Figure S1. Indirect-allowed (IA) TP spectra for 2 monoclinic BiVO$_4$ samples characterized using the diffuse reflectance (DR) technique. For each sample, end points of the piecewise linear fit (red circles) Tauc line segments (dotted magenta), baseline segments (dotted black) and the estimate of $E_{g}^{IA}$ are shown.
Figure S2. Plots of $TP^D_A$ vs photon illumination energy for the 60 samples used to compare band gap estimation between expert scientists and the automated algorithm.
Figure S3. The loss function (for the piece-wise linear fit) and $S_T - S_B$ (difference in slope between the Tauc and Base line segments) are shown for true-positive (blue) and false-positive (red) samples from the test dataset of Fig. S2. The results suggest that small values of $S_T - S_B$ may lead to increased incidence of false-positive band gap detection and higher loss function (poorer fit) for the piece-wise linear model, both of which correspond to a lower confidence in the band gap identification.

**Expert Scientist Guidelines for Band Gap Estimation:**

- If multiple band gaps are observed, estimate band gap using the Tauc regions that explain higher proportion of Tauc property change.
- In cases where a clear baseline is not observed but a trend for transition between the baseline and the absorption tail is observed, estimate band gap using best approximation of baseline.
- Do not estimate a band gap when neither a clear baseline nor a trend for transition between the baseline and the absorption tail are observed.
- Do not estimate band gap when only a lower limit of the band gap energy can be determined (due to the absorption transient extending beyond the high-energy limit of the spectrometer).