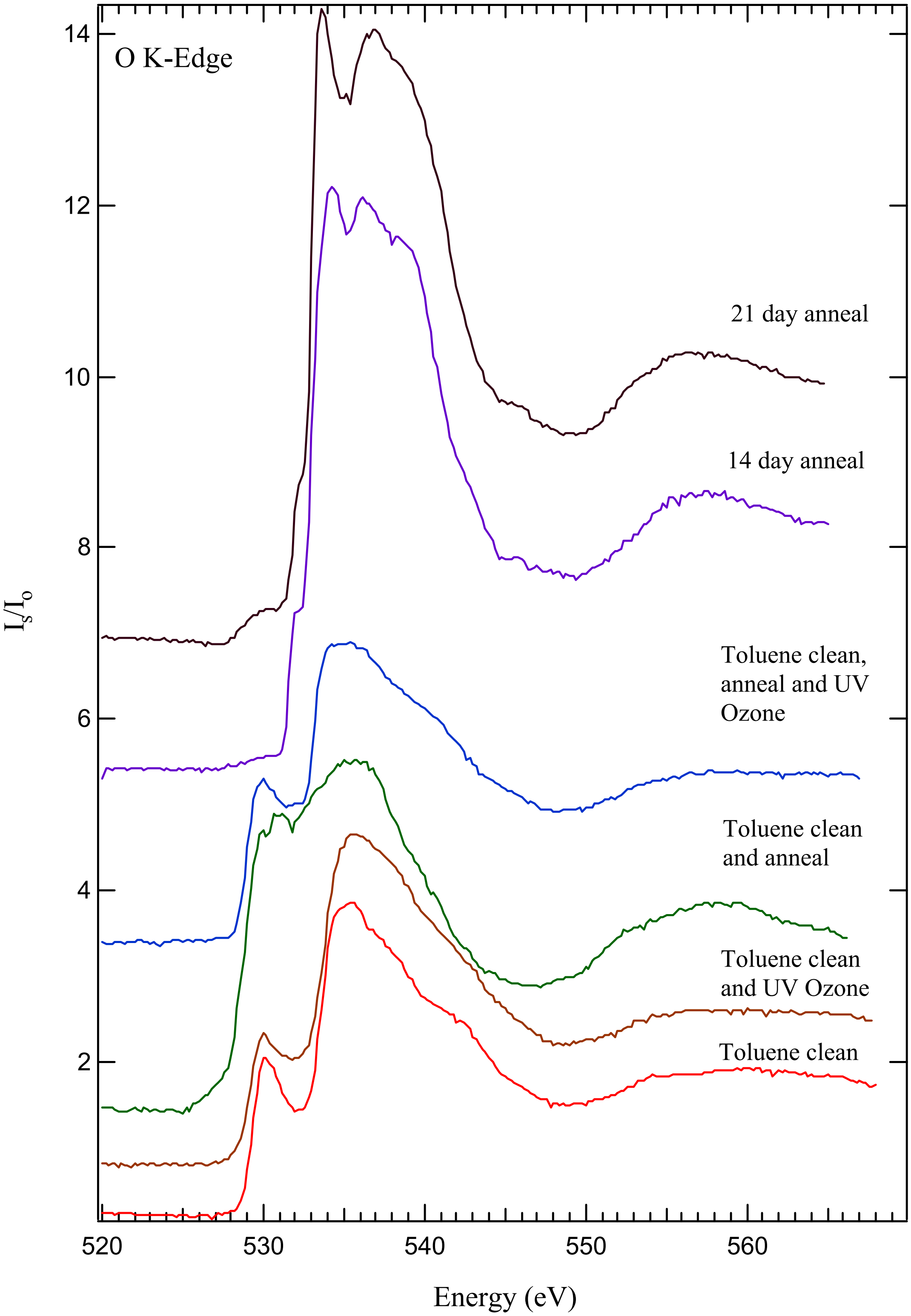
O K-Edge
21 day anneal
14 day anneal
Toluene clean, anneal and UV Ozone
Toluene clean and anneal
Toluene clean and UV Ozone
Toluene clean
I_s/I_o
14
12
10
8
6
4
2
520
530
540
550
560
Energy (eV)

Figure 6.

