Supplementary Information

Raman spectroscopy study of K-birnessite single crystals

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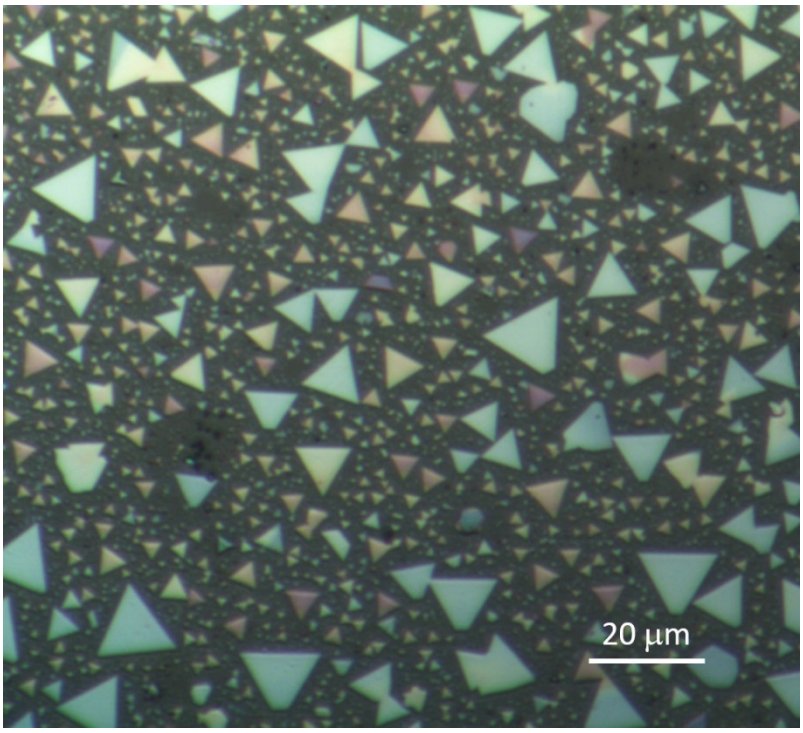

Figure S1. Light microscopy image of K-birnessite single crystals on c-sapphire substrate.

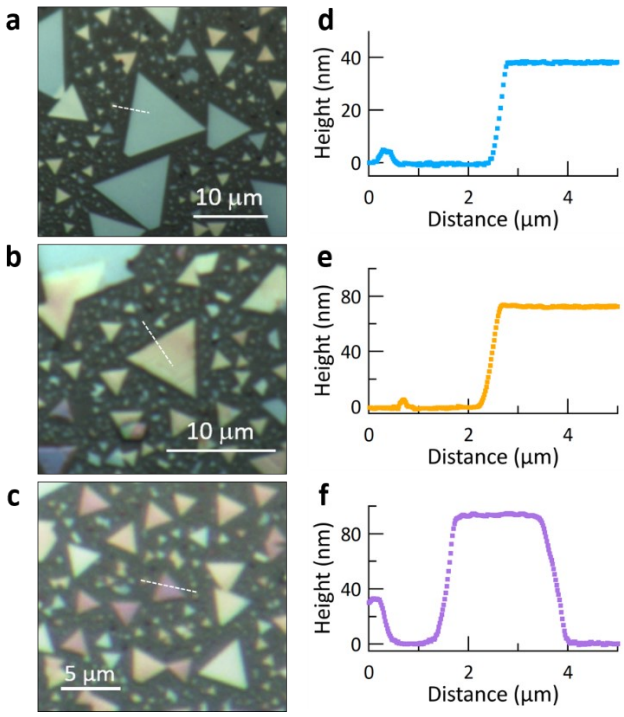

Figure S2. (a–c) Light microscopy images of blue, yellow, and purple K-birnessite single crystals on c-sapphire. (d–f) AFM height profiles of blue, yellow, and purple K- birnessite single crystals measured along the dashed lines shown in the light microscopy images.

