

Chemistry – An Asian Journal

Supporting Information

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Electronic Supporting Information

Intercalated Water Drives Anomalous Thermal Expansion in the Tetragonal Zircon Structured Bismuth Vanadate BiVO₄ Photocatalyst

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Synthesis Procedure

A 100 mL solution of 12.4 mmol NH_4VO_3 was prepared. NH_4VO_3 (1.4506 g, The British Drug House, 98+%) was added to a 100 mL volumetric flask and made up to volume using HNO_3 (10 mL, Univar, 70%) and deionized water (100 mL, 0.124 M). The solution was stirred at 60 °C for 20 minutes until the red precipitate turned to a golden yellow color solution. A 50 mL solution of 31.0 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was prepared. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (15.0372 g, Sigma-Aldrich, 98+%) was added to a 50 mL volumetric flask and made up to volume using HNO_3 (5 mL, Univar, 70%) and deionized water (50 mL, 0.62 M). The solution was sonicated to help dissolve the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. A 100 mL solution of 3 M NH_4OH was prepared. NH_4OH (22.4 mL, Merck, 25% Extra Pure) was added to a 100 mL volumetric flask and made up to volume using deionized water.

The NH_4VO_3 (0.124 M, 50 mL, 6.2 mmol) and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.62 M, 10 mL, 6.2 mmol) were stirred for 10 minutes whilst being heated at 60 °C, before NH_4OH (3 M, 7.5 mL) was added dropwise. Upon dropping, a milky white color appeared before disappearing due to the solution mixing. After the NH_4OH was added, an additional amount of NH_4OH (3 M, 25 mL) was added in one pour, before the light-yellow precipitate was immediately vacuum filtered out and washed three times with deionized water. The light-yellow precipitate was then dried at 120 °C for two hours. If the yellow precipitate was left, the sample could sometimes partially transform from the *tz*- to the *mf*-polymorph under ambient conditions. Therefore, the sample was never analyzed more than two weeks after the initial synthesis. The sample was not ground, as applying pressure can result in the partial transformation from the *tz*- to the *mf*-polymorph.

Neutron powder diffraction measurements were performed on Echidna, the high-resolution powder diffractometer at the Open Pool Australian Lightwater (OPAL) reactor, operated by the Australian Nuclear Science and Technology Organisation (ANSTO). Powder samples were loaded into 6 mm diameter vanadium cans, with data collected over the range $5 \leq 2\theta \leq 162^\circ$ with a step size of 0.05° at a wavelength of 1.62 Å. The same samples were then run on Wombat, the high-intensity neutron diffractometer at the OPAL reactor, operated by ANSTO. The vanadium can was affixed to a sample stick and loaded into an ILL-type high-vacuum furnace operated at $<10^{-4}$ Pa. Variable temperature NPD data were collected on heating the sample from 50-750 K. Due to a heating malfunction, data were not collected above 750 K, and data were not collected upon cooling.

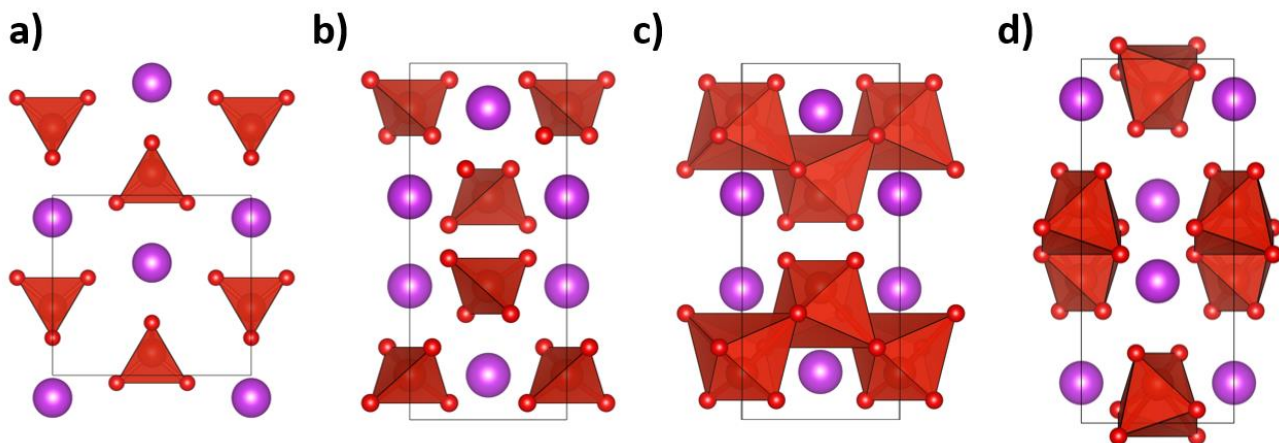


Figure S1: The four different polymorphs of BiVO_4 . (a) tetragonal-zircon $I4_1/amd$, (b) tetragonal-scheelite $I4_1/a$, (c) monoclinic-fergusonite $I2/b$, and (d) orthorhombic $Pnca$. The Bi^{3+} cations are shown as purple spheres, the VO_4 or VO_6 polyhedra are shown in orange, and the oxygen anions are shown as red spheres.