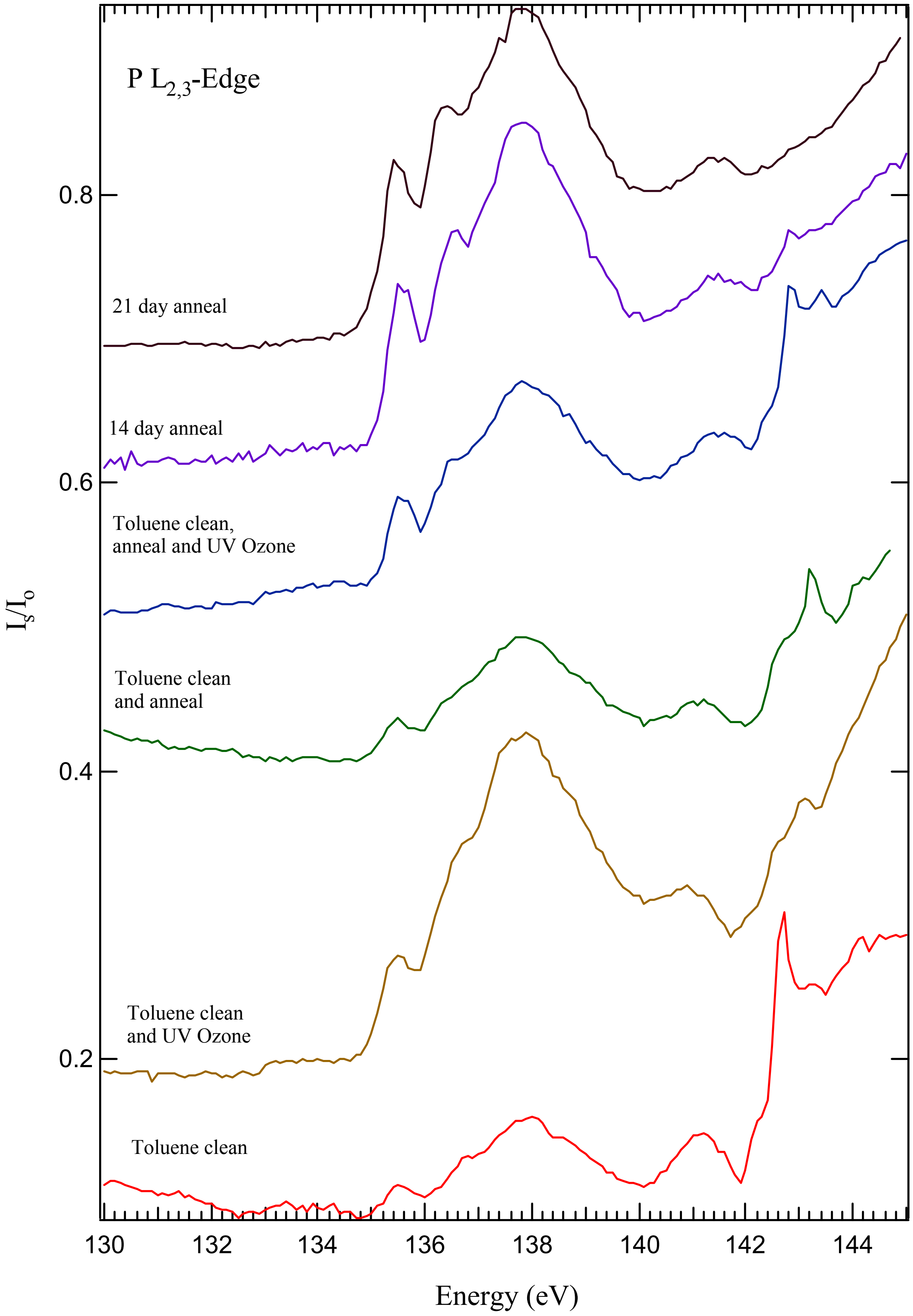
P $L_{2,3}$-Edge
21 day anneal
14 day anneal
Toluene clean,
anneal and UV Ozone
Toluene clean
and anneal
Toluene clean
and UV Ozone
Toluene clean
I_s/I_o
0.8
0.6
0.4
0.2
130
132
134
136
138
140
142
144
Energy (eV)

Figure 7.

