# S=1/2 chain in $BiVO_3F$: spin-dimers versus photoanodic properties

Olivier Mentré*, Miguel A. Juárez-Rosete, Sebastien Saitzek Cintli Aguilar-Maldonado, Marie Colmont, Ángel M. Arévalo-López

Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181, UCCS, Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

***Supporting Information***

## S1. Polycrystalline phase analysis

The synthesis of single phase powder sample was tried using the protocol detailed in the Experimental part. At best , starting out of stoichiometry and after sonification stages to remove impurity, $BiVO_3F$ can be obtained as major phase (87.5 wt%) with two additional impurities: $BiF_3$ (4 wt%) and $Bi_7F_{11}O_5$ (8.5 wt%). A Rietveld refinement was performed using the Fullprof Suite [1] using the single-crystal structural model, leading to reliability factors $R_F$= 0.0697, Bragg $R_{Factor}$= 0.0957 and $R_{F\text{-}factor}$= 0.07 for $BiVO_3F$.

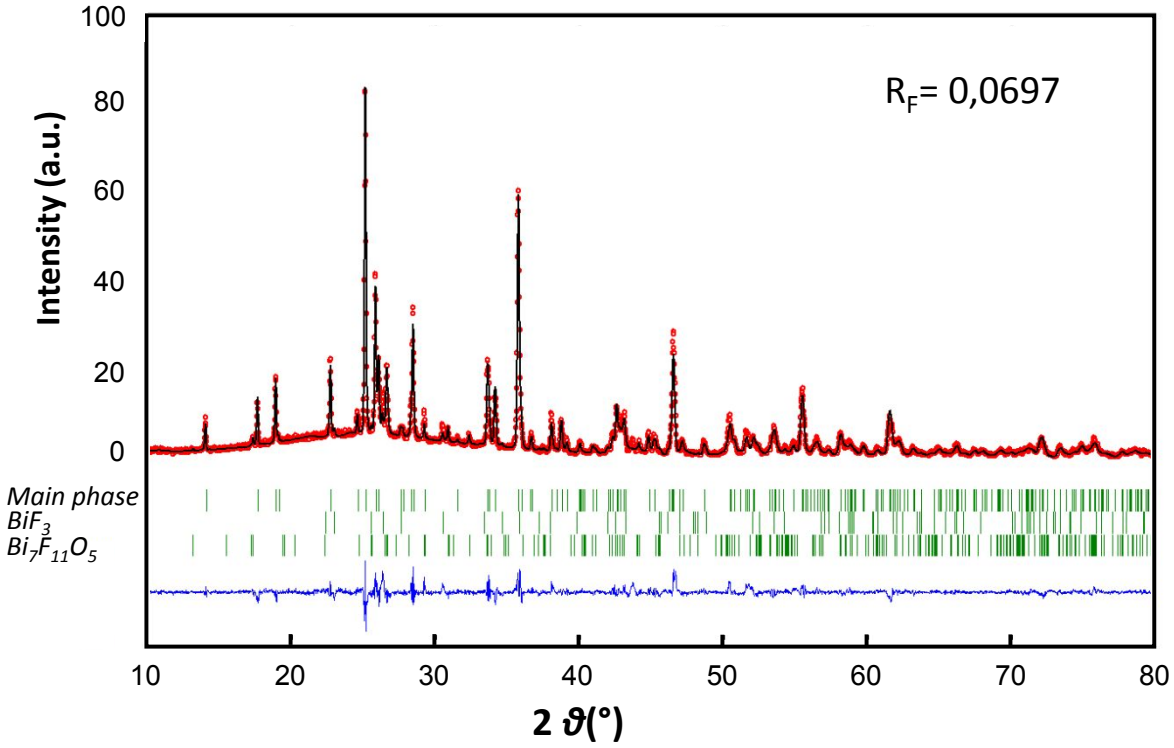


Figure S1 : XRD Rietveld refinement plots for $BiVO_3F$.

To date, our trials to synthesize the pure phase using solid state synthesis systematically failed. To do so, BiOF + $VO_2$ was weighted, mixed and sealed in tube under vaccum. It was heated at 600° for 90h and at 700° for 48h. The resulting powder sample is multiphased with evidence of Aurivilius$Bi_2V(O,F)_6$ under investigation and hollandite $Bi_xV_8O_{16}$.

*Table S1. Crystal and refinement data for $BiVO_3F$.*

| **Crystal Data (T=293K)** | |
|---|---|
| Formula | $BiVO_3F$ |
| Molar weight (g/mol) | 326.9 |
| Symmetry | Monoclinic |
| Space group | P 1 $2_1$/n 1 (14) |
| Unit cell (Å) and angle (°) | a = 5.2621(3) |
| | b = 4.9721(3) |
| | c = 12.6149(7) |
| | β = 95.590(2) |
| Volume | 328.48(3) |
| Z | 4 |
| **Data collection** | |
| Equipment | Bruker |
| λ (Ag Kα (graphite monochromator); Å) | 0.56087 |
| density calc. (g/cm$^3$) | 6.6105 |
| Colour | black |
| θ (min-max) (°) | 2.56 – 46.04 |
| μ (mm-1; for λ Kα=0,71073Å) | 30.689 |
| $R_{int}$ (%) | 6.45 |
| Recording reciprocal space | -13≤ h ≤13 -10 ≤ k ≤12 -32≤ l ≤31 |
| Number of measured reflections | 51579 |
| Number of independent reflections (I > 3σ(I)) | 914/885 |
| Crystal dimension (μm) | 100*100*50 |
| **Refinement** | |
| Number of refined parameters | 56 |
| Refinement method, program | Least square on F |
| Weighting scheme | Unit |
| R1(F)[I > 3σ(I)]/R1(F²) [All data, %] | 1.59 |
| wR²(F²)[I > 3σ(I)]/wR2(F²) [All data, %] | 1.81 |
| GOF | 1,03 |
| Max/min residual electronic density (e-/Å$^3$) | 2.43 / -1.08 |
| Refined extinction coefficient | 5(13) |

