**Supplementary Information**

Table S1. Crystal data and structure refinement for OD23K

|  |  |
| --- | --- |
| Refined composition | Bi1.902Sr2CuO5.885 |
| *M*r | 730.48 |
| Crystal system, space group | Orthorhombic, *Ccc*2 (37) |
| Temperature (K) | 298 |
| *a*, *b*, *c* (Å) | 5.3947(6), 24.605(3), 5.2786(6) |
| *V* (Å3) | 700.68(15) |
| *Z* | 4 |
| Radiation type | Mo *K*α |
| μ (mm−1) | 65.708 |
| Crystal size (mm) | 0.04×0.03×0.01 |
|  | |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE |
| Absorption correction | Multi-scan |
| No. of measured, independent and observed  [*I* > 2σ(*I*)] reflections | 6333, 984, 808 |
| *R*int | 0.077 |
| (sin θ/λ)max (Å−1) | 0.693 |
|  | |
| Refinement | |
| *R*[*F*2 > 2σ(*F*2)], *wR*(*F*2), *S* | 0.0478, 0.1119, 1.089 |
| No. of reflections | 984 |
| No. of parameters | 37 |
| No. of restraints | 1 |
|  | [*w* = 1/[σ2(*F*o2) + (0.0257*P*)2 + 125.5544*P*]  where *P* = (*F*o2 + 2*F*c2)/3](file:///D:\(Pb,Bi)2Sr2CuO6\bscoa_0m%20_refine_ls_weighting_details) |
| Δρmax, Δρmin (e Å−3) | 3.262, -2.687 |
| Absolute structure | Refined as an inversion twin |
| Absolute structure parameter | 0.47(6) |

Table S2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å2×103) for OD23K. Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom | x/*a* | y/*b* | z/*c* | Ueq | Occ. |
| Bi1 | 0.2676(1) | 0.43697(4) | 0.27412(2) | 17.8(3) | 0.951(11) |
| Sr1 | 0.2466(4) | 0.67736(11) | 0.2540(8) | 19.4(9) | 1 |
| Cu1 | 1/4 | 3/4 | 0.757(1) | 16.2(11) | 1 |
| O1 | -0.003(8) | 0.7517(8) | 0.513(6) | 20(4) | 1 |
| O2 | 0.231(3) | 0.3544(7) | 0.247(5) | 20 | 0.94(5) |
| O3 | 0.650(4) | 0.4322(9) | 0.374(4) | 20 | 1 |

Table S3. Anisotropic Displacement Parameters (Å2×103) for OD23K. The Anisotropic displacement factor exponent takes the form: -2π2[h2a\*2U11+2hka\*b\*U12+…].

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
| Bi1 | 15.2(5) | 22.7(5) | 15.5(5) | 4.4(6) | -4.1(12) | 0.5(4) |
| Sr1 | 12.1(11) | 29.3(13) | 16.7(19) | -0.4(16) | -5(2) | -2.3(8) |
| Cu1 | 9.2(18) | 28(2) | 11(3) | 0 | 0 | 0.5(15) |

Table S4. Crystal data and structure refinement for OD3K

|  |  |
| --- | --- |
| Refined composition | Bi1.88CuO5.73Sr2 |
| *M*r | 722.82 |
| Crystal system, space group | Orthorhombic, *Ccc*2 (37) |
| Temperature (K) | 298 |
| *a*, *b*, *c* (Å) | 5.3878(4), 24.553(2), 5.2646(4) |
| *V* (Å3) | 696.43(9) |
| *Z* | 4 |
| Radiation type | Mo *K*α |
| μ (mm−1) | 65.477 |
| Crystal size (mm) | 0.05×0.03×0.01 |
|  | |
| Data collection | |
| Diffractometer | Bruker D8 VENTURE |
| Absorption correction | Multi-scan |
| No. of measured, independent and observed  [*I* > 2σ(*I*)] reflections | 12508, 1070, 855 |
| *R*int | 0.1170 |
| (sin θ/λ)max (Å−1) | 0.693 |
|  | |
| Refinement | |
| *R*[*F*2 > 2σ(*F*2)], *wR*(*F*2), *S* | 0.0852, 0.1731, 1.162 |
| No. of reflections | 1070 |
| No. of parameters | 41 |
| No. of restraints | 1 |
|  | [*w* = 1/[σ2(*F*o2) + (0.0](file:///D:\(Pb,Bi)2Sr2CuO6\bscoa_0m%20_refine_ls_weighting_details)533[*P*)2 + 201.8843*P*]  where *P* = (*F*o2 + 2*F*c2)/3](file:///D:\(Pb,Bi)2Sr2CuO6\bscoa_0m%20_refine_ls_weighting_details) |
| Δρmax, Δρmin (e Å−3) | 6.58, -2.57 |
| Absolute structure | Refined as an inversion twin |
| Absolute structure parameter | 0.40(11) |

Table S5. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å2×103) for OD3K. Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom | x/*a* | y/*b* | z/*c* | Ueq | Occ. |
| Bi1A | 0.2672(2) | 0.43701(7) | 0.2747.5(2) | 25.4(5) | 0.904(1) |
| Bi1B | 0.2630(70) | 0.4070(20) | 0.2600(200) | 25(4) | 0.034(1) |
| Sr1 | 0.2473(6) | 0.6772.5(18) | 0.2570(20) | 39.3(17) | 1 |
| Cu1 | 1/4 | 3/4 | 0.7590(50) | 40(2) | 1 |
| O1 | 0.0030(80) | 0.7521(11) | 0.4930(70) | 25(6) | 0.87(2) |
| O2 | 0.2270(50) | 0.3539(11) | 0.2480(90) | 25 | 1 |
| O3 | 0.6480(60) | 0.4321(13) | 0.3850(60) | 25 | 1 |

Table S6. Anisotropic Displacement Parameters (Å2×103) for OD3K. The Anisotropic displacement factor exponent takes the form: -2π2[h2a\*2U11+2hka\*b\*U12+…].

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
| Bi1A | 18.2(7) | 21.4(9) | 36.5(8) | 5.8(13) | -8.1(14) | 0.8(6) |
| Bi1B | 18(11) | 21.4(7) | 36.5(9) | 5.8(8) | -8.1(13) | 0.8(14) |
| Sr1 | 14.8(16) | 34.6(19) | 69(5) | -4(4) | -17(4) | -3.4(13) |
| Cu1 | 13(3) | 35(3) | 71(7) | 0 | 0 | -1(2) |