# New complex phosphates $Cs_3M^{II}Bi(P_2O_7)_2$ ($M^{II}$ – Ca, Sr, Pb): synthesis, characterization, crystal and electronic structure

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## SUPPORTING INFORMATION

**Table 1S.**

**The atomic coordinates and their equivalent isotropic thermal parameters ofCsCaBiP (I), CsSrBiP (II) and CsPbBiP(III).**

| Atom | | *x* | *y* | *z* | $U_{iso}/U_{eq}$ |
|---|---|---|---|---|---|
| Bi1 | I | 0.730090(19) | 0.146186(18) | 0.249723(11) | 0.01228(5) |
| | II | 0.73077(2) | 0.14783(3) | 0.254473(13) | 0.01103(5) |
| | III | 0.732104(17) | 0.143512(18) | 0.257008 (9) | 0.01048(4) |
| Ca1 | I | 0.06336(10) | 0.31751(9) | 0.13101(5) | 0.00563(14) |
| Sr1 | II | 0.06838(6) | 0.31685(6) | 0.13283(3) | 0.00851(11) |
| Pb1 | III | 0.063661(19) | 0.31885(2) | 0.129076 (11) | 0.01434(4) |
| Cs1 | I | 0.11567(4) | 0.48665(3) | 0.498757(19) | 0.01702(7) |
| | II | 0.11406(5) | 0.49088(5) | 0.49919(2) | 0.01854(10) |
| | III | 0.10796(4) | 0.49466(4) | 0.498867 (18) | 0.01948(7) |
| Cs2 | I | 0.27066(4) | 0.14483(4) | 0.33569(2) | 0.02659(8) |
| | II | 0.26460(5) | 0.14586(6) | 0.33554(3) | 0.02746(11) |
| | III | 0.26279(4) | 0.15021(4) | 0.33278 (2) | 0.02978(8) |
| Cs3 | I | 0.11909(5) | 0.00324(4) | 0.56563(3) | 0.02840(9) |
| | II | 0.10135(6) | 0.00063(6) | 0.57290(3) | 0.03275(13) |
| | III | 0.09721(4) | 0.00268(4) | 0.58219 (2) | 0.02932(9) |
| P1 | I | 0.98245(15) | 0.42848(14) | 0.29832(7) | 0.0111(2) |
| | II | 0.97857(19) | 0.42420(18) | 0.30136(9) | 0.0109(3) |
| | III | 0.97027(14) | 0.41774(15) | 0.30476 (7) | 0.0140(2) |
| P2 | I | 0.88579(15) | 0.20625(13) | 0.41201(7) | 0.0121(2) |
| | II | 0.46603(17) | 0.3570(2) | 0.18494(9) | 0.0119(3) |
| | III | 0.87971(14) | 0.20448(14) | 0.41927 (7) | 0.0140(2) |
| P3 | I | 0.45687(13) | 0.35239(15) | 0.18091(7) | 0.0109(2) |
| | II | 0.46603(17) | 0.3570(2) | 0.18494(9) | 0.0119(3) |
| | III | 0.47486(12) | 0.35913(15) | 0.18855 (7) | 0.0128(2) |
| P4 | I | 0.68042(15) | 0.25624(15) | 0.07269(8) | 0.0126(2) |
| | II | 0.68618(19) | 0.2688(2) | 0.07489(10) | 0.0142(4) |
| | III | 0.69144(13) | 0.27470(15) | 0.07602 (7) | 0.0132(2) |
| O1 | I | 0.8729(6) | 0.3723(5) | 0.2433(3) | 0.0275(10) |
| | II | 0.8752(5) | 0.3613(5) | 0.2444(2) | 0.0167(9) |
| | III | 0.8717(4) | 0.3510(5) | 0.2455 (2) | 0.0243(9) |
| O2 | I | 1.1294(5) | 0.4159(5) | 0.2606(3) | 0.0226(9) |
| | II | 1.1288(5) | 0.4176(5) | 0.2692(3) | 0.0178(10) |
| | III | 1.1200(4) | 0.4217(5) | 0.2733 (2) | 0.0243(9) |
| O3 | I | 0.9548(5) | 0.5738(5) | 0.3306(3) | 0.0236(9) |
| | II | 0.9385(7) | 0.5661(6) | 0.3309(3) | 0.0266(12) |
| | III | 0.9170(6) | 0.5501(5) | 0.3358 (3) | 0.0411(12) |
| O4 | I | 0.7382(5) | 0.2216(5) | 0.3733(2) | 0.0238(9) |
| | II | 0.7313(6) | 0.2307(6) | 0.3781(3) | 0.0236(11) |
| | III | 0.7332(4) | 0.2187(4) | 0.3825 (2) | 0.0219(8) |

| | | | | | |
|---|---|---|---|---|---|
| O5 | I | 0.9520(6) | 0.0634(5) | 0.3963(3) | 0.0315(11) |
| | II | 0.9362(7) | 0.0708(6) | 0.3952(4) | 0.0429(18) |
| | III | 0.9403(6) | 0.0662(5) | 0.4003 (4) | 0.0577(18) |
| O6 | I | 0.8813(6) | 0.2505(5) | 0.4932(3) | 0.0256(9) |
| | II | 0.8784(7) | 0.2477(7) | 0.4969(3) | 0.0377(16) |
| | III | 0.8829(6) | 0.2433(6) | 0.5009 (2) | 0.0386(12) |
| O7 | I | 0.9921(5) | 0.3187(4) | 0.3688(2) | 0.0170(8) |
| | II | 0.9859(5) | 0.3218(5) | 0.3736(3) | 0.0185(11) |
| | III | 0.9837(4) | 0.3108(5) | 0.3752 (2) | 0.0266(9) |
| O8 | I | 0.5296(5) | 0.2739(5) | 0.2460(3) | 0.0249(9) |
| | II | 0.5387(5) | 0.2804(6) | 0.2492(3) | 0.0241(11) |
| | III | 0.5464(4) | 0.2797(5) | 0.2520 (2) | 0.0265(9) |
| O9 | I | 0.4353(5) | 0.5064(4) | 0.2043(3) | 0.0262(10) |
| | II | 0.4432(7) | 0.5067(6) | 0.2098 (4) | 0.0352 (15) |
| | III | 0.4495(5) | 0.5050(5) | 0.2159 (3) | 0.0355(11) |
| O10 | I | 0.3262(5) | 0.2861(5) | 0.1490(3) | 0.0278(10) |
| | II | 0.3374(6) | 0.2900(7) | 0.1527 (3) | 0.0304 (14) |
| | III | 0.3481(4) | 0.2925(6) | 0.1538 (3) | 0.0385(13) |
| O11 | I | 0.6235(5) | 0.2412(5) | −0.0066(3) | 0.0242(9) |
| | II | 0.6207(6) | 0.2422(6) | −0.0009 (3) | 0.0284 (13) |
| | III | 0.6161(5) | 0.2477(6) | 0.0024 (2) | 0.0323(10) |
| O12 | I | 0.8286(4) | 0.3182(5) | 0.0788(3) | 0.0250(9) |
| | II | 0.8282(5) | 0.3378(7) | 0.0737 (3) | 0.0302 (14) |
| | III | 0.8308(4) | 0.3464(6) | 0.0680 (2) | 0.0303(10) |
| O13 | I | 0.6637(5) | 0.1199(4) | 0.1188(2) | 0.0210(8) |
| | II | 0.6829(6) | 0.1377(6) | 0.1238 (3) | 0.0276 (12) |
| | III | 0.6999(5) | 0.1462(4) | 0.1254 (2) | 0.0276(9) |
| O14 | I | 0.5767(4) | 0.3713(4) | 0.1157(2) | 0.0177(8) |
| | II | 0.5828(5) | 0.3789(5) | 0.1197 (3) | 0.0169 (10) |
| | III | 0.5928(4) | 0.3823(4) | 0.1235 (2) | 0.0177(7) |

