Electronic Supplementary Information for

# Searching Better X-Ray and γ-Ray Photodetector: Structure-Composition Properties in the $TlPb_2Br_{5-x}I_x$ Quaternary System

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**Table S1.** Parameters of selected detector materials.

| Compound | Density, g/cm$^3$ | Band gap, eV | $\mu\tau_e$, cm$^2$/V | $\mu\tau_h$, cm$^2$/V |
|---|---|---|---|---|
| CZT | 5.78 | 1.57 | $4.5\cdot10^{-2}$ | $1\cdot10^{-4}$ |
| TlBr | 7.56 | 2.68 | $5\cdot10^{-3}$ | $1\cdot10^{-4}$ |
| $PbI_2$ | 6.2 | 2.32 | $8\cdot10^{-6}$ | $9\cdot10^{-7}$ |
| $HgI_2$ | 6.4 | 2.15 | $8\cdot10^{-4}$ | $3\cdot10^{-5}$ |
| $PbGa_2Se_4$ | 6.04 | 2.3 | $1\cdot10^{-6}$ | – |
| $TlGaSe_2$ | 6.4 | 1.93 | $6\cdot10^{-5}$ | $9.2\cdot10^{-6}$ |
| $Cs_2Hg_6S_7$ | 6.94 | 1.63 | $1.2\cdot10^{-3}$ | $1.0\cdot10^{-4}$ |
| $CsHgInS_3$ | 5.16 | 2.30 | $3.6\cdot10^{-5}$ | $2.9\cdot10^{-5}$ |
| $Tl_6SeI_4$ | 7.38 | 1.86 | $7\cdot10^{-3}$ | $6\cdot10^{-4}$ |
| $Tl_6SI_4$ | 7.25 | 2.03 | $2.1\cdot10^{-3}$ | $2.3\cdot10^{-5}$ |
| $CsPbCl_3$ | 4.24 | 2.86 | $1.0\cdot10^{-4}$ | $9.01\cdot10^{-5}$ |
| $CsPbBr_3$ | 4.86 | 2.25 | $1.7\cdot10^{-3}$ | $1.3\cdot10^{-3}$ |
| $Tl_4CdI_6$ | 6.88 | 2.83 | $6.05\cdot10^{-4}$ | $1.0\cdot10^{-4}$ |

**Table S2.** List of ternary and quaternary samples, used to study quasi-binary $TlPb_2Br_5$–‘ $TlPb_2I_5$’ phase diagram.

| Nominal composition | mol.% of $TlPb_2Br_5$ | mol.% of ‘$TlPb_2I_5$’ | Phase |
|---|---|---|---|
| $TlPb_2Br_5$ | 100 | 0 | Monoclinic $TlPb_2Br_5$ |
| $TlPb_2Br_{4.75}I_{0.25}$ | 95 | 5 | Monoclinic $TlPb_2Br_5$ |
| $TlPb_2Br_{4.5}I_{0.5}$ | 90 | 10 | Monoclinic $TlPb_2Br_5$ |
| $TlPb_2Br_4I$ | 80 | 20 | Two phases |
| $TlPb_2Br_{3.875}I_{1.125}$ | 77.5 | 22.5 | Two phases |
| $TlPb_2Br_{3.75}I_{1.25}$ | 75 | 25 | Tetragonal $TlPb_2BrI_4$ |
| $TlPb_2Br_{3.625}I_{1.375}$ | 72.5 | 27.5 | Tetragonal $TlPb_2BrI_4$ |
| $TlPb_2Br_{3.5}I_{1.5}$ | 70 | 30 | Tetragonal $TlPb_2BrI_4$ |
| $TlPb_2Br_{3.25}I_{1.75}$ | 65 | 35 | Tetragonal $TlPb_2BrI_4$ |
| $TlPb_2Br_3I_2$ | 60 | 40 | Tetragonal $TlPb_2BrI_4$ |
| $TlPb_2Br_{2.5}I_{2.5}$ | 50 | 50 | Tetragonal $TlPb_2BrI_4$ |
| $TlPb_2Br_2I_3$ | 40 | 60 | Tetragonal $TlPb_2BrI_4$ |
| $TlPb_2Br_{1.5}I_{3.5}$ | 30 | 70 | Tetragonal $TlPb_2BrI_4$ |
| $TlPb_2BrI_4$ | 20 | 80 | Tetragonal $TlPb_2BrI_4$ |
| $TlPb_2Br_{0.75}I_{4.25}$ | 15 | 85 | Tetragonal $TlPb_2BrI_4$ |
| $TlPb_2Br_{0.5}I_{4.5}$ | 10 | 90 | Tetragonal $TlPb_2BrI_4$ |
| $TlPb_2Br_{0.375}I_{4.625}$ | 7.5 | 92.5 | Three phases |
| $TlPb_2Br_{0.25}I_{4.75}$ | 5 | 95 | Three phases |
| $TlPb_2Br_{0.125}I_{4.875}$ | 2.5 | 97.5 | Three phases |
| $TlPb_2I_5$ | 0 | 100 | Two phases |

