**Supplementary material**

(to the paper "Synthesis and cation distribution in the new bismuth oxyhalides with the Sillén – Aurivillius intergrowth structures" by D.O. Charkin, V.S. Akinfiev, A.M. Alekseeva, M. Batuk, A.M. Abakumov, and S.M. Kazakov)

**Table S1.** Atomic coordinates and displacement parameters for $Ba_2Bi_3Nb_2O_{11}I$, $Ca_{1.25}Sr_{0.75}Bi_3Nb_2O_{11}Cl$ and $BaCaBi_3Nb_2O_{11}Br$

| Atom | Site | $Ba_2Bi_3Nb_2O_{11}I$ | | | $Ca_{1.25}Sr_{0.75}Bi_3Nb_2O_{11}Cl$ | | | $BaCaBi_3Nb_2O_{11}Br$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *z* | Occupancy | $U_{iso}$, Å$^2$ | *z* | Occupancy | $U_{iso}$, Å$^2$ | *z* | Occupancy | $U_{iso}$, Å$^2$ |
| *A* | 1*a* (0 0 0) | 0 | 0.93(1) Ba<br>0.07(1) Bi | 0.0421(7) | 0 | 0.596(7) Ca<br>0.404(7) Sr | 0.0187(9) | 0 | 1 Ca | 0.028(6) |
| *M*1 | 2*g* (0 0 *z*) | 0.2355(1)<br>0.2666(1) | 0.56(1) Ba<br>0.44(1) Bi | 0.035(1)<br>0.0395(8) | 0.26368(5) | 0.645(2) Bi<br>0.355(2) Ca | 0.0239(3) | 0.237(2)<br>0.264(1) | 0.50(1) Ba<br>0.50(1) Bi | 0.013(7)<br>0.022(3) |
| *M*2 | 2*h* (½ ½ *z*) | 0.3818(1) | 1 Bi | 0.0374(3) | 0.39413(4) | 0.878(3) Bi<br>0.122(3) Sr | 0.0145(3) | 0.3893(1) | 1 Bi | 0.013(2) |
| Nb | 2*h* (½ ½ *z*) | 0.1131(1) | 1 Nb | 0.0324(6) | 0.11221(7) | 1 Nb | 0.0098(4) | 0.1090(2) | 1 Nb | 0.003(1) |
| X | 1*b* (0 0 ½) | ½ | 1 I | 0.0429(7) | ½ | 1 Cl | 0.031(2) | ½ | 1 Br | 0.020(2) |
| O1 | 1*c* (½ ½ 0) | 0 | 1 O | 0.024(4) | 0 | 1 O | 0.037(4) | 0 | 1 O | 0.042(7) |
| O2 | 8*s* (0*xz*) | 0.1052(4)[1] | 1 O | 0.030(2) | *x*= 0.601(1)<br>*z*= 0.1012(5) | 0.5 O | 0.033(3) | *x*= 0.599(1)<br>*z*= 0.104(1) | 0.5 O | 0.036(8) |
| O3 | 2*h* (½ ½ *z*) | 0.2074(5) | 1 O | 0.028(3) | 0.2175(4) | 1 O | 0.028(3) | 0.209(1) | 1 O | 0.027(7) |
| O4 | 4*i* (0 ½ *z*) | 0.3287(4) | 1 O | 0.042(2) | 0.3360(3) | 1 O | 0.014(2) | 0.330(1) | 1 O | 0.028(6) |

[1]Site 4*i* (0 ½ *z*)