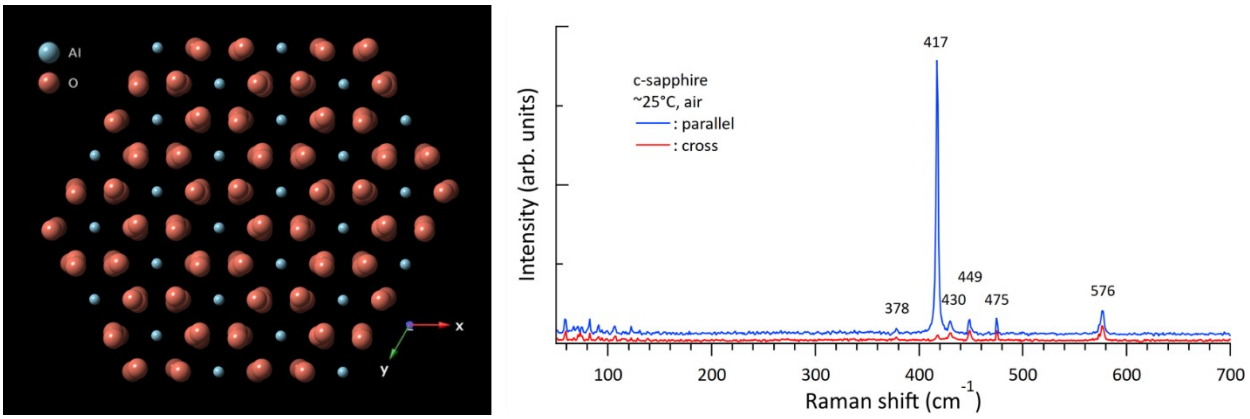

Figure S3. (left) Atomic arrangement in the c-plane direction of sapphire (α-Al_2O_3) with space group $R\bar{3}c$. (right) Polarization configuration dependence of the Raman spectrum of c-sapphire obtained in backscattering geometry. The blue (parallel) and red (cross) spectra were obtained with parallel and perpendicular polarization directions, respectively, of the incident and scattered light.

