**Supporting inforamtion**

**Synthesis and Characterization of the Aurivillius Phase CoBi2O2F4**

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**Table S1**

Atomic coordinates and equivalent isotropic displacement parameters (Å2) for CoBi2O2F4.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Atom | x | y | z | U(eq) |
| Bi(1) | 0.5000 | 0.5000 | 0.32714 (4) | 0.0090(2) |
| Co(1) | 0.0000 | 0.0000 | 0.5000 | 0.0063(6) |
| F(1A) | 0.091(13) | -0.088(14) | 0.381(4) | 0.010(6) |
| F(1B) | 0.073(14) | 0.057(19) | 0.376(4) | 0.010(6) |
| F(2A) | 0.069(10) | 0.494(15) | 0.537(3) | 0.014(5) |
| F(2B) | 0.118(10) | 0.494(11) | 0.477(2) | 0.014(5) |
| O(1) | 0.5000 | 0.0000 | 0.2500 | 0.006(7) |
| O(2) | 0.0000 | 0.5000 | 0.2500 | 0.012(8) |

**Table S2**

Selected bond Lengths (Å) and Angles (o) for CoBi2O2F4.

|  |  |  |  |
| --- | --- | --- | --- |
| Bi1—O1(x2)  | 2.2980(4)  | Co1—F1B(x4) | 2.059(60) |
| Bi1—O2(x2) | 2.2980(4)  | Co1—F2A(x4) | 2.011(57) |
| Bi1—F1A (x2) | 2.398(58) | Co1—F2A(x4)  | 2.053(57) |
| Bi1—F1B(x2) | 2.495(55) | Co1—F2B(x4) | 1.986(44) |
| Co1—F1A(x4) | 2.002 (68) | Co1—F2B(x4) | 2.033(43) |

**Table S3**

Bond valence sum (BVS) calculation results for CoBi2O2F4

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Atoms** | **Bonding Distance** | **Bond Valence** | **Atoms** | **Bonding Distance** | **Bond Valence** |
| Bi1—O1(x2) | 2.2980(4)  | 0.865 | F1A—Co1 | 2.002(68) | 0.374 |
| Bi1—O2(x2) | 2.2980(4)  | 0.865 | F1A—Bi1 | 2.398(58) | 0.331 |
| Bi1—F1A(x2) | 2.398(58) | 0.5 |  |  | **0.70** |
| Bi1—F1B(x2) | 2.495(55) | 0.66 | F1B—Co1 | 2.059(60) | 0.321 |
|  |  | **3.40** | F1B—Co1 | 2.495(55) | 0.255 |
|  |  |  |  |  | **0.58** |
| Co—F1A(x4) | 2.002(68) | 0.375 | F2A—Co1 | 2.011(57) | 0.321 |
| Co—F1B(x4) | 2.059(60) | 0.323 | F2A—Co1ii | 2.053(57) | 0.366 |
| Co—F2A(x4) | 2.053(57) | 0.327 |  |  | **0.68** |
| Co—F2A(x4) | 2.011(57) | 0.366 |  |  |  |
| Co—F2B(x4) | 1.986(44) | 0.785 | F2B—Co1 | 1.986(44) | 0.388 |
| Co—F2B(x4) | 2.033(43) | 0.345 | F2B—Co1ii | 2.033(43) | 0.348 |
|  |  | **2.13** |  |  | **0.74** |
|  |  |  |  |  |  |
| O1—Bi1 | 2.298(4) | 0.576 |  |  |  |
| O1—Bi1xi | 2.298(4) | 0.576 |  |  |  |
| O1—Bi1xii | 2.298(4) | 0.576 |  |  |  |
| O1—Bi1xiii | 2.298(4) | 0.576 |  |  |  |
|  |  | **2.30** |  |  |  |



Figure S1 Experimental powder pattern of the CoBi2O2F4 compound and the Bragg peak assignment for the calculated pattern. The blue lines correspond to the CoBi2O2F4 phase and the green lines correspond to a minor BiOF impurity phase.