**Table S2.** Selected interatomic distances (in Å) for $Ba_2Bi_3Nb_2O_{11}I$, $Ca_{1.25}Sr_{0.75}Bi_3Nb_2O_{11}Cl$ and $BaCaBi_3Nb_2O_{11}Br$

| | $Ba_2Bi_3Nb_2O_{11}I$ | $Ca_{1.25}Sr_{0.75}Bi_3Nb_2O_{11}Cl$ | $BaCaBi_3Nb_2O_{11}Br$ |
|---|---|---|---|
| *A*−8O2 | 2.822(1) | 2.432(7) | 2.51(3) |
| 4O1 | 2.851(7) | 2.7423(1) | 2.763(1) |
| *M*1–4O4 | Ba 2.664(6) Bi 2.322(5) | 2.352(4) | Ba 2.62(3) Bi 2.31(2) |
| 4O3 | Ba 2.875(4) Bi 3.038(4) | 2.871(2) | Ba 2.81(1) Bi 2.96(1) |
| *M*2−4O4 | 2.247(4) | 2.214(3) | 2.25(1) |
| 1O3 | 3.35(1) | 3.249(8) | 3.215(4) |
| 4*X* | 3.6246(6) | 3.3631(4) | 3.463(4) |
| Nb−1O3 | 1.83(1) | 1.935(8) | 1.88(2) |
| 4O2 | 2.0007(7) | 1.987(2) | 1.993(7) |
| 1O1 | 2.181(2) | 2.063(1) | 2.057(4) |

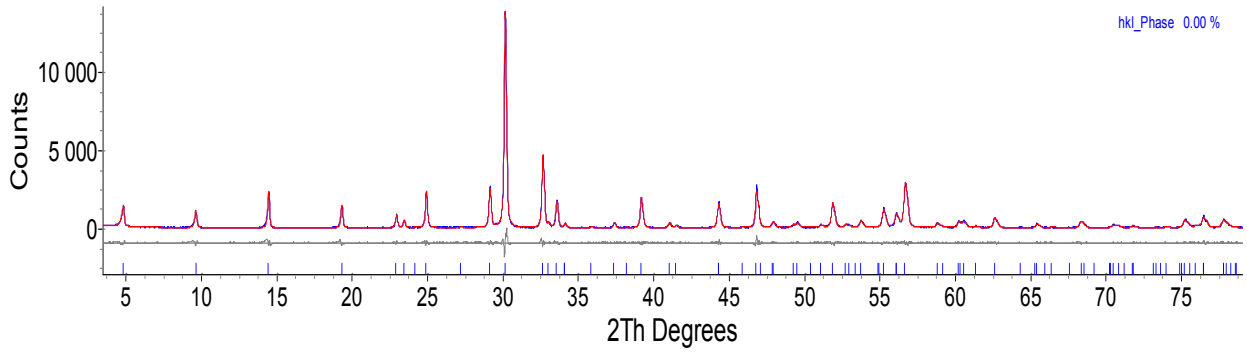
**Table S3.** Atomic coordinates and displacement parameters for $Sr_2Bi_3Nb_2O_{11}Cl$

| Atom | Site | *z* | Occupancy | $U_{iso}$, Å$^2$ |
|---|---|---|---|---|
| *A* | 1*a* (000) | 0 | 0.94(1) Sr<br>0.06(1) Bi | 0.011(1) |
| *M*1 | 2*g* (00*z*) | 0.2646(1) | 0.40(1) Sr<br>0.60(1) Bi | 0.032(1) |
| *M*2 | 2*h* (½½*z*) | 0.3949(1) | 0.13(1) Sr<br>0.87(1) Bi | 0.025(1) |
| Nb | 2*h* (½½*z*) | 0.1143(1) | 1 Nb | 0.011(1) |
| X | 1*b* (00½) | ½ | 1 Cl | 0.019(2) |
| O1 | 1*c* (½½0) | 0 | 1 O | 0.025 [1] |
| O2 | 8*s* (0*xz*) | *x* = 0.543(9)<br>*z* = 0.1070(4) | 1 O | 0.025 [1] |
| O3 | O3 (½½*z*) | 0.2104(8) | 1 O | 0.025 [1] |
| O4 | O4 (0½*z*) | 0.3357(5) | 1 O | 0.025 [1] |

[1] Not refined.