**Table 2S.**

**The bond lengths (Å) in the coordination polyhedra of $PO_4$ and $CsO_x$ for CsCaBiP (I), CsSrBiP (II) and CsPbBiP(III).**

| | I | II | III | | I | II | III |
|---|---|---|---|---|---|---|---|
| ***PO$_4$tetrahedra*** | | | | Cs(1)–O(12)$^{iii}$ | 3.451(5) | 3.620(7) | 3.662(5) |
| P(1)–O(1) | 1.502(5) | 1.524(5) | 1.537(4) | Cs(1)–O(9)$^{ii}$ | 3.653(5) | 3.756(7) | 3.843(6) |
| P(1)–O(3) | 1.505(4) | 1.510(5) | 1.485(5) | Cs(1)–O(5)$^{iv}$ | 3.660(6) | 3.605(7) | 3.645(6) |
| P(1)–O(2) | 1.522(4) | 1.523(5) | 1.515(4) | ***Cs(2)O$_x$ polyhedra*** | | | |
| P(1)–O(7) | 1.619(4) | 1.614(5) | 1.620(4) | Cs(2)–O(14)$^{v}$ | 3.065(4) | 3.047(5) | 3.038(4) |
| P(2)–O(6) | 1.490(5) | 1.482(6) | 1.481(5) | Cs(2)–O(9)$^{v}$ | 3.108(5) | 3.158(6) | 3.174(5) |
| P(2)–O(5) | 1.506(5) | 1.499(6) | 1.499(5) | Cs(2)–O(7)$^{i}$ | 3.118(4) | 3.191(5) | 3.148(4) |
| P(2)–O(4) | 1.537(5) | 1.544(6) | 1.530(4) | Cs(2)–O(8) | 3.123(5) | 3.262(5) | 3.276(4) |
| P(2)–O(7) | 1.637(4) | 1.641(5) | 1.621(4) | Cs(2)–O(2)$^{i}$ | 3.162(4) | 3.138(5) | 3.142(4) |
| P(3)–O(10) | 1.476(5) | 1.483(5) | 1.489(4) | Cs(2)–O(1)$^{v}$ | 3.212(5) | 3.350(5) | 3.458(4) |
| P(3)–O(9) | 1.523(4) | 1.522(6) | 1.517(5) | Cs(2)–O(6)$^{iv}$ | 3.335(5) | 3.309(6) | 3.294(5) |
| P(3)–O(8) | 1.523(5) | 1.515(5) | 1.512(4) | Cs(2)–O(5)$^{i}$ | 3.239(6) | 3.340(7) | 3.362(6) |
| P(3)–O(14) | 1.609(4) | 1.605(5) | 1.608(4) | Cs(2)–O(12)$^{v}$ | 3.550(5) | 3.482(6) | 3.541(5) |
| P(4)–O(12) | 1.499(5) | 1.491(6) | 1.494(4) | Cs(2)–O(10) | 3.585(6) | 3.579(6) | 3.522(5) |
| P(4)–O(11) | 1.500(4) | 1.495(5) | 1.497(4) | Cs(2)–O(3)$^{v}$ | 3.662(5) | 3.587(6) | 3.543(5) |
| P(4)–O(13) | 1.528(4) | 1.530(6) | 1.522(4) | ***Cs(3)O$_x$ polyhedra*** | | | |
| P(4)–O(14) | 1.636(4) | 1.641(5) | 1.629(4) | Cs(3)–O(4)$^{iv}$ | 3.019(5) | 2.989(6) | 3.060(4) |
| ***Cs(1)O$_x$ polyhedra*** | | | | Cs(3)–O(13)$^{vi}$ | 3.020(5) | 3.118(6) | 3.242(5) |
| Cs(1)–O(7)$^{i}$ | 3.011(4) | 3.003(5) | 3.044(4) | Cs(3)–O(12)$^{v}$ | 3.123(5) | 3.097(6) | 3.114(4) |
| Cs(1)–O(14)$^{ii}$ | 3.039(4) | 3.086(5) | 3.128(4) | Cs(3)–O(10)$^{vi}$ | 3.140(5) | 3.185(6) | 3.176(6) |
| Cs(1)–O(6)$^{i}$ | 3.115(5) | 3.223(6) | 3.237(5) | Cs(3)–O(5)$^{i}$ | 3.410(6) | 3.564(8) | 3.569(7) |
| Cs(1)–O(13)$^{iii}$ | 3.173(4) | 3.218(5) | 3.193(4) | Cs(3)–O(6)$^{i}$ | 3.456(5) | 3.443(7) | 3.404(6) |
| Cs(1)–O(4)$^{iv}$ | 3.198(5) | 3.234(5) | 3.166(4) | Cs(3)–O(11)$^{vi}$ | 3.465(5) | 3.394(6) | 3.453(5) |
| Cs(1)–O(6)$^{iv}$ | 3.333(5) | 3.385(6) | 3.474(5) | Cs(3)–O(6)$^{iv}$ | 3.521(6) | 3.764(7) | 3.934(6) |
| Cs(1)–O(11)$^{ii}$ | 3.395(5) | 3.387(6) | 3.277(5) | Cs(3)–O(11)$^{v}$ | 3.592(5) | 3.825(7) | 3.956(6) |
| Cs(1)–O(11)$^{iii}$ | 3.413(5) | 3.474(6) | 3.581(5) | Cs(3)–O(3)$^{iv}$ | 3.687(5) | 3.652(6) | 3.378(6) |
| Cs(1)–O(3)$^{i}$ | 3.418(5) | 3.475(6) | 3.420(5) | Cs(3)–O(8)$^{iv}$ | 4.015(5) | 3.828(7) | 3.627(4) |
| Cs(1)–O(10)$^{ii}$ | 3.448(6) | 3.465(6) | 3.440(6) | Cs(3)–O(9)$^{iv}$ | - | 4.115(8) | 3.804(5) |

Symmetrycodes: (i) −1+*x*, *y*, *z*;(ii) 0.5−*x*, 1 −*y*, *z*+0.5;(iii) 1−*x*, *y*+0.5, 0.5−*z*; (iv) −0.5+*x*, 0.5−*y*, 1−*z*;(v) 1−*x*, −0.5+*y*, 0.5−*z*;(vi) 0.5−*x*, −*y*, *z*+0.5;(vii) 2−*x*, *y*−0.5, 0.5−*z*;(viii) *x*+1, *y*, *z*;(ix) *x*+0.5, 0.5−*y*, 1−*z*; (x) 0.5−*x*, 0.5−*y*, −*z*; (xi)−*x*, *y*−0.5, 0.5−*z*;(xii) −*x*+0.5, 1−*y*, *z*−0.5; (xiii) −*x*, *y*+0.5, 0.5−*z*; (xiv) 0.5−*x*, −*y*, *z*−0.5; (xv) 2−*x*, *y*+0.5, 0.5−*z*; (xvi) *x*+0.5, 0.5−*y*, −*z*.