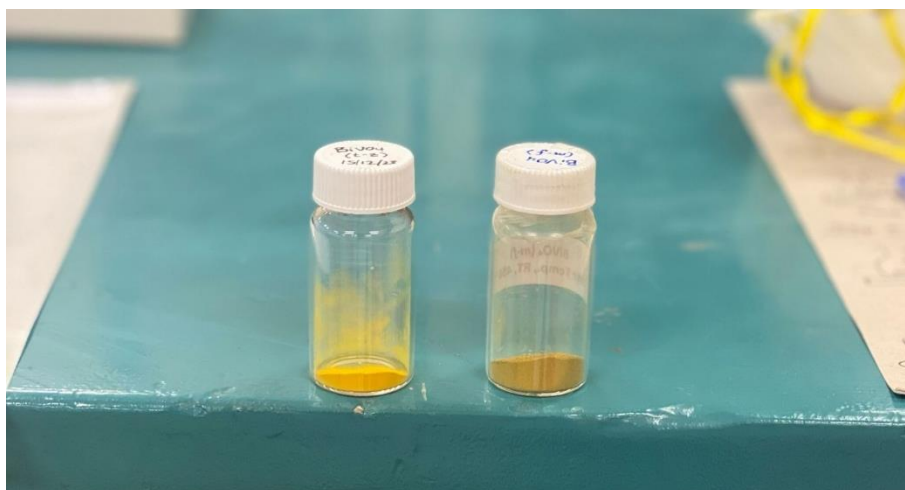


Figure S2: (Left) Synthesis of $tz\text{-BiVO}_4$ prepared using a coprecipitation method, and (right) $mf\text{-BiVO}_4$ prepared using a solid-state chemistry method.

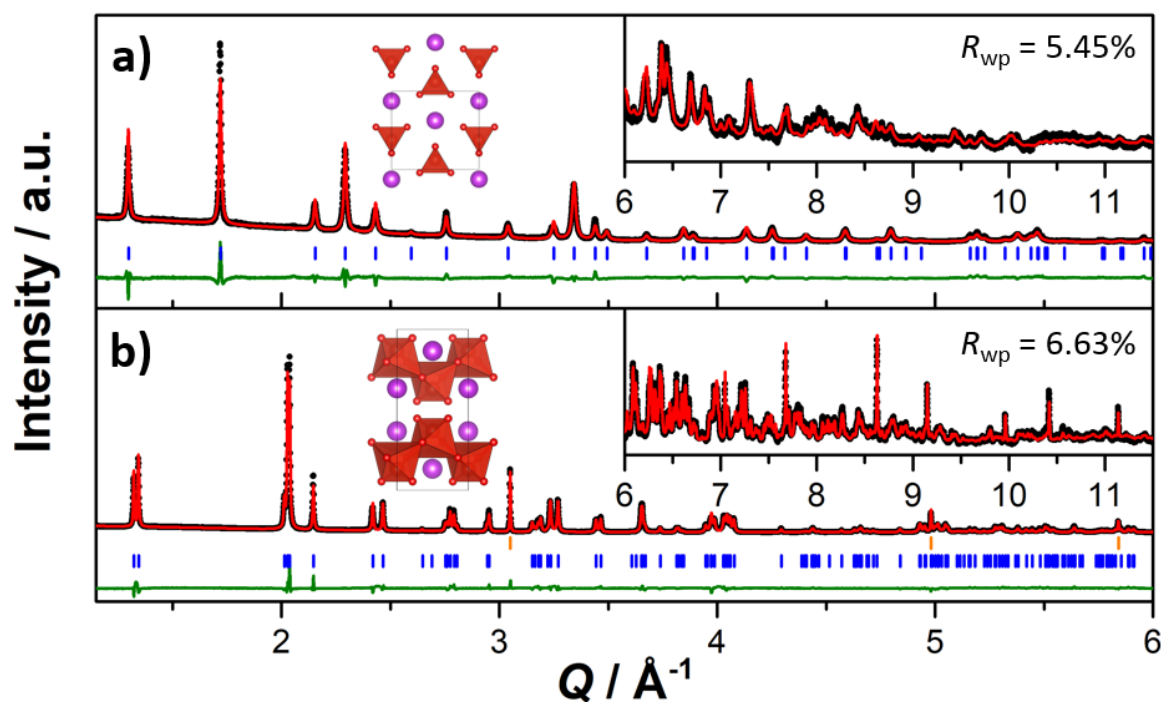


Figure S3: Rietveld refinements to the X-ray diffraction data taken from the Powder Diffraction beamline of the Australian Synchrotron at room temperature of (a) *tz*-BiVO₄ and (b) *mf*-BiVO₄. The black circles represent the data, the red line represents the fit to the data, the green line represents the difference between the two, and the orange and blue ticks represent the space group-allowed *hkl* reflections. The inset highlights the high quality of the fit to the data at high Q .