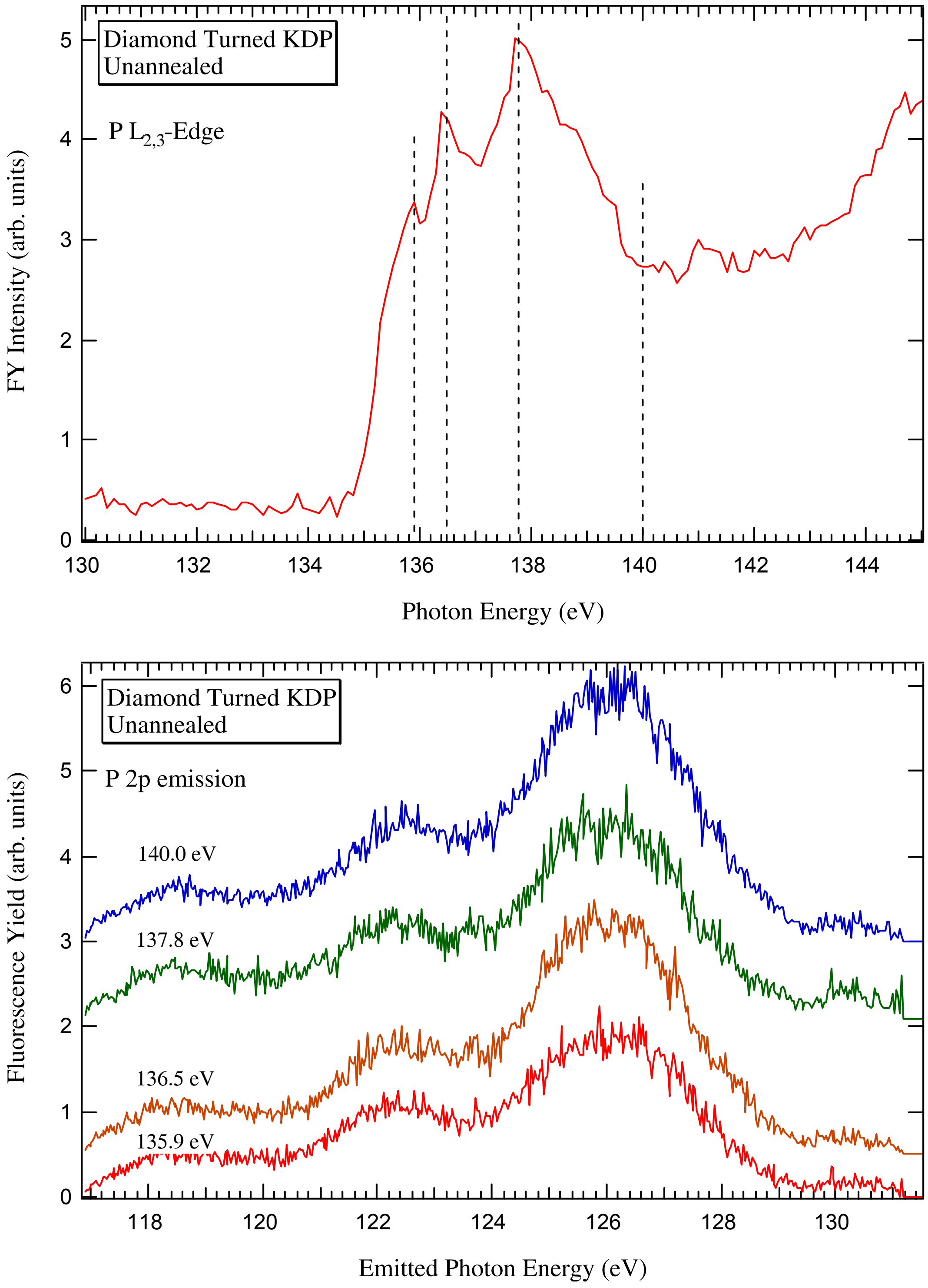
Diamond Turned KDP
Unannealed
P $L_{2,3}$-Edge
FY Intensity (arb. units)
0
1
2
3
4
5
130
132
134
136
138
140
142
144
Photon Energy (eV)
Diamond Turned KDP
Unannealed
P 2p emission
140.0 eV
137.8 eV
136.5 eV
135.9 eV
Fluorescence Yield (arb. units)
0
1
2
3
4
5
6
118
120
122
124
126
128
130
Emitted Photon Energy (eV)

Figure 8.