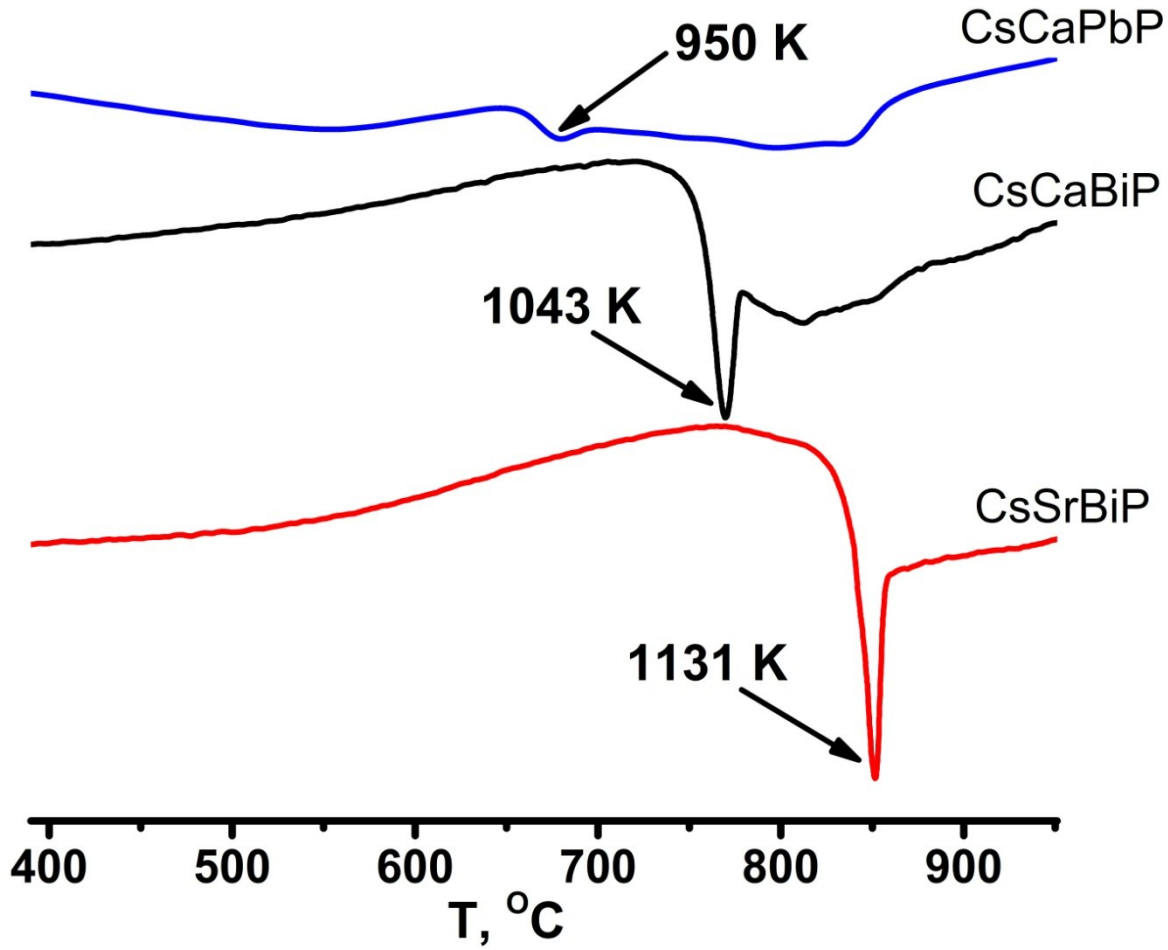


**Fig 1S.** DTA-curvesat heating mode for complex phosphates $Cs_3M^{II}Bi(P_2O_7)_2$ (melting points are indicated by arrows).

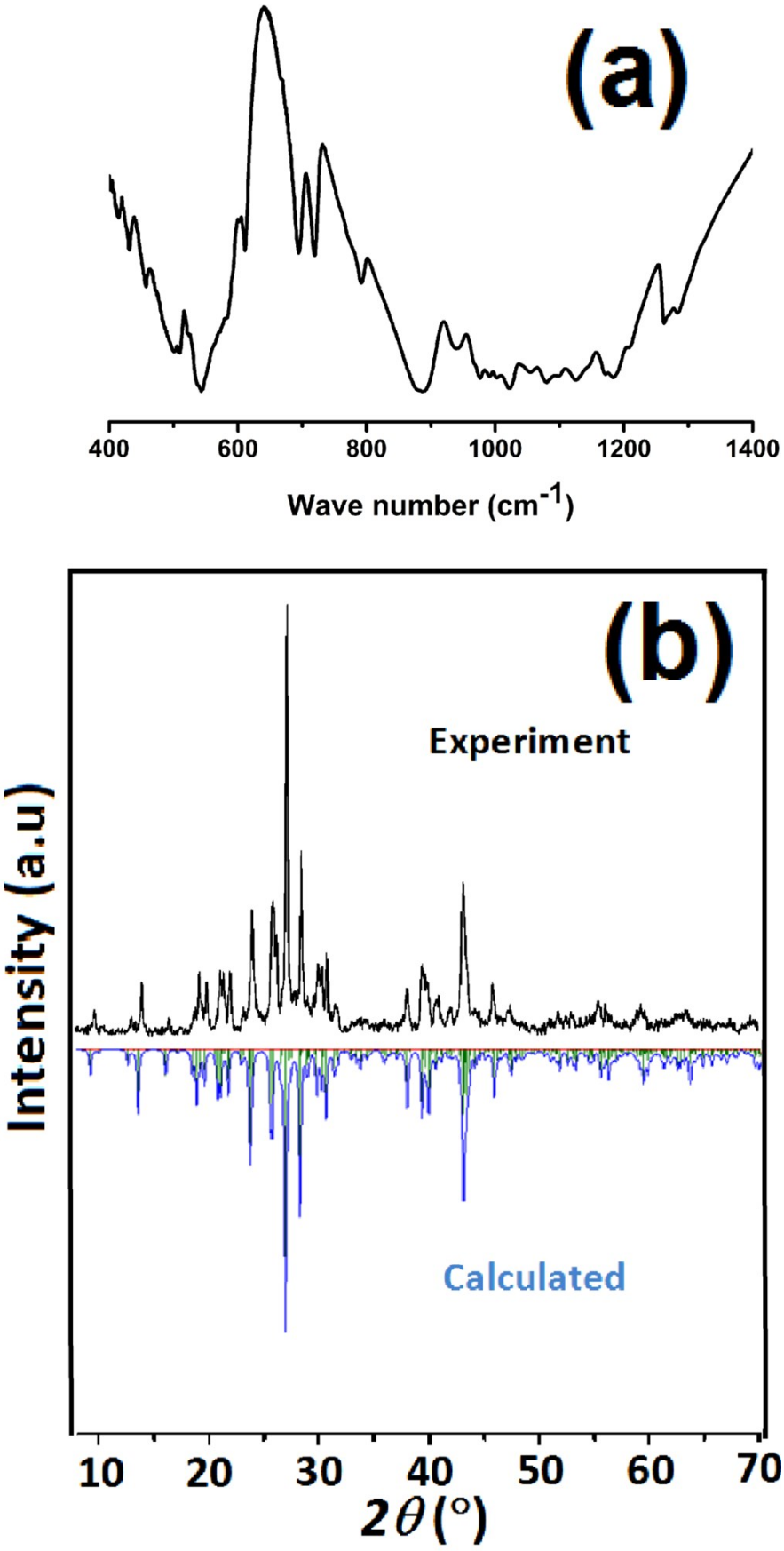


**Fig 2S.** FTIR-spectra (a) and XRD powder data (b) of glass-ceramic $Cs_3CaBi(P_2O_7)_2$.

# Details of calculations of Voronoi-Dirichlet polyhedron (VDP)

***CN*** *– Coordination number*

***Rsd****– Radius of spherical domain*

***D(CP)*** *– The shift of an atom from the centroid of its coordination polyhedron and coordinates of the centroid*

***D(VDP)****– The shift of an atom from the centroid of its Voronoi-Dirichlet polyhedron andcoordinates of the centroid*

***Atom, Top*** *– The values of division coefficients used for bonds between central atom and atoms,forming Voronoi-Dirichlet polyhedron, if they differ from 0.5*

***CN*****(*m*:*l*:*n*)** *– Total coordination number of the atom, written as n:m:l, where n, m and l are thenumbers of 'direct', 'half-direct' and 'indirect' neighbours*

