Electronic Supplementary Information for: “The electronic structure and the formation of polarons in Mo-doped BiVO₄, measured by angle-resolved photoemission spectroscopy”

Mansour Mohamed,¹,² Matthias M. May,³ Michael Kanis,³,⁴ Mario Brützam,⁵ Reinhard Uecker,⁵ Roel van de Krol,³ Christoph Janowitz,¹ and Mattia Mulazzi¹,⁶

¹) Institut für Physik, Humboldt-Universität zu Berlin, D-12489 Berlin, Germany.
²) Department of Physics, Faculty of Science, Assiut University, 71515 Assiut, Egypt.
³) Institute for Solar Fuels, Helmholtz-Zentrum Berlin, D-14109 Berlin, Germany.
⁴) OUT e.V., D-12555 Berlin, Germany.
⁵) Leibniz-Institut für Kristallzüchtung, D-12489 Berlin, Germany.
⁶) Institute Functional Oxides for Energy-Efficient IT, Helmholtz-Zentrum Berlin, D-14109 Berlin, Germany.
In ESI Fig. 1 we show the dispersion measured using the second angular degree of freedom of our manipulator. For these measurements, the angular step is about $1^\circ$, measured by tilting the sample in the plane perpendicular to the analyzer slit.

**FIG. 1.** ARPES maps measured perpendicular to the (a) YZ direction with a photon energy of 35 eV and (b) the $\Gamma Z'$ direction with a photon energy of 29 eV. Since BiVO$_4$ has a monoclinic cell, the wavevectors spanned are approximately parallel to the YA’ and and $\Gamma A'$ directions, respectively (see main text).
FIG. 2. X-ray photoelectron spectroscopy around the Mo 3d signal with a monochromated Al K\(\alpha\) source.

FIG. 3. Madelung graph used for the determination of the inner potential, \(U_0\), by means of a least square fit according to \(E = l^2c - U_0\), where \(c\) is a constant and \(E\) the energy, at which a maximum of the primary Bragg peak was observed (including half-order peaks).
FIG. 4. Detail view of the in-gap signal from Fig. 8 (of the main manuscript) as a function of temperature. The intensity was normalised with respect to the total photon flux.