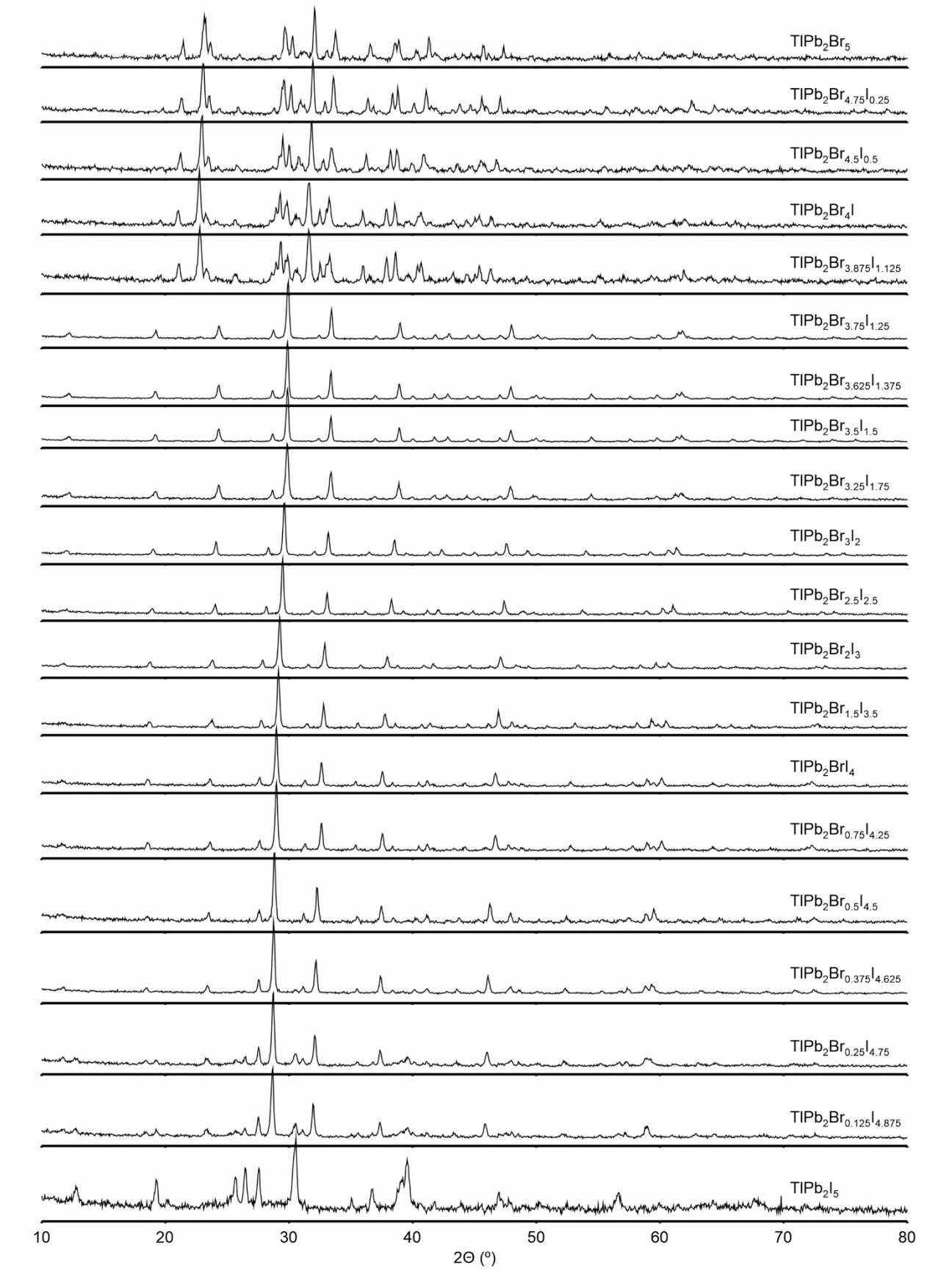


**Figure S1.** X-ray diffractograms of ternary and quaternary samples, used to study quasi-binary $TlPb_2Br_5$–‘ $TlPb_2I_5$’ phase diagram.