***NV*** *– The number of vertices of Voronoi-Dirichlet polyhedron*

***V*** *– Volume of Voronoi-Dirichlet polyhedron/coordination polyhedron*

***S*** *– Surface area of Voronoi-Dirichlet polyhedron*

***Cpac*** *– Packing coefficient*

**C***cov – Covering coefficient*

**G***3 – Dimensionless second moment of inertia of Voronoi-Dirichlet polyhedron*

***Face distribution*** *– Combinatorial properties of VDP faces written as the number of vertices (edges)of a face/the number of such faces*

***Vertex distribution*** *– Combinatorial properties of VDP vertices written as the number of edges(faces), that meet in a vertex/the number of such vertices*

***Dist*** *– The distance between central atom and Xi atom*

***S****Seg – The area of the face*

***V****Seg – The volume of a pyramid with the face in a bottom and the central atom in the top*

***S****Ang – The solid angle of the face*

***NV*** *– The number of vertices (edges) of the face*

***Phi*** *– The angle (Xi–central atom–VDP centroid)*

**Table 3S.**

## Calculations VDP for atoms Bi and Cs in $Cs_3CaBi(P_2O_7)_2$.

***Central atom: Bi1*** *0.230 0.354 0.750*

**Rsd:** 1.483; **D(CP):** 0.655 ( 0.2961 0.3320 0.7562 ); **D(VDP):** 0.225 ( 0.2534 0.3560 0.7537 );

**Atom:** 2.180<r<3.601, <r> = 2.927; **Top:** 1.675<R<2.224, <R> = 1.930; **CN** = 8:0:5;

**NV** =22; **V** = 13.668/44.203; **S** = 32.856; **Cpac** = 0.397; **Ccov** = 3.371; **G3** = 0.085805893;

**Face distribution:** {3/1 4/4 5/3 6/3 7/2} ; **Vertex distribution:** {3/22}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O9** | 0.065 | 0.494 | 0.704 | 2.180 | 14.48 | 12.65 | 16.33 | 5 | 136.05 |
| 2 | **O8** | 0.030 | 0.226 | 0.754 | 2.218 | 12.69 | 11.28 | 15.00 | 5 | 147.86 |
| 3 | **O4** | 0.238 | 0.278 | 0.627 | 2.291 | 13.43 | 12.33 | 14.95 | 6 | 104.57 |
| 4 | **O13** | 0.164 | 0.380 | 0.881 | 2.400 | 15.85 | 15.25 | 15.62 | 7 | 88.82 |
| 5 | **O1** | 0.373 | 0.128 | 0.757 | 2.513 | 15.57 | 15.67 | 14.53 | 7 | 63.87 |
| 6 | **O2** | 0.371 | 0.584 | 0.761 | 2.540 | 15.09 | 15.36 | 14.20 | 4 | 53.82 |
| 7 | **O3** | 0.545 | 0.426 | 0.831 | 3.322 | 6.31 | 8.40 | 4.69 | 6 | 12.04 |
| 8 | **O5** | 0.452 | 0.437 | 0.604 | 3.395 | 3.87 | 5.27 | 2.77 | 6 | 66.46 |
| 9 | **O14** | 0.077 | 0.129 | 0.884 | 3.480 | 0.47 | 0.65 | 0.35 | 4 | 105.47 |
| 10 | **O12** | 0.329 | 0.182 | 0.921 | 3.540 | 1.24 | 1.75 | 0.91 | 4 | 64.29 |
| 11 | **O7** | 0.492 | 0.181 | 0.631 | 3.601 | 0.63 | 0.91 | 0.39 | 5 | 63.22 |

***Central atom:Cs1*** *0.116 0.487 0.499*

**Rsd:** 1.842; **D(CP):** 0.220 (0.1206 0.5070 0.5043); **D(VDP):** 0.028 (0.1177 0.4844 0.4987);

**Atom:** 3.011<r< 4.750, <r> = 3.591; **Top:** 1.771<R<2.446, <R> = 2.159; **CN** = 15:0:5;

**NV** = 36; **V** = 26.174/102.730; **S** = 48.047; **Cpac** = 0.546; **Ccov** = 2.343; **G3** = 0.080441684 ;

**Face distribution:** {3/7 5/1 6/7 7/2 8/1 9/2}; **Vertex distribution:** {3/36}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O7** | -0.008 | 0.319 | 0.369 | 3.011 | 11.15 | 10.27 | 11.45 | 5 | 79.89 |
| 2 | **O14** | -0.077 | 0.629 | 0.616 | 3.038 | 9.88 | 9.18 | 10.71 | 6 | 139.32 |
| 3 | **O6** | -0.119 | 0.250 | 0.493 | 3.115 | 12.35 | 11.77 | 11.68 | 9 | 86.48 |
| 4 | **O13** | 0.336 | 0.620 | 0.381 | 3.173 | 9.97 | 9.67 | 9.91 | 8 | 79.81 |
| 5 | **O4** | 0.238 | 0.278 | 0.627 | 3.199 | 8.77 | 8.58 | 9.09 | 6 | 49.20 |
| 6 | **O6** | 0.381 | 0.250 | 0.507 | 3.333 | 9.55 | 9.74 | 8.79 | 7 | 7.93 |
| 7 | **O11** | -0.123 | 0.759 | 0.493 | 3.395 | 7.01 | 7.28 | 6.80 | 6 | 175.03 |
| 8 | **O11** | 0.377 | 0.741 | 0.507 | 3.413 | 5.32 | 5.56 | 5.49 | 6 | 92.64 |
| 9 | **O3** | -0.045 | 0.574 | 0.331 | 3.418 | 6.28 | 6.57 | 6.27 | 6 | 115.01 |
| 10 | **O10** | 0.174 | 0.714 | 0.649 | 3.448 | 5.79 | 6.11 | 5.81 | 9 | 113.40 |
| 11 | **O12** | 0.171 | 0.818 | 0.421 | 3.451 | 4.64 | 4.90 | 4.80 | 6 | 123.17 |
| 12 | **O9** | 0.065 | 0.494 | 0.704 | 3.652 | 2.95 | 3.30 | 2.81 | 6 | 98.94 |
| 13 | **O5** | 0.452 | 0.437 | 0.604 | 3.660 | 3.76 | 4.21 | 3.53 | 7 | 50.22 |

***Central atom:Cs2*** *0.771 0.355 0.664*

**Rsd:** 1.879; **D(CP)**: 0.281 (0.7888 0.3315 0.6626); **D(VDP)**: 0.104 (0.7745 0.3467 0.6611);

**Atom:** 3.065<r<5.063, <r> = 3.838; **Top:** 1.946<R<2.579, <R> = 2.302; **CN** = 13:0:7;

**NV** = 36; **V** = 27.770/120.452; **S** = 50.527; **Cpac** = 0.543; **Ccov** = 2.587; **G3** = 0.082202137;

**Face distribution:** {3/8 5/2 6/5 7/1 8/2 9/1 12/1}; **Vertex distribution:** {3/36}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O14** | 0.923 | 0.629 | 0.616 | 3.065 | 8.83 | 8.20 | 9.99 | 6 | 109.86 |
| 2 | **O9** | 1.065 | 0.494 | 0.704 | 3.108 | 9.25 | 8.72 | 9.63 | 9 | 98.33 |
| 3 | **O7** | 0.492 | 0.181 | 0.631 | 3.118 | 9.16 | 8.66 | 9.72 | 6 | 77.19 |
| 4 | **O8** | 1.030 | 0.226 | 0.754 | 3.124 | 11.11 | 10.53 | 11.16 | 8 | 73.06 |
| 5 | **O2** | 0.629 | 0.084 | 0.739 | 3.163 | 9.36 | 8.98 | 9.90 | 6 | 75.19 |
| 6 | **O1** | 0.627 | 0.628 | 0.743 | 3.212 | 9.48 | 9.23 | 9.96 | 8 | 172.49 |
| 7 | **O5** | 0.452 | 0.437 | 0.604 | 3.239 | 8.25 | 8.10 | 8.72 | 6 | 108.54 |
| 8 | **O6** | 0.881 | 0.250 | 0.493 | 3.334 | 16.09 | 16.27 | 13.92 | 12 | 34.93 |
| 9 | **O12** | 0.671 | 0.682 | 0.579 | 3.550 | 4.25 | 4.57 | 4.30 | 5 | 121.93 |
| 10 | **O10** | 0.826 | 0.214 | 0.851 | 3.586 | 5.13 | 5.58 | 4.88 | 7 | 99.09 |
| 11 | **O3** | 0.545 | 0.426 | 0.831 | 3.663 | 5.20 | 5.77 | 5.02 | 5 | 140.07 |
| 12 | **O8** | 0.970 | 0.726 | 0.746 | 4.212 | 0.01 | 0.01 | 0.01 | 3 | 132.28 |
| 13 | **O4** | 1.238 | 0.278 | 0.627 | 4.452 | 0.51 | 0.69 | 0.38 | 3 | 57.38 |
| 14 | **O13** | 0.836 | -0.120 | 0.619 | 4.591 | 2.19 | 3.05 | 1.53 | 6 | 27.00 |