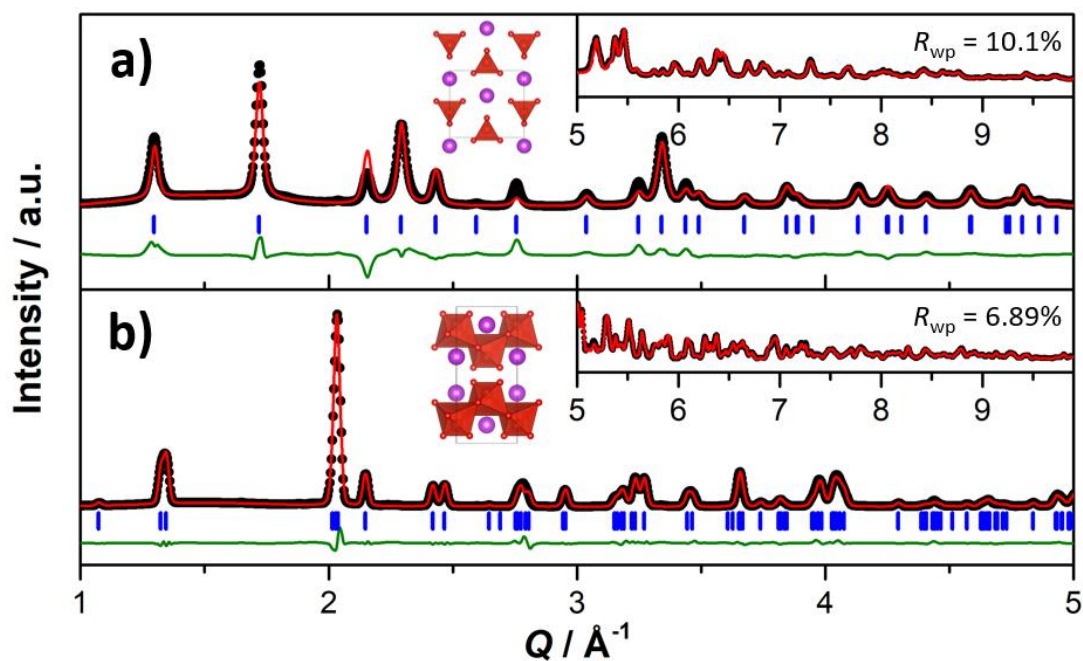


Figure S4: Rietveld refinements to the synchrotron X-ray diffraction data of (a) *tz*-BiVO₄ and (b) *mf*-BiVO₄. The black circles represent the data, the red line represents the fit to the data, the green line represents the difference between the two, and the blue ticks represent the space group-allowed *hkl* reflections. The inset highlights the high quality of the fit to the data at high Q .