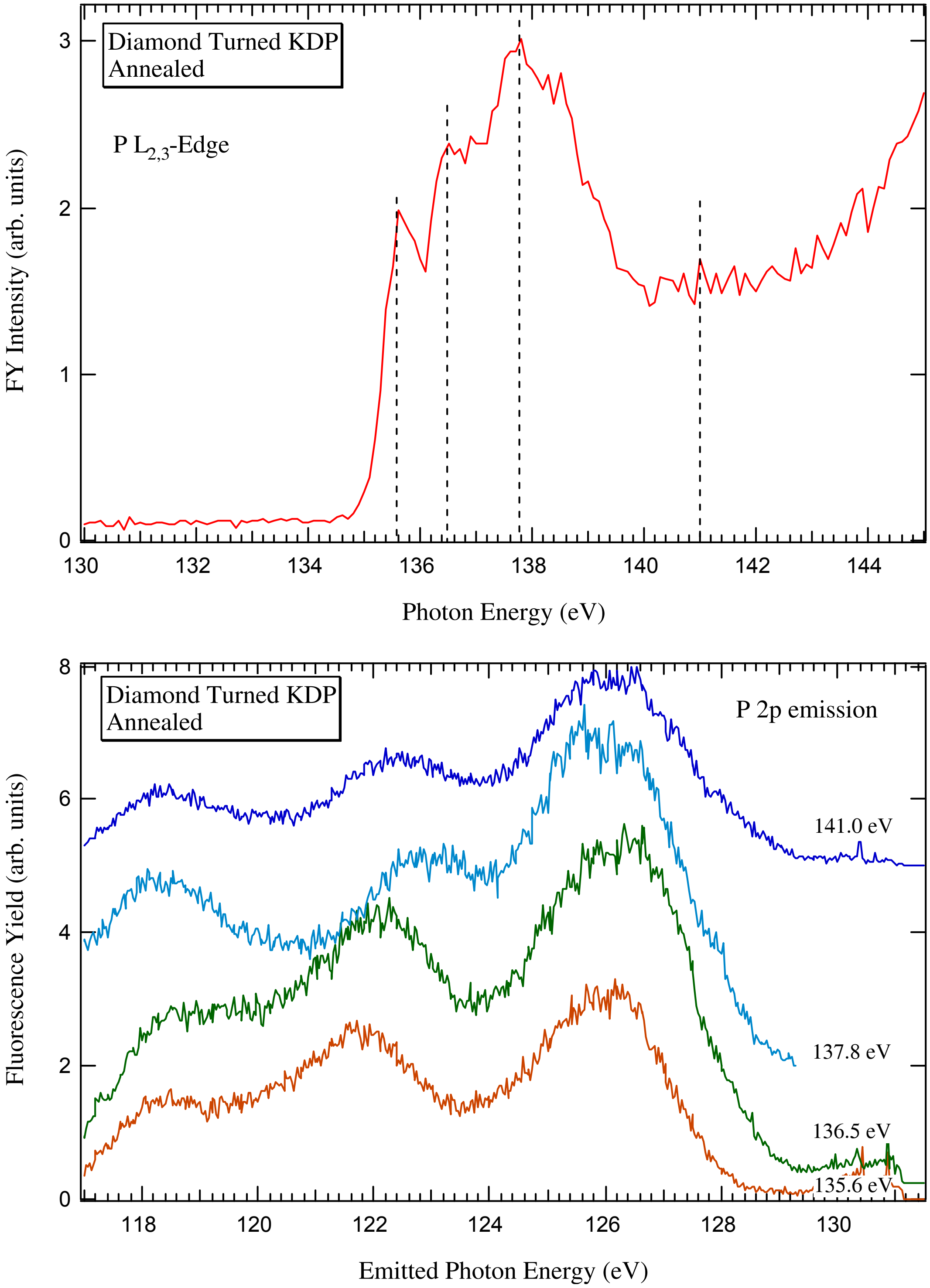
Diamond Turned KDP
Annealed
P $L_{2,3}$-Edge
FY Intensity (arb. units)
0
1
2
3
130
132
134
136
138
140
142
144
Photon Energy (eV)
Diamond Turned KDP
Annealed
P 2p emission
141.0 eV
137.8 eV
136.5 eV
135.6 eV
Fluorescence Yield (arb. units)
0
2
4
6
8
118
120
122
124
126
128
130
Emitted Photon Energy (eV)

Figure 9.