***Central atom: Cs3*** *0.619 0.497 0.434*

**Rsd:** 1.913; **D(CP):** 0.454 (0.6421 0.4924 0.4118); **D(VDP):** 0.111 (0.6239 0.4881 0.4309);

**Atom:** 3.019<r<5.063, <r> = 3.891; **Top:** 1.950<R<2.579 , <R> = 2.295; **CN** = 13:0:9;

**NV** = 40; **V** = 29.346/130.936; **S** = 51.967; **Cpac** = 0.491; **Ccov** = 2.448; **G3** = 0.081912637 ;

**Face distribution:** {3/8 4/1 5/1 6/6 7/3 9/1 10/1 11/1} ; **Vertex distribution:** {3/40}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O4** | 0.738 | 0.222 | 0.373 | 3.019 | 12.15 | 10.83 | 13.28 | 7 | 12.96 |
| 2 | **O13** | 0.336 | 0.620 | 0.381 | 3.020 | 12.57 | 11.20 | 13.33 | 9 | 117.81 |
| 3 | **O12** | 0.671 | 0.682 | 0.579 | 3.123 | 9.90 | 9.13 | 10.95 | 7 | 142.22 |
| 4 | **O10** | 0.674 | 0.786 | 0.351 | 3.140 | 11.26 | 10.44 | 11.90 | 10 | 108.74 |
| 5 | **O5** | 0.452 | 0.437 | 0.604 | 3.410 | 7.34 | 7.39 | 7.59 | 6 | 122.37 |
| 6 | **O6** | 0.381 | 0.250 | 0.507 | 3.456 | 9.80 | 10.00 | 9.25 | 6 | 87.78 |
| 7 | **O11** | 0.377 | 0.741 | 0.507 | 3.465 | 4.46 | 4.56 | 4.97 | 5 | 162.15 |
| 8 | **O6** | 0.881 | 0.250 | 0.493 | 3.521 | 9.03 | 9.39 | 8.06 | 11 | 52.71 |
| 9 | **O11** | 0.877 | 0.759 | 0.493 | 3.592 | 5.30 | 5.61 | 5.18 | 6 | 113.26 |
| 10 | **O3** | 0.955 | 0.574 | 0.331 | 3.687 | 6.73 | 7.32 | 6.41 | 7 | 62.27 |
| 11 | **O8** | 0.530 | 0.274 | 0.246 | 4.015 | 5.53 | 6.56 | 4.48 | 6 | 41.41 |
| 12 | **O7** | 0.992 | 0.319 | 0.369 | 4.019 | 0.79 | 0.94 | 0.74 | 4 | 35.72 |
| 13 | **O1** | 0.873 | 0.372 | 0.243 | 4.274 | 1.64 | 2.07 | 1.22 | 6 | 31.56 |
| 14 | **O8** | 0.470 | 0.774 | 0.254 | 4.340 | 0.05 | 0.06 | 0.04 | 3 | 100.10 |
| 15 | **O9** | 0.435 | 0.506 | 0.204 | 4.399 | 2.03 | 2.64 | 1.53 | 6 | 70.89 |
| 16 | **O14** | 0.923 | 0.629 | 0.616 | 4.442 | 0.25 | 0.33 | 0.18 | 3 | 109.82 |

**Table 4S.**

## Calculations VDP for atoms Bi and Cs in $Cs_3SrBi(P_2O_7)_2$.

***Central atom: Bi1*** *0.231 0.352 0.746 Rsd:1.487*

**D(CP):** 0.529 ( 0.2821 0.3661 0.7359 ); **D(VDP):** 0.232 ( 0.2544 0.3589 0.7464 );

**Atom:** 2.213 < r < 3.869 <r>=2.933; **Top:** 1.719 < R < 2.257 <R>=1.958; **CN** = 8:0:4;

**NV** = 20; **V** = 13.771/39.842; **S** = 33.242; **Cpac** = 0.412; **Ccov** = 3.495; **G3** = 0.085976891;

**Face distribution:** {3/3 4/2 5/2 6/3 7/1 8/1}; **Vertex distribution:** {3/20}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O8** | 0.039 | 0.220 | 0.751 | 2.213 | 12.38 | 11.02 | 14.98 | 5 | 160.08 |
| 2 | **O9** | 0.057 | 0.493 | 0.710 | 2.218 | 15.50 | 13.83 | 16.75 | 6 | 123.57 |
| 3 | **O4** | 0.231 | 0.269 | 0.622 | 2.324 | 12.88 | 12.04 | 14.50 | 6 | 98.83 |
| 4 | **O13** | 0.183 | 0.362 | 0.876 | 2.353 | 16.27 | 15.40 | 16.28 | 6 | 96.29 |
| 5 | **O1** | 0.375 | 0.139 | 0.756 | 2.470 | 16.38 | 16.28 | 15.33 | 7 | 72.65 |
| 6 | **O2** | 0.371 | 0.582 | 0.769 | 2.613 | 14.99 | 15.76 | 13.77 | 5 | 43.02 |
| 7 | **O5** | 0.436 | 0.429 | 0.605 | 3.233 | 6.71 | 8.72 | 4.99 | 8 | 54.01 |
| 8 | **O14** | 0.083 | 0.121 | 0.880 | 3.542 | 0.09 | 0.13 | 0.06 | 3 | 120.62 |
| 9 | **O3** | 0.562 | 0.434 | 0.831 | 3.543 | 4.37 | 6.23 | 3.04 | 4 | 21.64 |
| 10 | **O7** | 0.486 | 0.178 | 0.626 | 3.603 | 0.21 | 0.31 | 0.15 | 4 | 61.93 |
| 11 | **O10** | 0.163 | 0.710 | 0.653 | 3.869 | 0.00 | 0.00 | 0.00 | 3 | 86.35 |