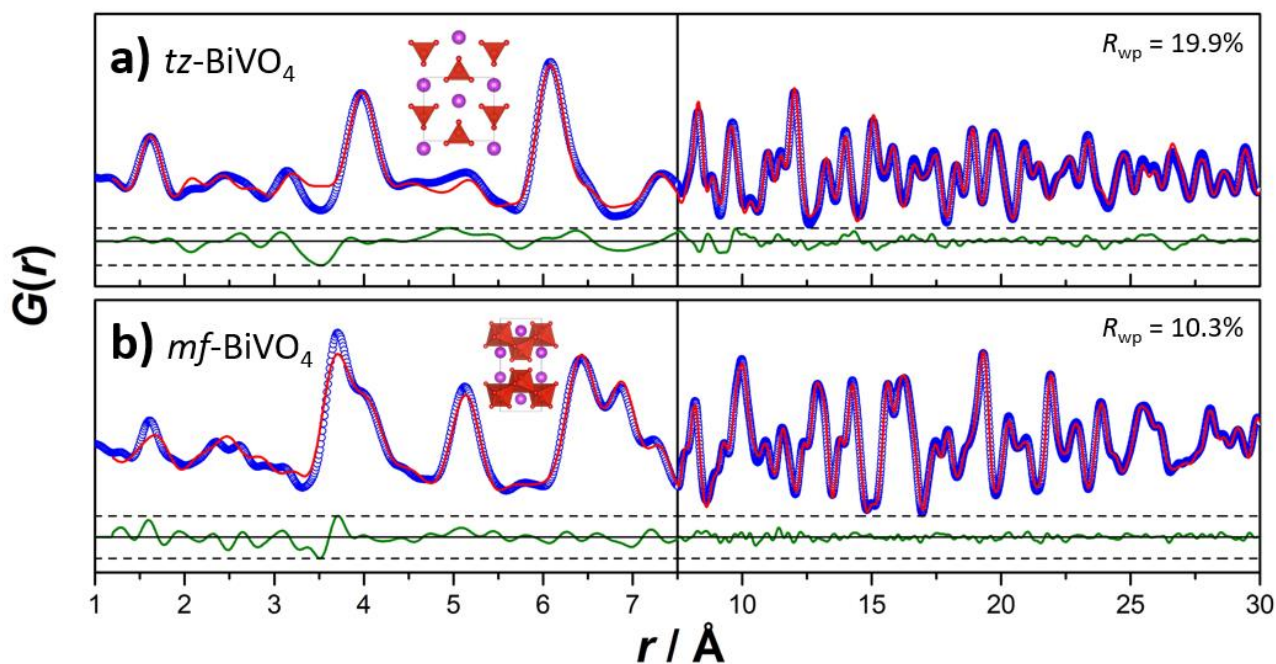


Figure S5: X-ray pair distribution function analysis of (a) tetragonal-zircon BiVO_4 and (b) monoclinic-fergusonite BiVO_4 . The data has been fitted over a range of 1.2-30 \AA . The blue circles represent the data, the red line represents the fit to the data, and the green line is the difference between the two.

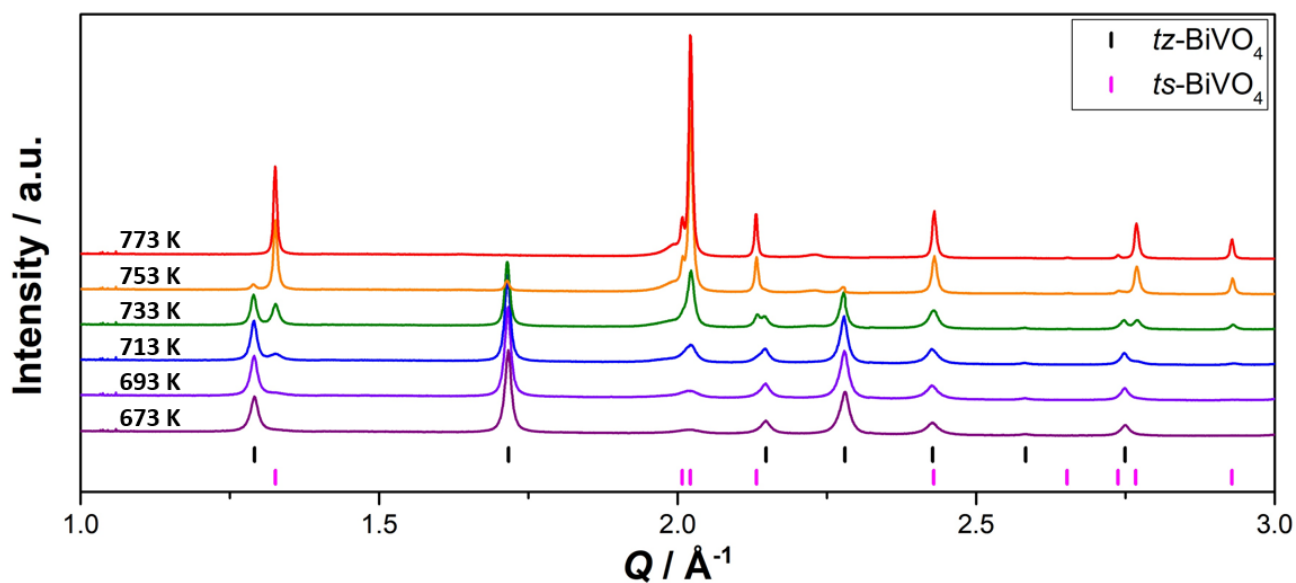


Figure S6: Temperature dependent synchrotron X-ray diffraction patterns of tetragonal-zircon BiVO_4 measured on heating from 673-773 K. The data were collected at $\lambda = 0.590067 \text{\AA}$.