*Table S2. Atomic Positions and equivalent isotropic thermal displacement for $BiVO_3F$.*

| Atom | Wick. | x | y | z | $U_{eq}$ (Å²) |
|---|---|---|---|---|---|
| Bi | 4e | 0.44052(7) | 0.69997(8) | 0.16736(3) | *0.00830(11)* |
| V | 4e | 0.5518(4) | 0.7256(4) | 0.43028(14) | *0.0099(5)* |
| O1 | 4e | 0.6721(15) | 0.5788(16) | 0.5685(6) | *0.0098(19)* |
| O2 | 4e | -0.1513(15) | 1.5971(16) | 0.1922(6) | *0.010(2)* |
| O3 | 4e | -0.2265(15) | -0.3711(19) | 0.3556(6) | *0.014(2)* |
| F | 4e | 0.7236(12) | 1.0607(14) | 0.4860(5) | *0.0110(17)* |

*Table S3. Anisotropic thermal displacement for $BiVO_3F$.*

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Bi | 0.00862(19) | 0.0088(2) | 0.00739(19) | 0.00071(12) | 0.00050(11) | 0.00005(12) |
| V | 0.0135(8) | 0.0070(8) | 0.0081(7) | -0.0003(6) | -0.0033(6) | 0.0005(6) |
| O1 | 0.016(3) | 0.005(3) | 0.008(3) | -0.003(3) | -0.005(3) | -0.001(3) |
| F | 0.012(3) | 0.009(3) | 0.012(3) | -0.002(2) | 0.003(2) | -0.002(2) |
| O2 | 0.015(3) | 0.006(4) | 0.008(3) | -0.005(3) | -0.001(3) | -0.001(3) |
| O3 | 0.014(4) | 0.017(4) | 0.012(3) | 0.005(3) | 0.002(3) | 0.000(3) |

*Table S4. Bond valence sum calculations using distances < 3 Å*

| *Atom* | *BVS* |
|---|---|
| Bi | 3.18(3) |
| V | 4.10(3) |
| O1 | 2.26(3) |
| O2 | 2.18(3) |
| O3 | 1.87(4) |
| F | 0.976(9) |

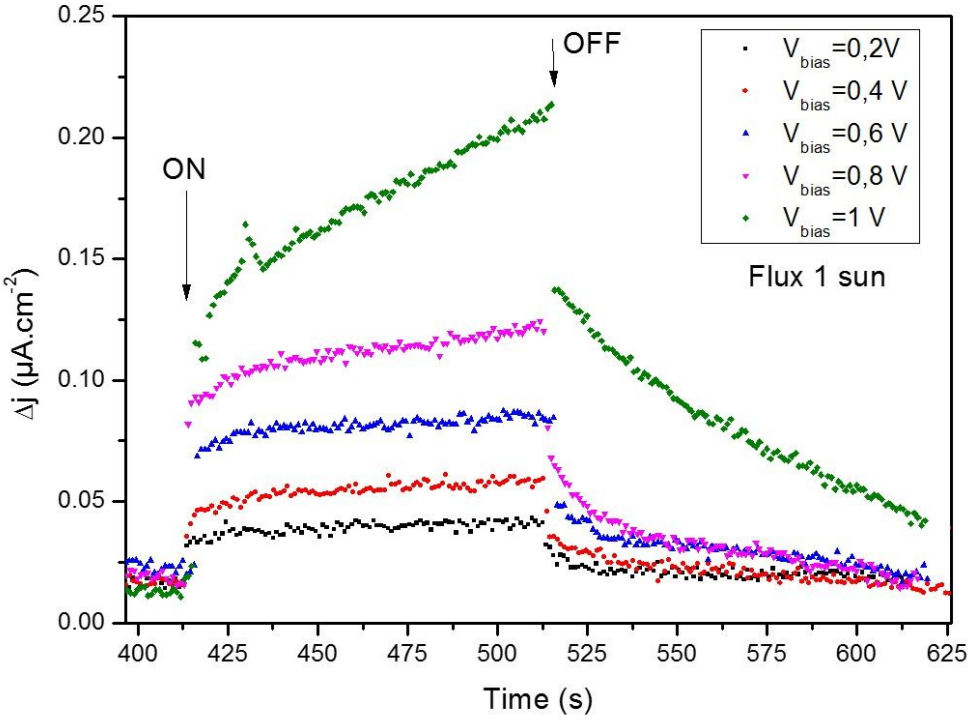


**Figure S2.** Variation of current density under illumination (AM1.5G one-sun (100 mW.cm$^{-2}$)) or dark depending on the applied potential ($V_{bias}$) *vs.* Ag/AgCl.