***Central atom: Cs1*** *0.114 0.491 0.499*

**Rsd:** 1.869; **D(CP):** 0.216 (0.1116 0.5091 0.4922); **D(VDP):** 0.027 (0.1167 0.4900 0.4988);

**Atom:** 3.003<r<4.984, <r> = 3.705; **Top:** 1.791<R<2.523, <R> = 2.197; **CN** = 16:0:7;

**NV** = 42; **V** = 27.358/117.390; **S** = 49.459; **Cpac** = 0.518; **Ccov** = 2.459; **G3** = 0.080492504;

**Face distribution:** {3/8 4/1 5/1 6/5 7/4 8/1 9/3}; **Vertex distribution:** {3/42}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O7** | -0.014 | 0.322 | 0.374 | 3.003 | 11.32 | 10.24 | 11.94 | 6 | 90.19 |
| 2 | **O14** | -0.083 | 0.621 | 0.620 | 3.086 | 9.68 | 9.00 | 10.50 | 6 | 148.88 |
| 3 | **O13** | 0.317 | 0.638 | 0.376 | 3.218 | 10.20 | 9.89 | 10.15 | 8 | 54.11 |
| 4 | **O6** | -0.122 | 0.248 | 0.497 | 3.223 | 11.10 | 10.78 | 10.48 | 9 | 113.65 |
| 5 | **O4** | 0.231 | 0.269 | 0.622 | 3.234 | 8.64 | 8.42 | 9.03 | 6 | 70.37 |
| 6 | **O6** | 0.378 | 0.252 | 0.503 | 3.384 | 9.41 | 9.59 | 8.61 | 7 | 29.08 |
| 7 | **O11** | -0.121 | 0.758 | 0.499 | 3.387 | 7.74 | 7.89 | 7.56 | 7 | 145.92 |
| 8 | **O10** | 0.163 | 0.710 | 0.653 | 3.465 | 6.25 | 6.52 | 6.28 | 9 | 105.96 |
| 9 | **O11** | 0.379 | 0.742 | 0.501 | 3.474 | 5.62 | 5.88 | 5.71 | 6 | 63.96 |
| 10 | **O3** | -0.062 | 0.566 | 0.331 | 3.475 | 6.24 | 6.54 | 6.15 | 9 | 105.69 |
| 11 | **O5** | 0.436 | 0.429 | 0.605 | 3.605 | 4.62 | 5.02 | 4.46 | 7 | 47.13 |
| 12 | **O12** | 0.172 | 0.838 | 0.426 | 3.621 | 3.91 | 4.27 | 3.88 | 7 | 92.99 |
| 13 | **O9** | 0.057 | 0.493 | 0.710 | 3.757 | 2.61 | 2.95 | 2.44 | 6 | 113.33 |
| 14 | **O2** | 0.129 | 0.418 | 0.269 | 4.124 | 0.56 | 0.69 | 0.43 | 5 | 69.80 |

***Central atom: Cs2*** *0.765 0.354 0.664*

**Rsd:** 1.895; **D(CP):** 0.284 (0.7835 0.3315 0.6671); **D(VDP):** 0.088 (0.7673 0.3466 0.6620);

**Atom:** 3.048<r<5.008, <r> = 3.885; **Top:** 1.961<R<2.584, <R> = 2.333; **CN** = 11:0:9;

**NV** = 36; **V** = 28.497/128.215; **S** = 51.515; **Cpac** = 0.520; **Ccov** = 2.537; **G3** = 0.081924722;

**Face distribution:** {3/6 4/2 5/3 6/4 7/2 8/1 9/1 12/1}; **Vertex distribution:** {3/36}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O14** | 0.917 | 0.621 | 0.620 | 3.048 | 8.83 | 8.11 | 10.23 | 6 | 115.10 |
| 2 | **O2** | 0.629 | 0.082 | 0.731 | 3.138 | 10.57 | 9.99 | 10.97 | 7 | 67.76 |
| 3 | **O9** | 1.057 | 0.493 | 0.710 | 3.159 | 9.14 | 8.70 | 9.47 | 9 | 102.70 |
| 4 | **O7** | 0.486 | 0.178 | 0.626 | 3.191 | 8.64 | 8.31 | 9.13 | 5 | 72.55 |
| 5 | **O8** | 1.039 | 0.220 | 0.751 | 3.261 | 10.09 | 9.92 | 9.93 | 8 | 71.17 |
| 6 | **O6** | 0.878 | 0.248 | 0.497 | 3.308 | 16.76 | 16.70 | 14.56 | 12 | 37.70 |
| 7 | **O5** | 0.436 | 0.429 | 0.605 | 3.340 | 8.07 | 8.12 | 8.28 | 6 | 106.82 |
| 8 | **O1** | 0.625 | 0.639 | 0.744 | 3.350 | 8.01 | 8.08 | 8.42 | 7 | 172.78 |
| 9 | **O12** | 0.672 | 0.662 | 0.574 | 3.482 | 5.49 | 5.76 | 5.58 | 5 | 122.76 |
| 10 | **O10** | 0.837 | 0.210 | 0.847 | 3.580 | 5.37 | 5.79 | 5.32 | 6 | 94.29 |
| 11 | **O3** | 0.562 | 0.434 | 0.831 | 3.587 | 6.84 | 7.39 | 6.62 | 6 | 137.43 |
| 12 | **O8** | 0.961 | 0.720 | 0.749 | 4.247 | 0.01 | 0.01 | 0.01 | 3 | 136.54 |
| 13 | **O4** | 1.231 | 0.269 | 0.622 | 4.524 | 0.42 | 0.57 | 0.31 | 3 | 59.19 |
| 14 | **O13** | 0.817 | -0.138 | 0.624 | 4.815 | 0.96 | 1.39 | 0.62 | 5 | 24.74 |

***Central atom: Cs3*** *0.601 0.499 0.427 Rsd:1.930*

**D(CP):** 0.487 ( 0.6327 0.4933 0.4054 ); **D(VDP):** 0.095 ( 0.6053 0.4914 0.4246 );

**Atom:** 2.989<r<5.008, <r> = 3.900; **Top:** 2.022<R<2.584, <R> = 2.324; **CN** = 12:0:9;

**NV** = 38; **V** = 30.104/133.938; **S** = 52.948; **Cpac** = 0.464; **Ccov** = 2.402; **G3** = 0.081806697;

**Face distribution:** {3/6 4/2 5/3 6/5 7/1 8/1 9/2 10/1}; **Vertex distribution:** {3/38}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O4** | 0.731 | 0.231 | 0.378 | 2.989 | 12.35 | 10.82 | 13.87 | 7 | 10.23 |
| 2 | **O12** | 0.672 | 0.662 | 0.574 | 3.098 | 11.25 | 10.21 | 12.24 | 6 | 134.58 |
| 3 | **O13** | 0.317 | 0.638 | 0.376 | 3.117 | 11.68 | 10.67 | 12.24 | 9 | 123.04 |
| 4 | **O10** | 0.663 | 0.790 | 0.347 | 3.185 | 11.09 | 10.36 | 11.83 | 9 | 115.60 |
| 5 | **O11** | 0.379 | 0.742 | 0.501 | 3.394 | 5.48 | 5.45 | 6.20 | 5 | 164.99 |
| 6 | **O6** | 0.378 | 0.252 | 0.503 | 3.442 | 10.69 | 10.78 | 10.09 | 6 | 82.00 |
| 7 | **O5** | 0.436 | 0.429 | 0.605 | 3.565 | 6.30 | 6.59 | 6.29 | 6 | 114.70 |
| 8 | **O3** | 0.938 | 0.566 | 0.331 | 3.652 | 7.88 | 8.44 | 7.46 | 8 | 65.88 |
| 9 | **O6** | 0.878 | 0.248 | 0.497 | 3.764 | 7.12 | 7.85 | 5.93 | 10 | 50.48 |
| 10 | **O11** | 0.879 | 0.758 | 0.499 | 3.825 | 3.82 | 4.28 | 3.48 | 5 | 113.95 |
| 11 | **O8** | 0.539 | 0.280 | 0.249 | 3.828 | 6.44 | 7.22 | 5.56 | 6 | 41.06 |
| 12 | **O7** | 0.986 | 0.322 | 0.374 | 4.108 | 0.56 | 0.67 | 0.49 | 4 | 38.67 |
| 13 | **O9** | 0.443 | 0.507 | 0.210 | 4.115 | 3.67 | 4.43 | 3.10 | 6 | 74.38 |
| 14 | **O8** | 0.461 | 0.780 | 0.251 | 4.329 | 0.03 | 0.04 | 0.03 | 3 | 107.00 |
| 15 | **O1** | 0.875 | 0.361 | 0.244 | 4.335 | 0.93 | 1.18 | 0.70 | 5 | 35.40 |