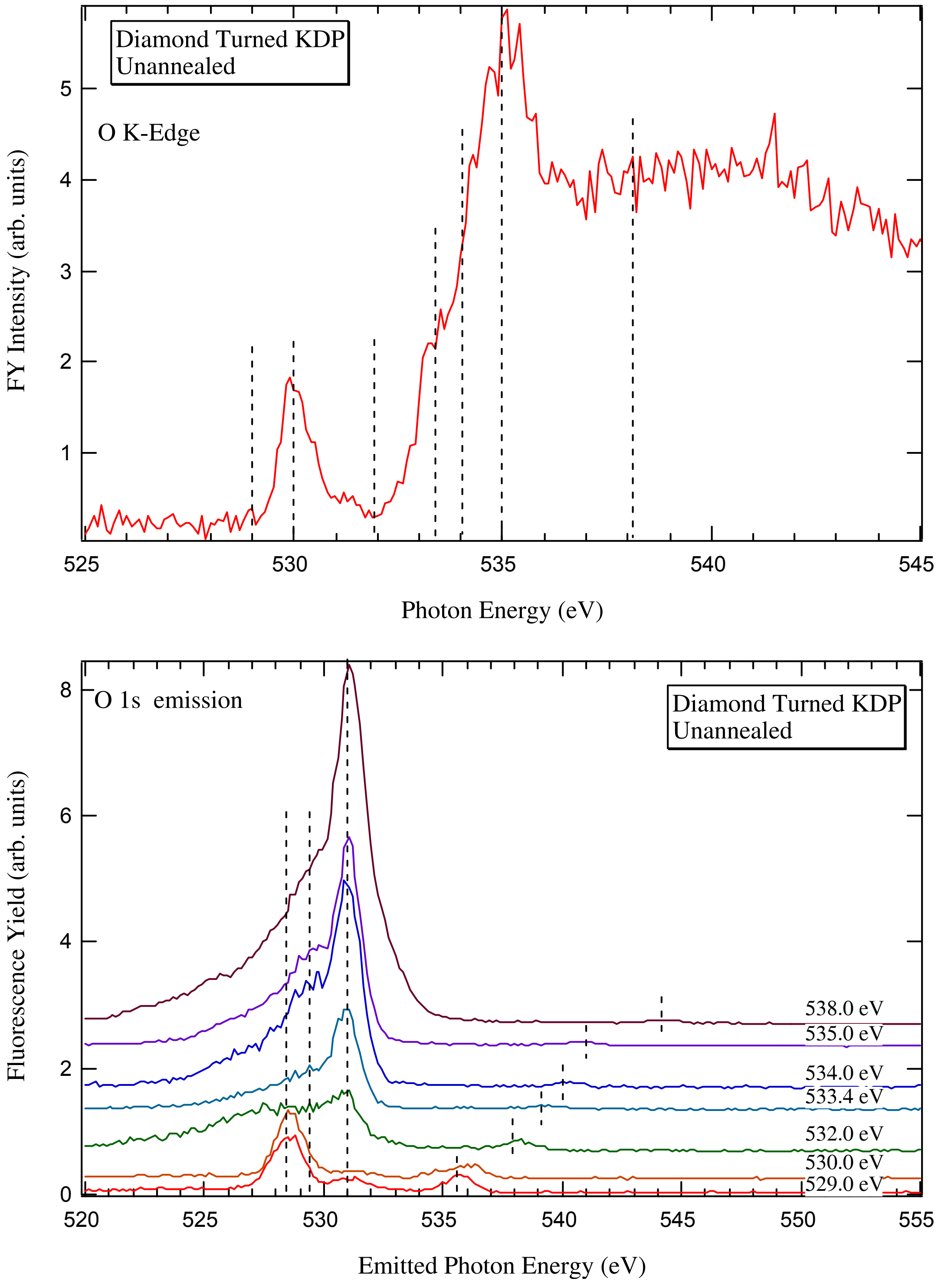
Diamond Turned KDP
Unannealed
O K-Edge
FY Intensity (arb. units)
1
2
3
4
5
525
530
535
540
545
Photon Energy (eV)
O 1s emission
Diamond Turned KDP
Unannealed
Fluorescence Yield (arb. units)
0
2
4
6
8
538.0 eV
535.0 eV
534.0 eV
533.4 eV
532.0 eV
530.0 eV
529.0 eV
520
525
530
535
540
545
550
555
Emitted Photon Energy (eV)

Figure 10.