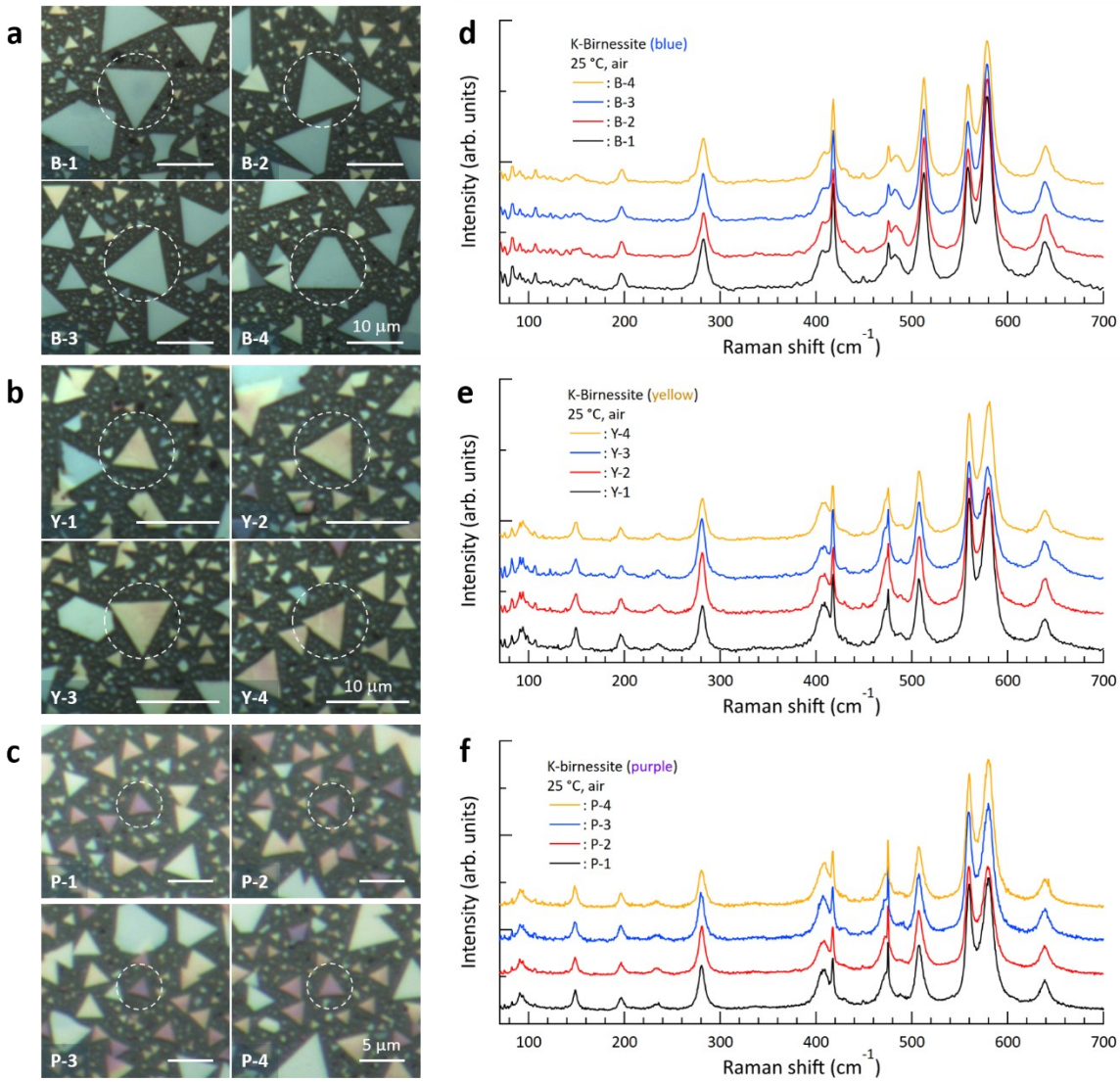

Figure S4. (a–c) Light microscopy images of blue, yellow, and purple K-birnessite single crystals on c-sapphire. (d–f) Raman spectra of the blue, yellow, and purple crystals in the dashed circles in a, b, and c panels. The incident light was vertically polarized in each figure, but no analyzer was used in the scattered light path. Black circles (●) represent the Raman peaks of c-sapphire.