**Table 5S.**

## Calculations VDP for atoms Bi and Cs in $Cs_3PbBi(P_2O_7)_2$.

***Central atom: Bi1*** *0.232 0.356 0.743*

**Rsd:** 1.486; **D(CP):** 0.570 ( 0.2882 0.3724 0.7348 ); **D(VDP):** 0.247 ( 0.2559 0.3669 0.7421 );

**Atom:** 2.197<r<3.830, <r> = 2.944; **Top:** 1.738<R<2.343, <R> = 1.978; **CN** = 7:0:5;

**NV** = 20; **V** = 13.732/40.181; **S** = 33.424; **Cpac** = 0.404; **Ccov** = 3.922; **G3** = 0.087098949;

**Face distribution:** {3/3 4/2 5/2 6/3 7/1 8/1}; **Vertex distribution:** {3/20}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O8** | 0.046 | 0.220 | 0.748 | 2.197 | 12.07 | 10.75 | 14.97 | 5 | 167.19 |
| 2 | **O9** | 0.051 | 0.495 | 0.716 | 2.229 | 16.06 | 14.53 | 16.99 | 6 | 115.84 |
| 3 | **O4** | 0.233 | 0.281 | 0.618 | 2.318 | 13.48 | 12.68 | 14.94 | 6 | 93.79 |
| 4 | **O13** | 0.200 | 0.354 | 0.875 | 2.327 | 15.75 | 14.87 | 16.23 | 6 | 100.70 |
| 5 | **O1** | 0.372 | 0.149 | 0.755 | 2.417 | 16.34 | 16.02 | 15.58 | 7 | 81.61 |
| 6 | **O2** | 0.380 | 0.578 | 0.773 | 2.623 | 16.53 | 17.59 | 14.53 | 5 | 36.00 |
| 7 | **O5** | 0.440 | 0.434 | 0.600 | 3.275 | 6.57 | 8.73 | 4.74 | 8 | 46.57 |
| 8 | **O7** | 0.484 | 0.189 | 0.625 | 3.544 | 0.47 | 0.67 | 0.32 | 4 | 62.87 |
| 9 | **O14** | 0.093 | 0.118 | 0.877 | 3.549 | 0.00 | 0.00 | 0.00 | 3 | 130.33 |
| 10 | **O3** | 0.583 | 0.450 | 0.836 | 3.796 | 2.28 | 3.52 | 1.42 | 4 | 30.27 |
| 11 | **O10** | 0.152 | 0.708 | 0.654 | 3.830 | 0.26 | 0.41 | 0.15 | 3 | 77.69 |

***Central atom: Cs1*** *0.108 0.495 0.499*

**Rsd:** 1.873; **D(CP):**0.180 ( 0.1055 0.5121 0.4957 ); **D(VDP):** 0.041 ( 0.1121 0.4937 0.4984 );

**Atom:** 3.044<r<5.019, <r> = 3.712; **Top:** 1.804<R<2.538, <R> = 2.196; **CN** = 14:0:9;

**NV** = 42; **V** = 27.511/115.607; **S** = 49.603; **Cpac** = 0.537; **Ccov** = 2.489; **G3** = 0.080544502;

**Face distribution:** {3/9 6/6 7/4 8/1 9/3}; **Vertex distribution:** {3/42}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O7** | -0.016 | 0.311 | 0.375 | 3.044 | 10.38 | 9.49 | 11.08 | 6 | 95.97 |
| 2 | **O14** | -0.093 | 0.618 | 0.623 | 3.128 | 9.22 | 8.67 | 9.87 | 6 | 142.47 |
| 3 | **O4** | 0.233 | 0.281 | 0.618 | 3.166 | 9.59 | 9.12 | 10.14 | 6 | 67.25 |
| 4 | **O13** | 0.300 | 0.646 | 0.375 | 3.193 | 10.71 | 10.28 | 10.74 | 7 | 55.87 |
| 5 | **O6** | -0.117 | 0.243 | 0.501 | 3.237 | 10.86 | 10.56 | 10.29 | 9 | 117.13 |
| 6 | **O11** | -0.116 | 0.752 | 0.502 | 3.277 | 8.46 | 8.33 | 8.60 | 7 | 142.59 |
| 7 | **O3** | -0.083 | 0.550 | 0.336 | 3.421 | 6.85 | 7.05 | 6.82 | 9 | 112.77 |
| 8 | **O10** | 0.152 | 0.708 | 0.654 | 3.440 | 6.90 | 7.14 | 6.93 | 9 | 99.57 |
| 9 | **O6** | 0.383 | 0.257 | 0.499 | 3.474 | 8.58 | 8.95 | 7.65 | 8 | 30.08 |
| 10 | **O11** | 0.384 | 0.748 | 0.498 | 3.581 | 4.99 | 5.37 | 4.91 | 6 | 57.41 |
| 11 | **O5** | 0.440 | 0.434 | 0.600 | 3.645 | 4.51 | 4.94 | 4.26 | 7 | 39.59 |
| 12 | **O12** | 0.169 | 0.846 | 0.432 | 3.662 | 3.51 | 3.86 | 3.46 | 7 | 90.26 |
| 13 | **O9** | 0.051 | 0.495 | 0.716 | 3.843 | 2.04 | 2.36 | 1.88 | 6 | 108.38 |
| 14 | **O2** | 0.120 | 0.422 | 0.273 | 4.019 | 1.19 | 1.43 | 0.95 | 6 | 75.73 |

***Central atom: Cs2*** *0.763 0.350 0.667*

**Rsd:** 1.895; **D(CP):** 0.314 ( 0.7834 0.3245 0.6673 ); **D(VDP):** 0.074 ( 0.7644 0.3435 0.6650 );

**Atom:** 3.038<r<4.892, <r> = 3.902; **Top:** 1.962<R<2.604, <R> = 2.346; **CN** = 11:0:10;

**NV** = 38; **V** = 28.504/120.469; **S** = 51.653; **Cpac** = 0.515; **Ccov** = 2.594; **G3** = 0.081728861;

**Face distribution:** {3/9 5/4 6/2 7/1 8/1 9/3 13/1}; **Vertex distribution:** {3/38}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O14** | 0.907 | 0.618 | 0.623 | 3.038 | 9.07 | 8.32 | 10.52 | 5 | 119.33 |
| 2 | **O2** | 0.620 | 0.078 | 0.727 | 3.142 | 11.09 | 10.52 | 11.21 | 9 | 63.99 |
| 3 | **O7** | 0.484 | 0.189 | 0.625 | 3.148 | 9.07 | 8.62 | 9.67 | 5 | 68.86 |
| 4 | **O9** | 1.051 | 0.495 | 0.716 | 3.174 | 8.85 | 8.49 | 9.24 | 9 | 109.33 |
| 5 | **O8** | 1.046 | 0.220 | 0.748 | 3.276 | 9.78 | 9.67 | 9.65 | 9 | 74.56 |
| 6 | **O6** | 0.883 | 0.243 | 0.501 | 3.295 | 16.86 | 16.78 | 14.70 | 13 | 37.91 |
| 7 | **O5** | 0.440 | 0.434 | 0.600 | 3.362 | 8.02 | 8.14 | 8.09 | 7 | 102.02 |
| 8 | **O1** | 0.628 | 0.649 | 0.745 | 3.458 | 6.78 | 7.08 | 7.10 | 6 | 168.60 |
| 9 | **O10** | 0.848 | 0.208 | 0.846 | 3.522 | 5.76 | 6.13 | 5.94 | 6 | 94.89 |
| 10 | **O12** | 0.669 | 0.654 | 0.568 | 3.540 | 5.20 | 5.56 | 5.16 | 5 | 119.49 |
| 11 | **O3** | 0.583 | 0.450 | 0.836 | 3.543 | 8.11 | 8.67 | 7.76 | 8 | 139.28 |
| 12 | **O9** | 0.949 | -0.005 | 0.784 | 4.382 | 0.02 | 0.02 | 0.01 | 3 | 60.20 |
| 13 | **O4** | 1.233 | 0.281 | 0.618 | 4.567 | 0.26 | 0.36 | 0.20 | 3 | 65.08 |
| 14 | **O13** | 0.800 | -0.146 | 0.625 | 4.892 | 0.52 | 0.77 | 0.32 | 5 | 24.23 |