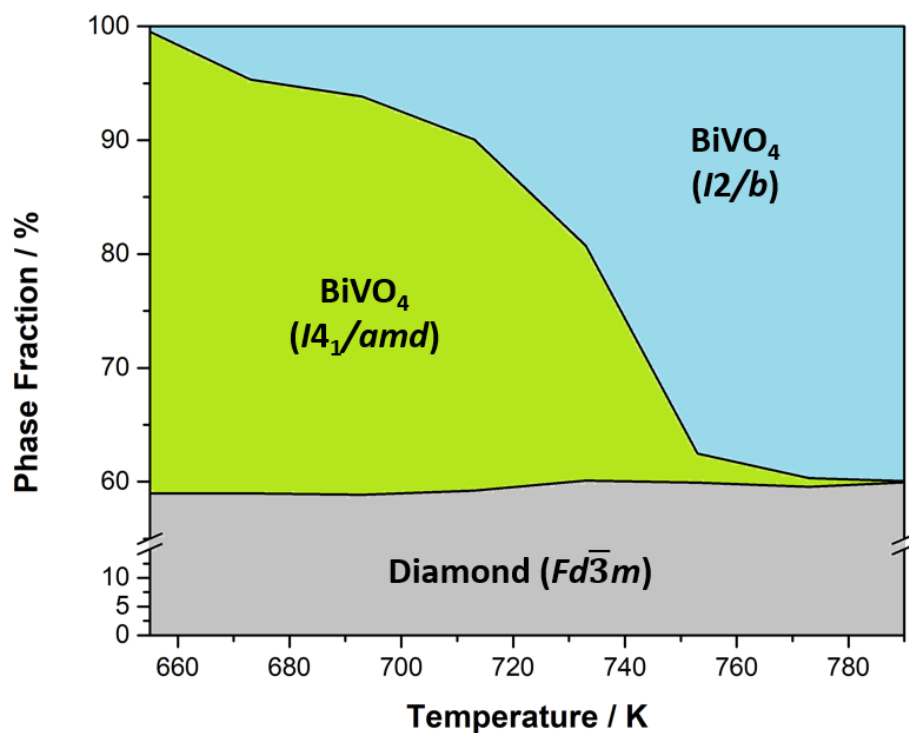


Figure S7: Phase diagram of BiVO₄ heating through the two-phase region of tetragonal-zircon *I*₄₁/*amd* and tetragonal-scheelite *I*₄₁/*a*.

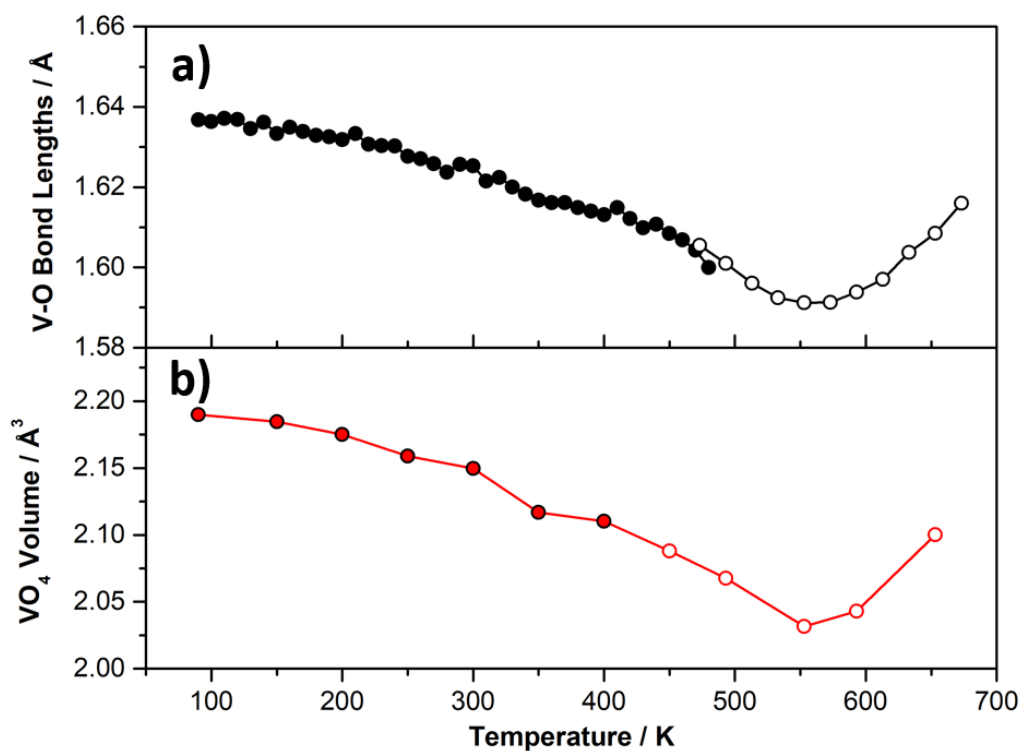


Figure S8: Rietveld refinement parameters from synchrotron X-ray diffraction data of *tz*-BiVO₄. (a) The V-O bond lengths, and (b) the VO₄ polyhedra volumes.