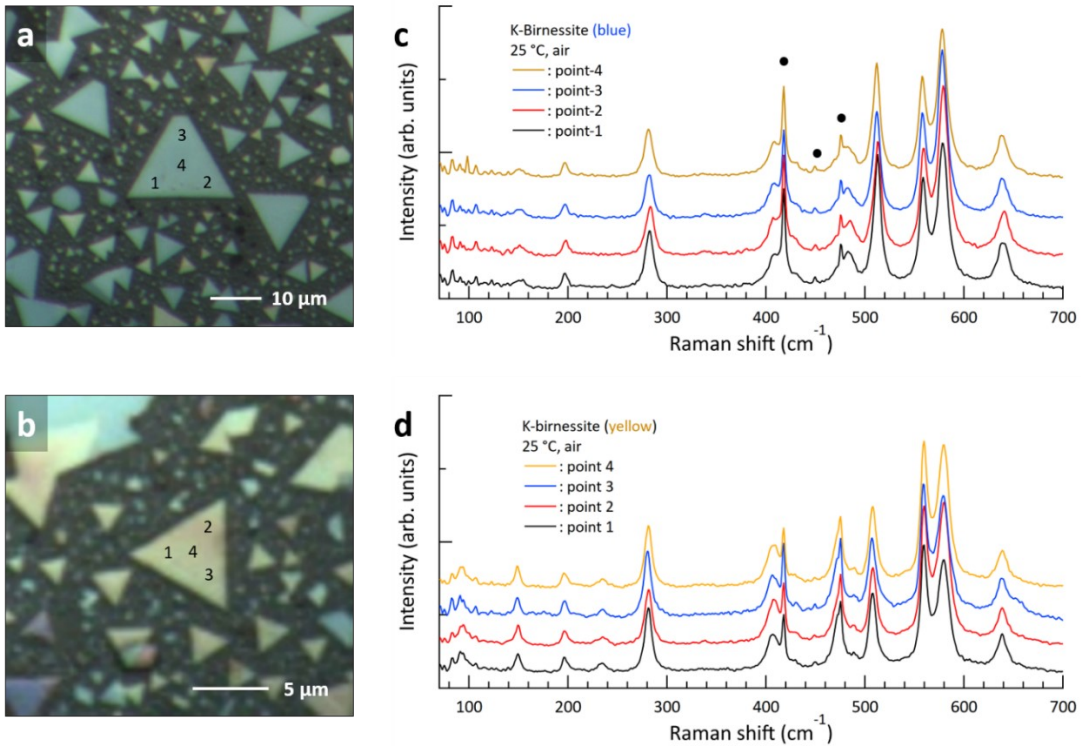

Figure S5. (a,b) Light microscopy images of blue and yellow K-birnessite single crystals on c-sapphire. (c,d) Raman spectra of different areas of the blue and yellow crystals shown in a and b panels. The incident light was vertically polarized in each figure, but no analyzer was used in the scattered light path. Black circles (●) represent the Raman peaks of c-sapphire.

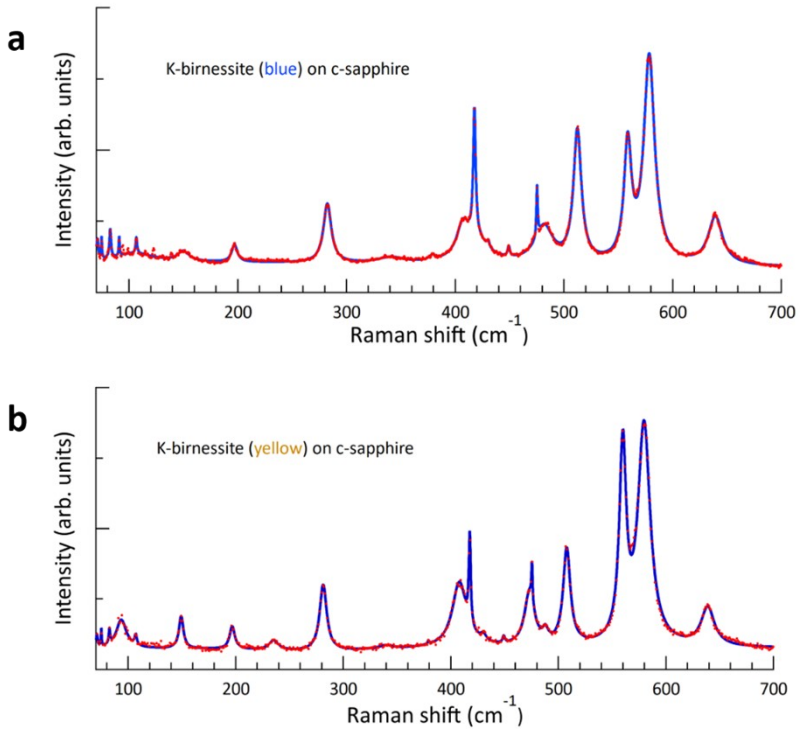

Figure S6. Deconvolution of the Raman peaks of (a) blue and (b) yellow K-birnessite and underlying c-sapphire substrate into Lorentzian functions. The red dots are the experimental results, and the blue lines are the fit results.