***Central atom: Cs3*** *0.597 0.497 0.418*

**Rsd:** 1.922; **D(CP):** 0.314 (0.6262 0.4880 0.4106); **D(VDP):** 0.073 (0.5979 0.4899 0.4171);

**Atom:** 3.061<r<5.019, <r> = 3.890; **Top:** 2.040<R<2.604, <R> = 2.330; **CN** = 13:0:7;

**NV** = 36; **V** = 29.729/127.466; **S** = 52.495; **Cpac** = 0.505; **Ccov** = 2.487; **G3** = 0.081318453;

**Face distribution:** {3/6 4/3 5/1 6/4 7/2 8/2 9/1 10/1}; **Vertex distribution:** {3/36}

| N | Atom | x | y | z | Dist. Å | SSeg. | VSeg. | SAng. | NV | Phi |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **O4** | 0.733 | 0.219 | 0.382 | 3.061 | 11.36 | 10.24 | 12.69 | 7 | 19.68 |
| 2 | **O12** | 0.669 | 0.654 | 0.568 | 3.115 | 11.60 | 10.63 | 12.31 | 6 | 126.70 |
| 3 | **O10** | 0.652 | 0.792 | 0.346 | 3.175 | 10.72 | 10.02 | 11.62 | 8 | 143.89 |
| 4 | **O13** | 0.300 | 0.646 | 0.375 | 3.242 | 10.69 | 10.20 | 10.87 | 8 | 118.73 |
| 5 | **O3** | 0.917 | 0.550 | 0.336 | 3.378 | 10.35 | 10.29 | 10.24 | 9 | 89.79 |
| 6 | **O6** | 0.383 | 0.257 | 0.499 | 3.404 | 11.07 | 11.09 | 10.45 | 6 | 56.55 |
| 7 | **O11** | 0.384 | 0.748 | 0.498 | 3.454 | 5.23 | 5.32 | 5.81 | 4 | 144.40 |
| 8 | **O5** | 0.440 | 0.434 | 0.600 | 3.568 | 6.20 | 6.51 | 6.08 | 6 | 90.87 |
| 9 | **O8** | 0.546 | 0.280 | 0.252 | 3.627 | 7.22 | 7.71 | 6.69 | 6 | 46.19 |
| 10 | **O9** | 0.449 | 0.505 | 0.216 | 3.804 | 5.76 | 6.45 | 5.27 | 7 | 84.30 |
| 11 | **O6** | 0.883 | 0.243 | 0.501 | 3.934 | 5.84 | 6.76 | 4.62 | 10 | 51.70 |
| 12 | **O11** | 0.884 | 0.752 | 0.502 | 3.956 | 2.57 | 2.99 | 2.28 | 5 | 127.85 |
| 13 | **O7** | 0.984 | 0.311 | 0.375 | 4.137 | 0.17 | 0.21 | 0.15 | 4 | 57.16 |
| 14 | **O1** | 0.872 | 0.351 | 0.245 | 4.224 | 0.71 | 0.88 | 0.58 | 4 | 59.65 |
| 15 | **O8** | 0.454 | 0.780 | 0.248 | 4.270 | 0.05 | 0.06 | 0.05 | 3 | 123.14 |

**Table 6S.**

**Experimental (obtained by X-ray structural analysis) and calculated (obtained after geometry optimization) lattice parameters of $Cs_3M^{II}Bi(P_2O_7)_2$ crystals.**

| Lattice constant/ UC volume | $Cs_3CaBi(P_2O_7)_2$ | | $Cs_3SrBi(P_2O_7)_2$ | | $Cs_3PbBi(P_2O_7)_2$ | |
|---|---|---|---|---|---|---|
| | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. |
| a, **Å** | 9.28730 | 9.46027 | 9.39780 | 9.60073 | 9.42430 | 9.72855 |
| b, **Å** | 9.42920 | 9.53013 | 9.62840 | 9.73125 | 9.72610 | 9.77751 |
| c, **Å** | 17.6162 | 18.0394 | 17.6552 | 18.0551 | 17.5291 | 18.1647 |
| V, **Å$^3$** | 1542.68 | 1626.39 | 1597.54 | 1686.83 | 1606.75 | 1727.85 |
| **$\Delta V^*$, %** | 5.4 | | 5.6 | | 7.5 | |

$^*\Delta V = ((V^{calc}-V^{exp})/ V^{exp})x100\%$

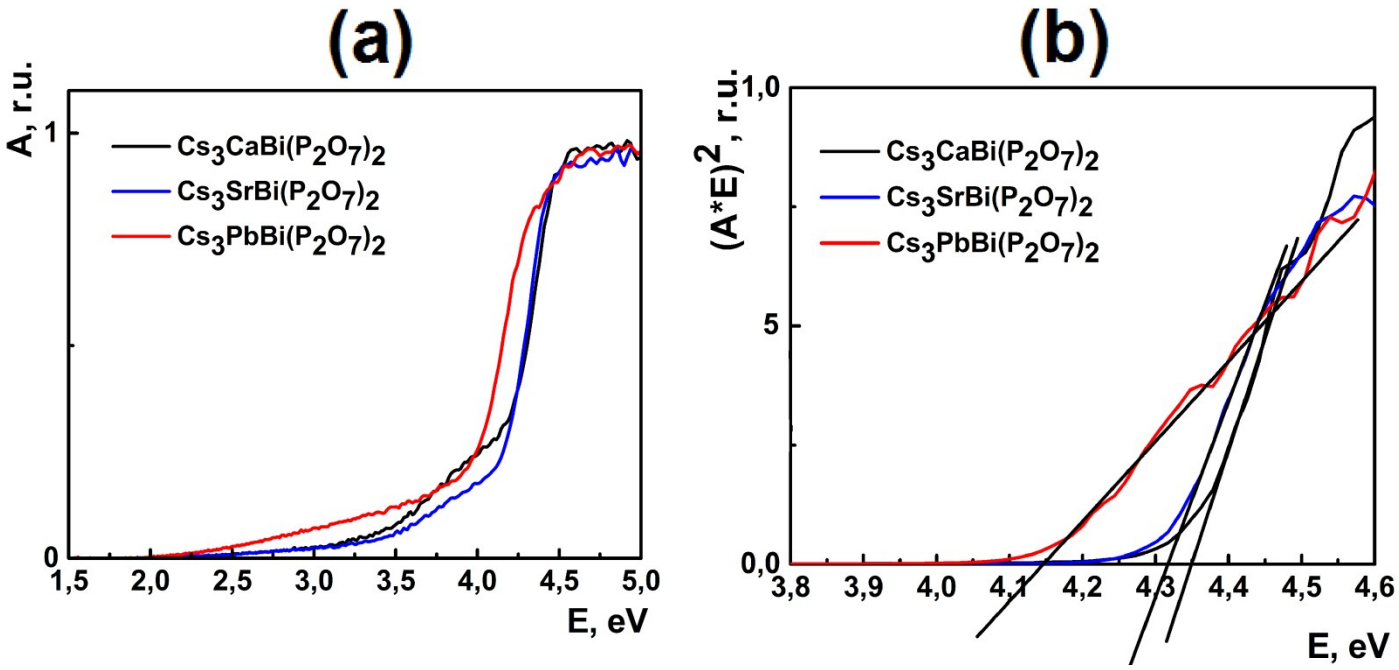


**Fig 3S.** UV-VIS absorbance spectra of $Cs_3M^{II}Bi(P_2O_7)_2$ crystals (a), and corresponding Tauc plots calculated for direct allowed transitions (b).