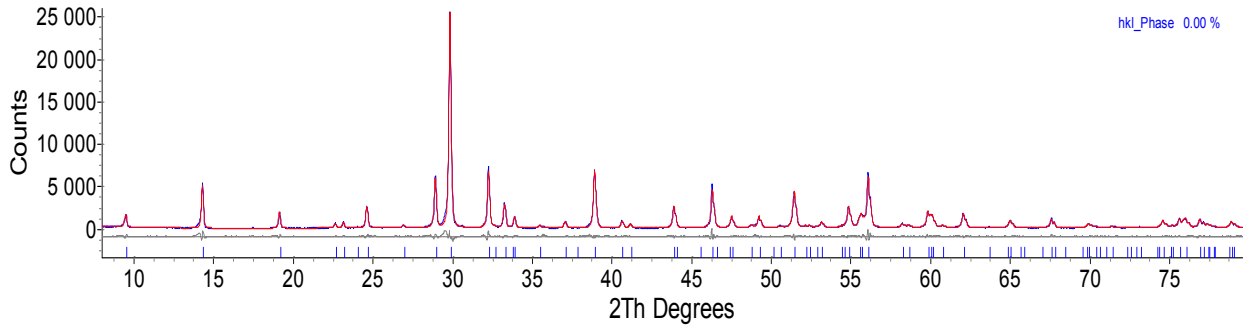
**$SrCaBi_3Nb_2O_{11}Cl$**

Space group *P*4/*nmm* (# 129), $Z = 2$, $a = 3.88007(6)$ Å, $c = 18.3983(4)$ Å; single phase sample.




**$Sr_2Bi_3Nb_2O_{11}Cl$**

Space group *P*4/*nmm* (# 129), $Z = 2$,$a = 3.91425(5)$ Å, $c = 18.4721(3)$ Å; single phase sample.




**$Sr_2Bi_3Nb_2O_{11}Br$**

Space group *P*4/*nmm* (# 129), $Z = 2$, $a = 3.92218(4)$Å, $c = 18.6618(2)$Å; 97.6(1) wt. % target phase, 2.4 (1) wt. % $SrBi_2Nb_2O_9$.