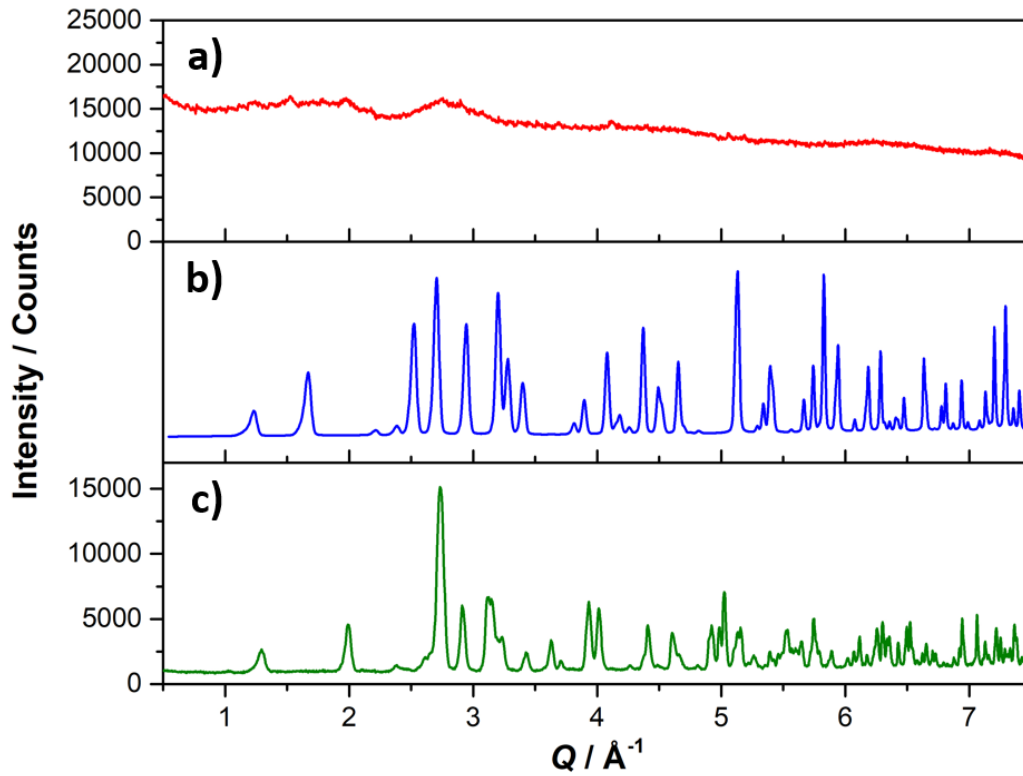


Figure S9: Neutron powder diffraction patterns for (a) *tz*-BiVO₄ collected for 18 hours, (b) simulated *tz*-BiVO₄, and (c) *mf*-BiVO₄ collected for four hours.

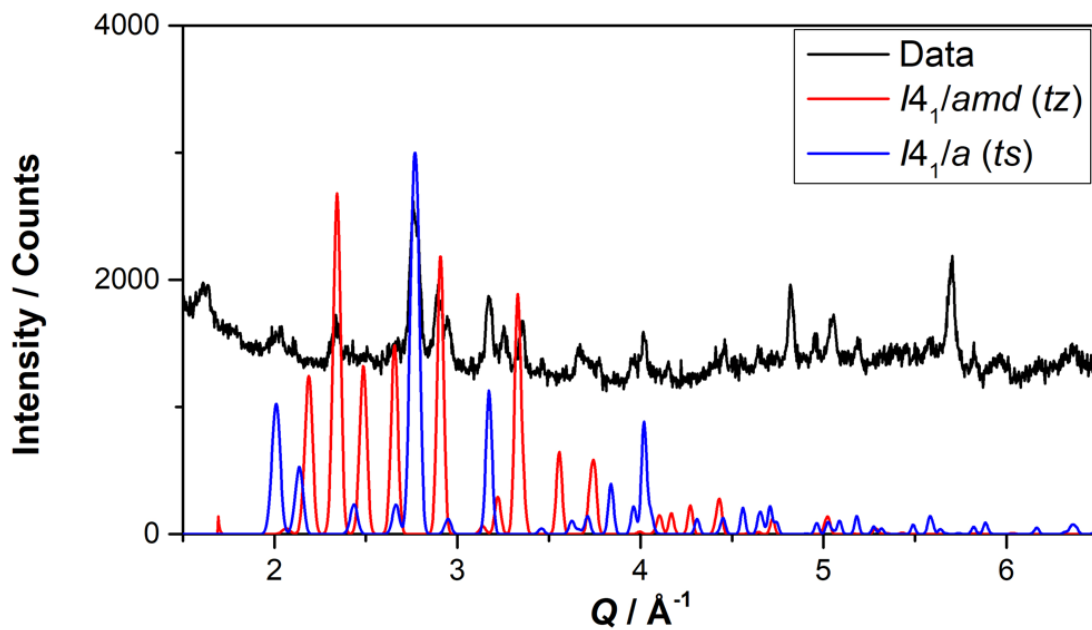


Figure S10: The collected neutron powder diffraction pattern of tetragonal-zircon BiVO₄ measured on the Wombat neutron diffractometer at 750 K. Despite the high background, reflections from both tetragonal-zircon and tetragonal-scheelite BiVO₄ are present, indicating the material did not completely transform. The red reflections are the simulated tetragonal-zircon phase, and the blue reflections are the simulated tetragonal-scheelite phase.