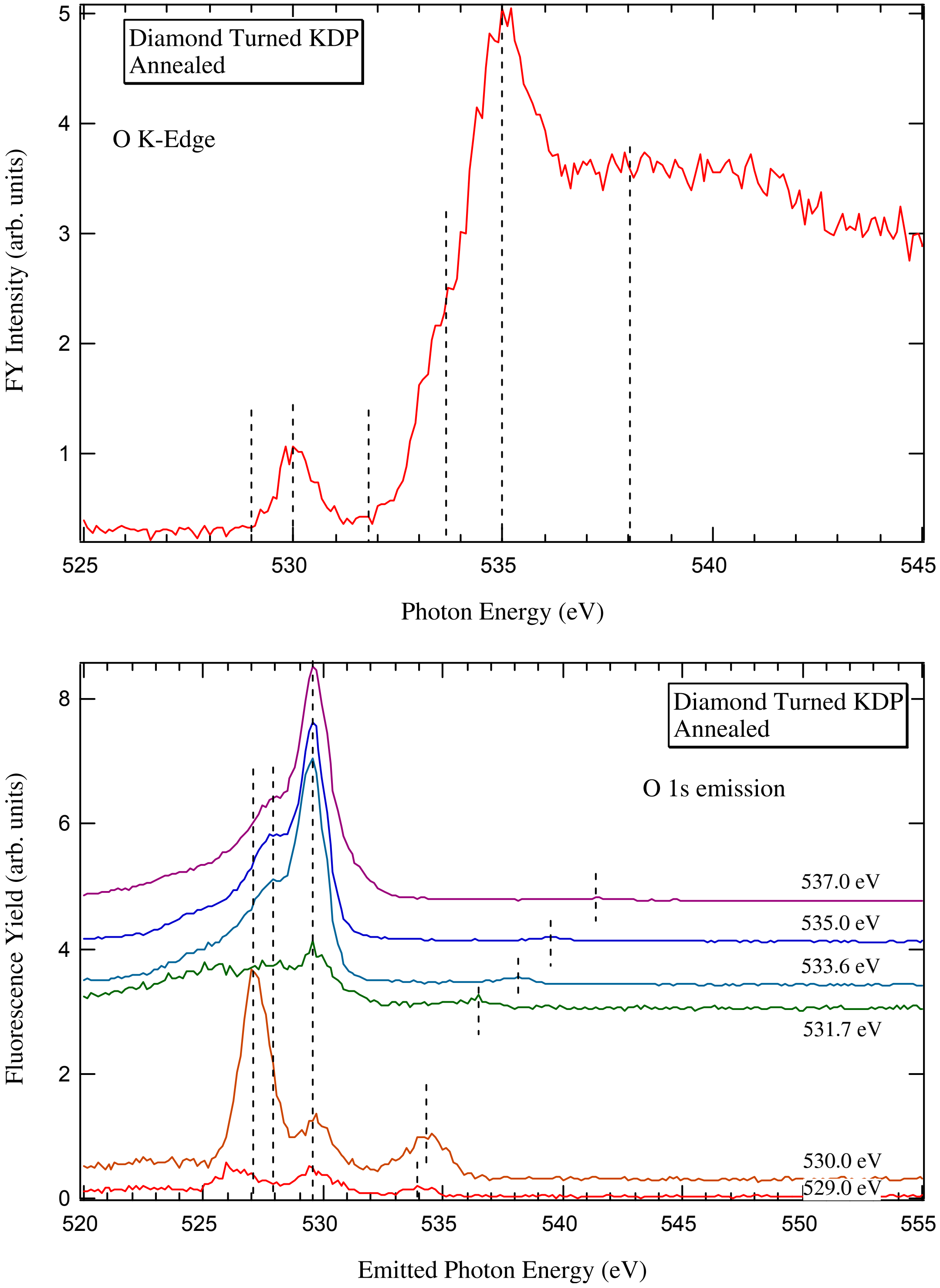
Diamond Turned KDP
Annealed
O K-Edge
FY Intensity (arb. units)
Photon Energy (eV)
525
530
535
540
545
1
2
3
4
5
Diamond Turned KDP
Annealed
O 1s emission
Fluorescence Yield (arb. units)
Emitted Photon Energy (eV)
537.0 eV
535.0 eV
533.6 eV
531.7 eV
530.0 eV
529.0 eV
520
525
530
535
540
545
550
555
0
2
4
6
8

Figure 11.