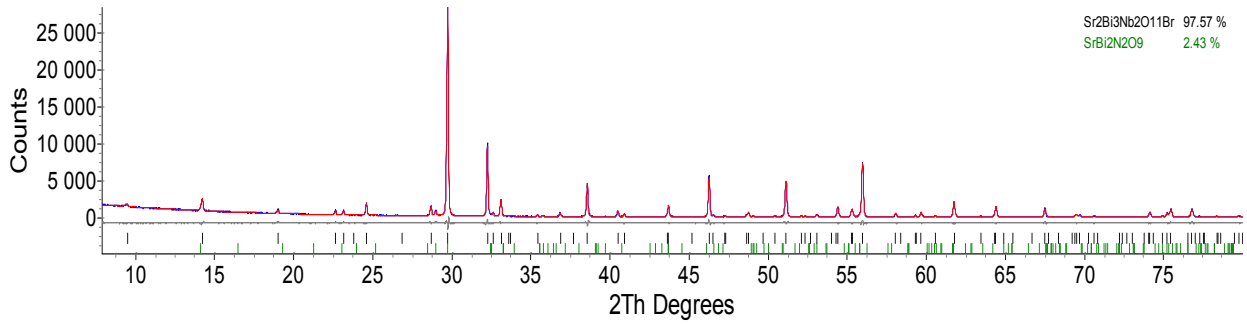



**Figure S1.** Typical LeBail fits for the $Me^1Me^2Bi_3Nb_2O_{11}X$ oxyhalides.

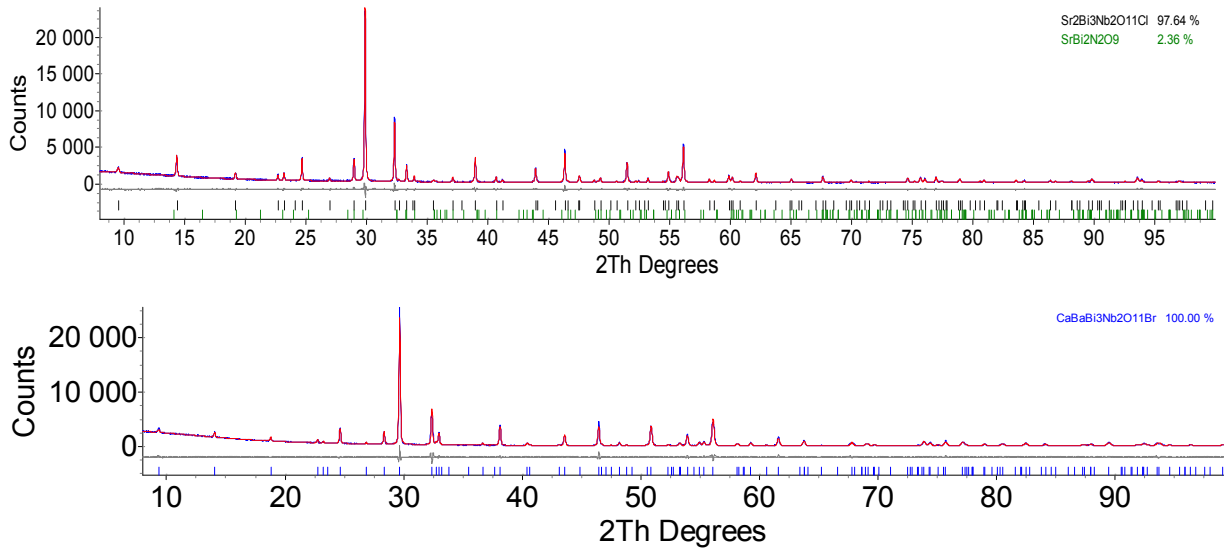



**Figure S2.** Experimental, calculated and difference PXRD profiles for $Sr_2Bi_3Nb_2O_{11}Cl$ (top) and $BaCaBi_3Nb_2O_{11}Br$ (bottom) for $2\theta < 100°$.

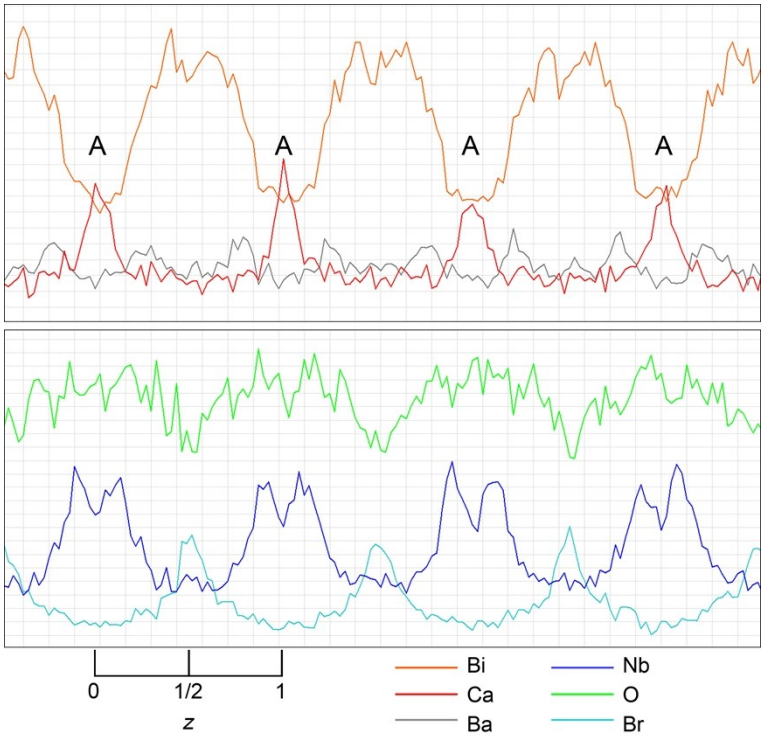



**Figure S3**. Elemental profiles for $BaCaBi_3Nb_2O_{11}Br$ measured along the *c* direction (the unit cell is outlined, the *A* positions are indicated).