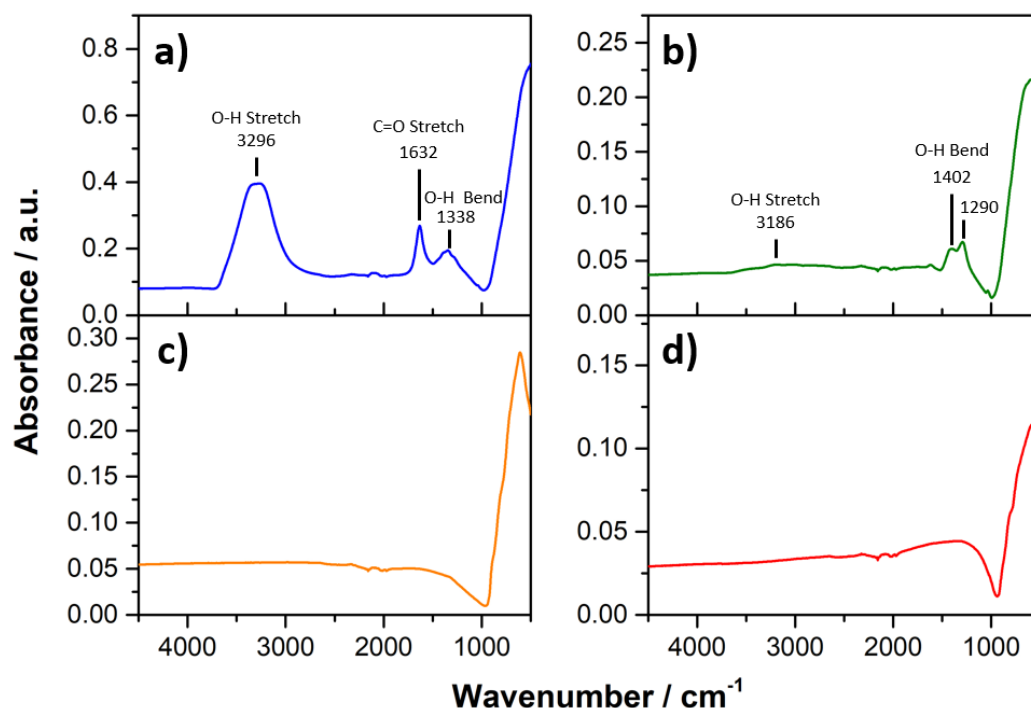


Figure S11: Fourier-transformed infrared spectroscopy collected on (a) BiVO_4 from the coprecipitation method, (b) BiVO_4 heated at 100 °C for one hour, (c) BiVO_4 heated at 600 °C for one hour, and (d) BiVO_4 heated at 750 °C for 12 hours.

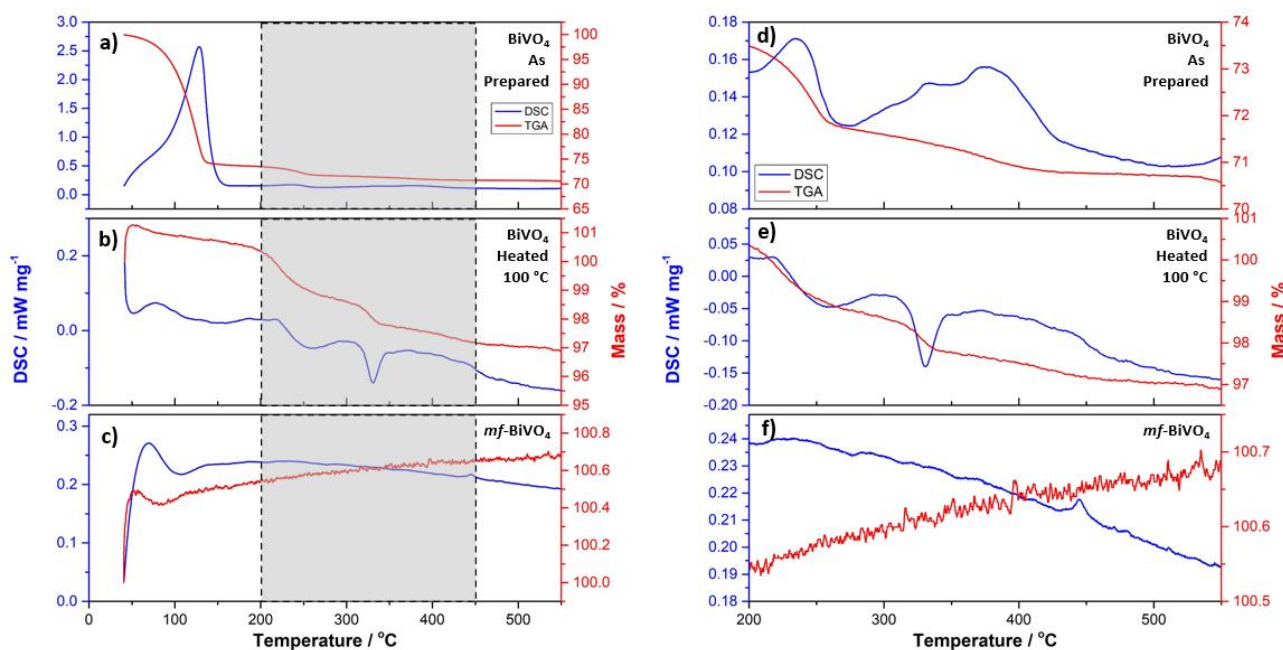


Figure S12: Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of three samples of BiVO_4 : (a) $tz\text{-BiVO}_4$ as prepared from the coprecipitation method, (b) heated to 100 °C for one hour after coprecipitation, and (c) $mf\text{-BiVO}_4$ after $tz\text{-BiVO}_4$ was heated to 750 °C for 12 hours. The blue line represents the DSC and the red line represents the TGA. The grey area is zoomed in for (d-f).