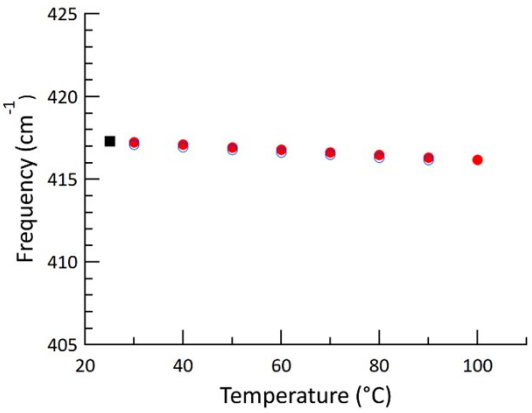

Figure S7. Frequency shift of the A_{1g} mode of c-sapphire substrate by increasing (red closed circles) and then decreasing (blue open circles) the temperature between 30 and 100 °C in vacuum. The black square represents the frequency measured in the laboratory environment.

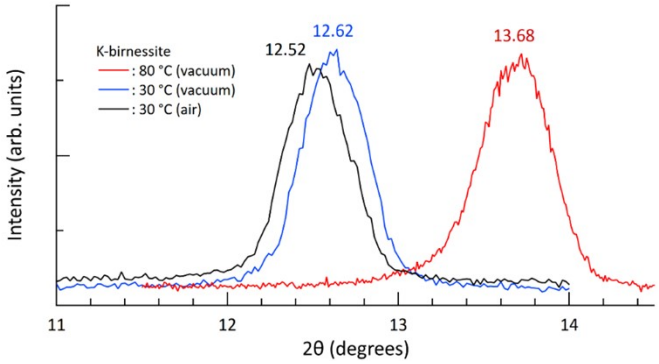

Figure S8. X-ray diffraction of the (*001*) peak of K-birnessite single crystals on c-sapphire measured at 30 °C (blue) and 80 °C (red) in vacuum. The c-axis lattice parameters are 0.71 nm (30 °C, air), 0.70 nm (30 °C, vacuum), and 0.65 nm (80 °C, vacuum).

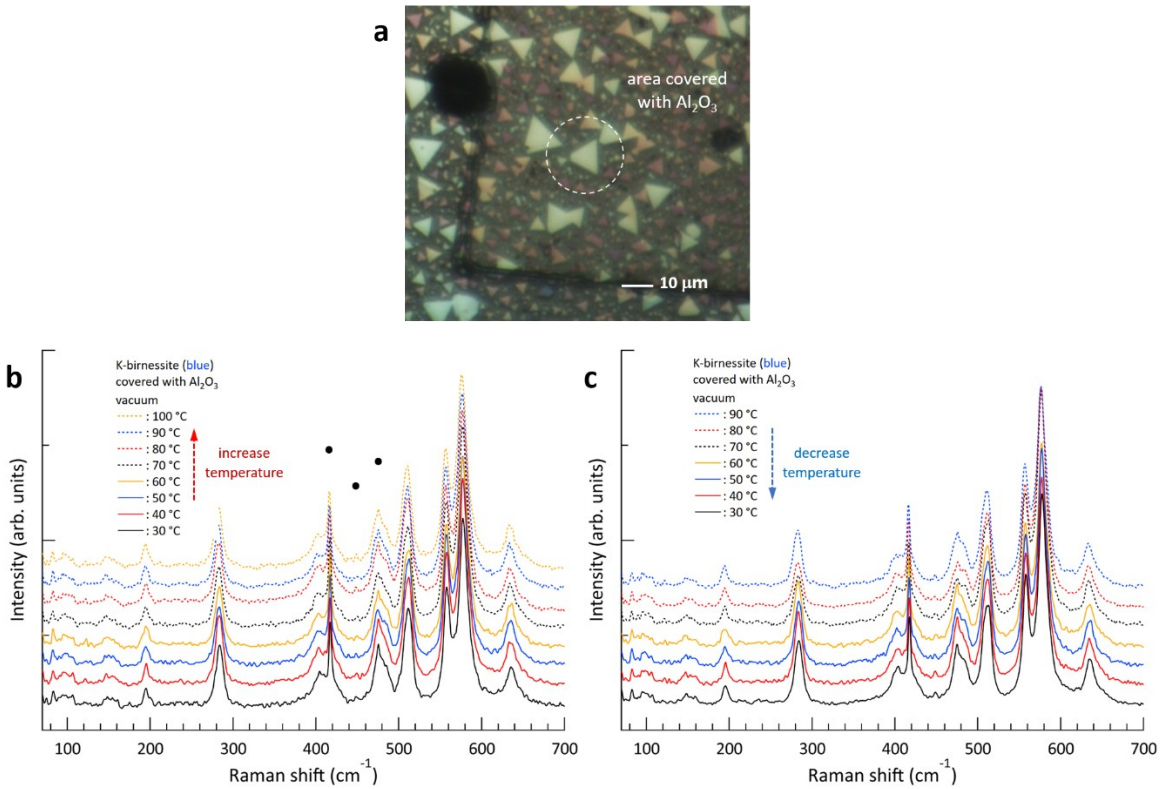

Figure S9. (a) Optical image of K-birnessite single crystals covered with 30 nm Al_2O_3. (b,c) Changes in the Raman spectrum of the blue K-birnessite single crystal in the dashed circle in the optical image with increasing (b) and then decreasing (c) temperature. All spectra were taken 10 min after reaching each target temperature. The small and narrow peaks below 150 cm^{-1} and those marked with black circles (●) represent the Raman peaks of c-sapphire.

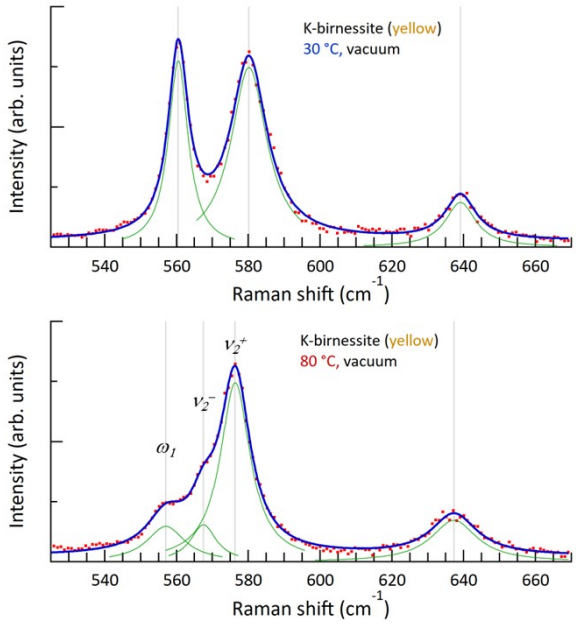

Figure S10. Deconvolution of the Raman peaks between 525 and 670 cm^{-1} of a yellow K-birnessite single crystal at 30 °C (top) and 80 °C (bottom) into Lorentzian curves. The red dots are the experimental results, the green lines are the individual peaks, and the blue lines are the fits.