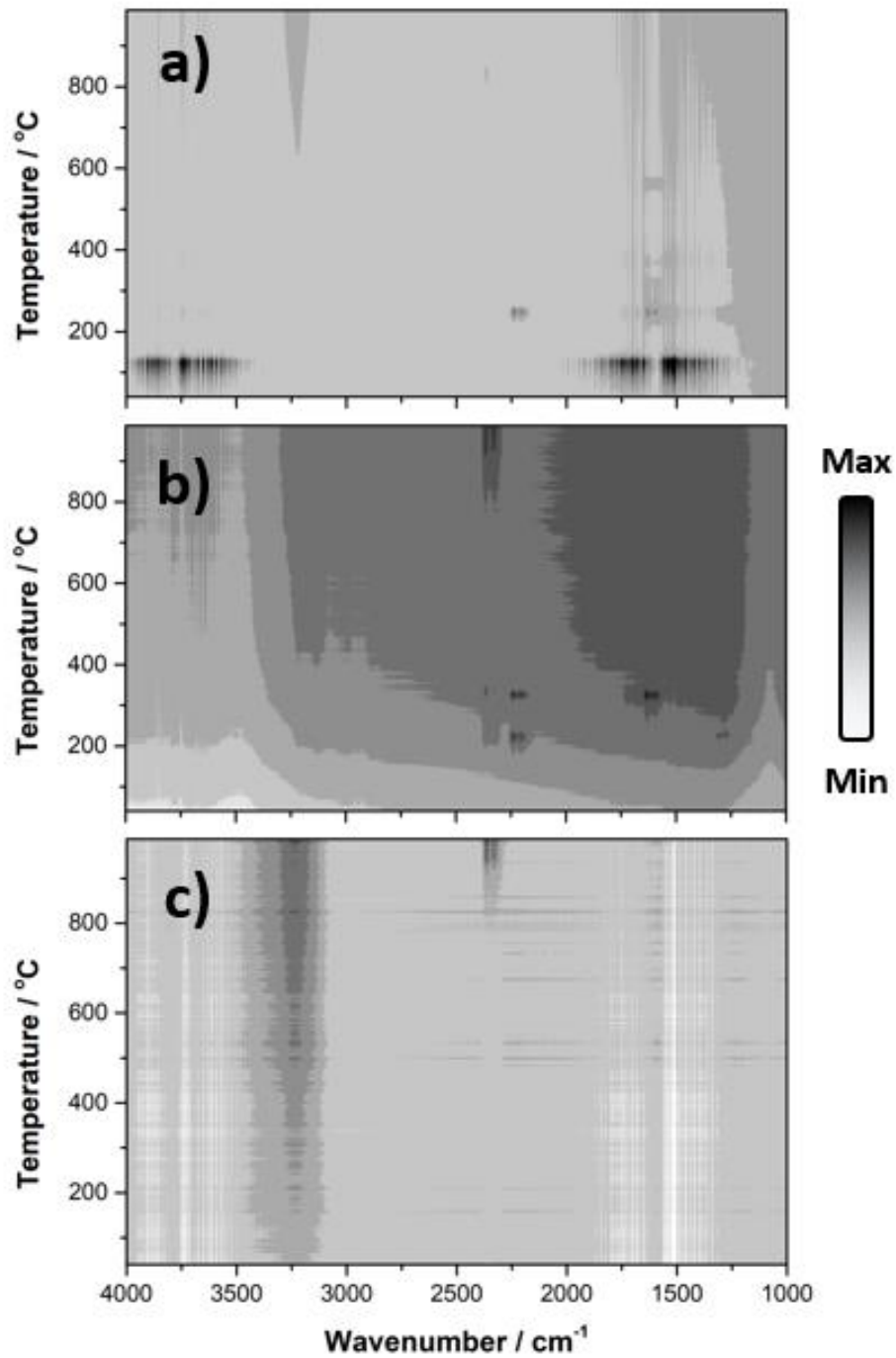


Figure S13: Variable temperature Fourier-transform infrared spectroscopy of (a) BiVO₄ from the coprecipitation reaction, (b) BiVO₄ heated at 100 °C for one hour, and (c) BiVO₄ heated at 750 °C for 12 hours.