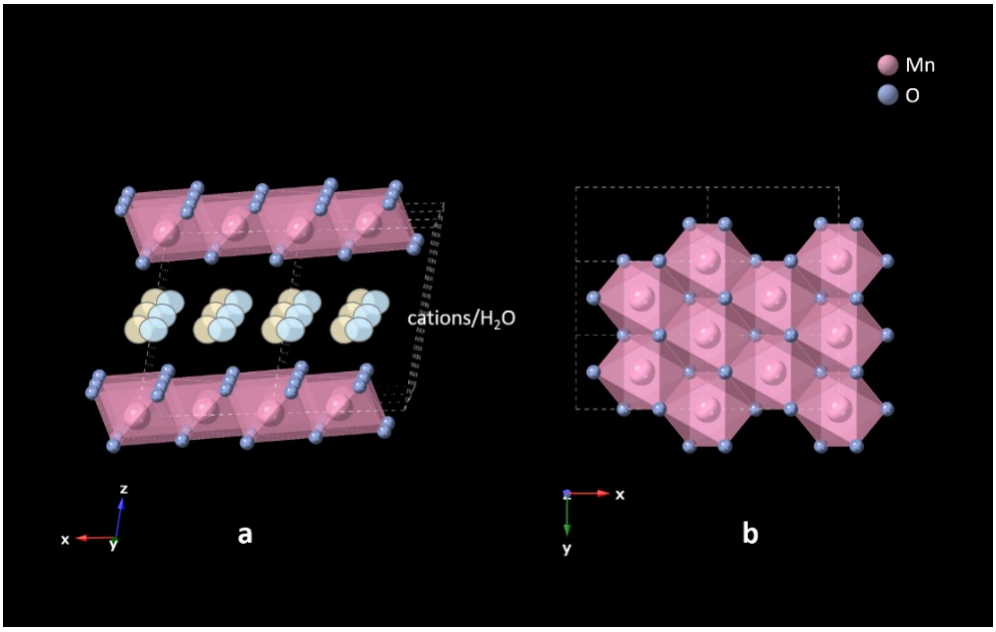

Figure S11. Crystal structure of K-birnessite from the side view (a) and top view (b) based on the atomic parameters obtained by Rietveld refinement of powder X-ray diffraction data by Post et al.[1] The dashed lines represent unit cells.

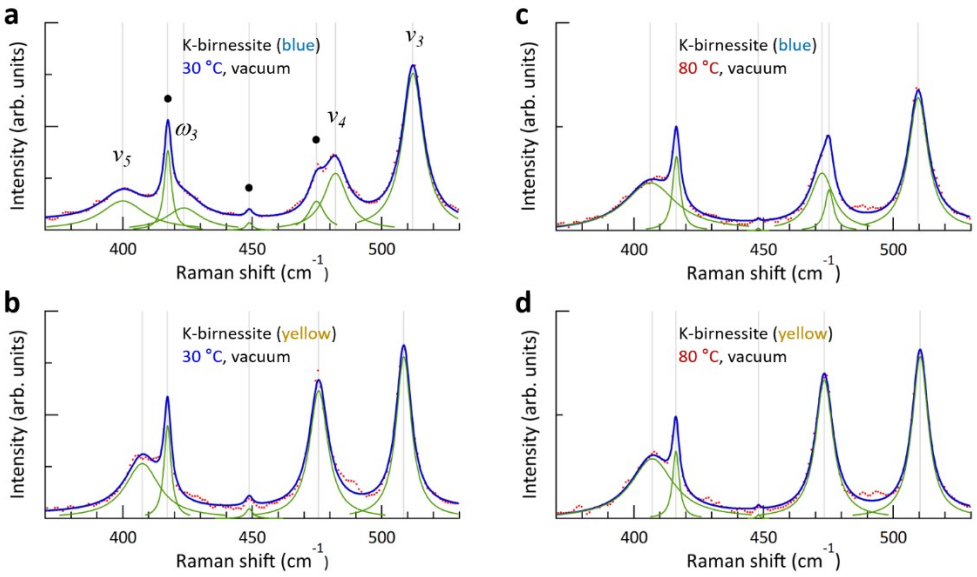

Figure S12. Raman peaks of blue and yellow K-birnessite single crystals at 30 °C (a,b) and 80 °C (c,d) between 370 and 530 cm^{-1} deconvoluted with Lorentzian curves. The red dots are the experimental results, the green lines are the individual peaks, and the blue lines are the fits. Black circles (●) represent the Raman peaks of sapphire. In (b,d), the peak of c-sapphire at 475 cm^{-1} is obscured by the ν_4 peak.

References

1 J. E. Post and D. R. Veblen, *Am. Mineral.*, 1990, **75**, 477-489.