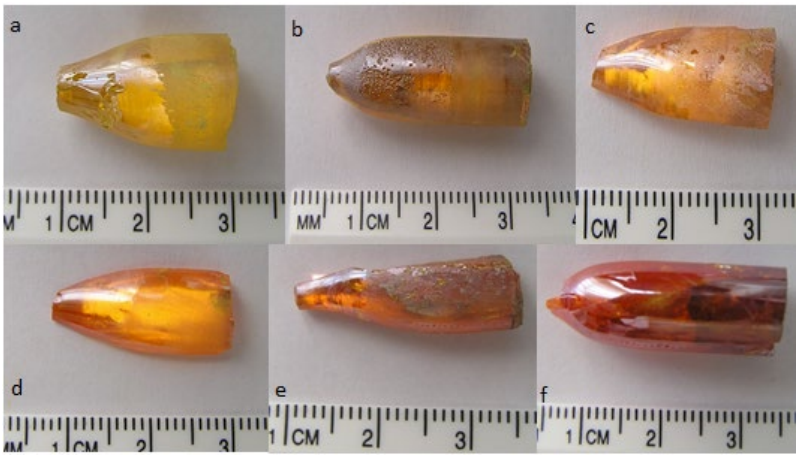


**Figure S2.** As-grown $TlPb_2Br_{5-x}I_x$ single crystals: a – $TlPb_2Br_3I_2$, b – $TlPb_2Br_{2.5}I_{2.5}$, c – $TlPb_2Br_2I_3$, d – $TlPb_2Br_{1.5}I_{3.5}$, e – $TlPb_2BrI_4$, f – $TlPb_2Br_{0.5}I_{4.5}$.

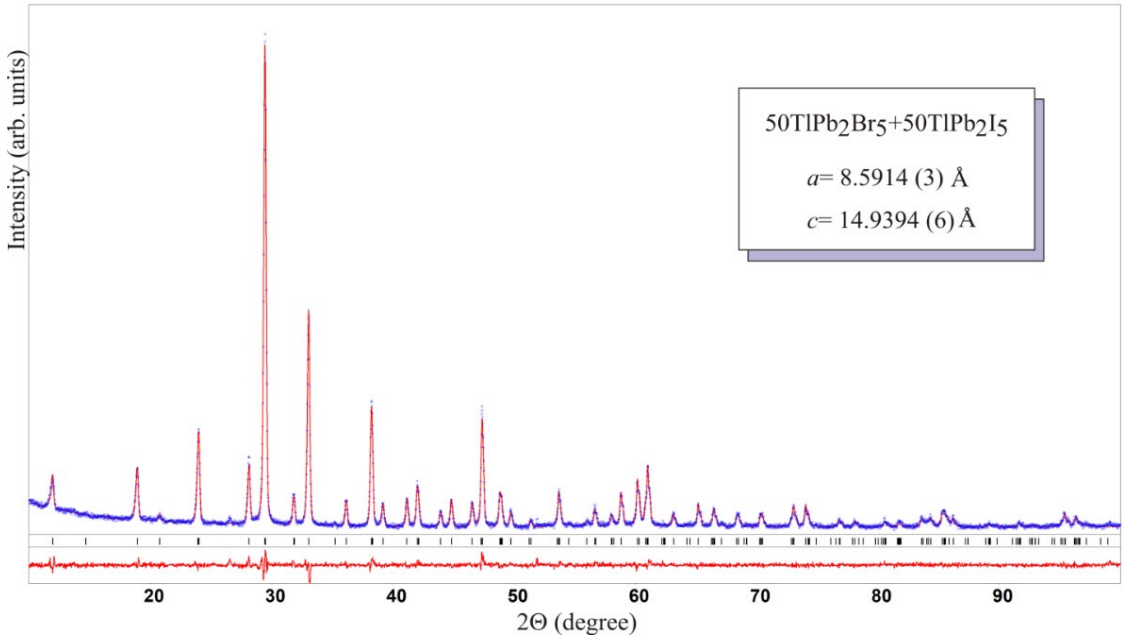


**Figure S3.** Experimental and calculated diffraction patterns for $TlPb_2Br_{2.5}I_{2.5}$ (i.e., 50 mol.% '$TlPb_2I_5$') and their difference.

**Table S3.** Coordinates and thermal displacement parameters of atoms in the $TlPb_2Br_{5-x}I_x$ (structure type $NH_4Pb_2Br_5$, space group I4/mcm)

| *Atom* | *Wyckoff site* | *x/a* | *y/b* | *z/c* | *B(is/eq)* |
|---|---|---|---|---|---|
| **$TlPb_2Br_{0.5}I_{4.5}$** (*a* = 8.80047(7)Å, *c* = 15.2176(1)Å), V=1178.58(2) Å$^3$, $R_p$ = 6.73, $R_{wp}$ = 8.67 | | | | | |
| Tl | 4*a* | 0 | 0 | ¼ | 1.38(8) |
| Pb | 8*h* | 0.16859(8) | x+1/2 | 0 | 1.08(4) |
| 0.50Br + 0.50I | 4*c* | 0 | 0 | 0 | 1.03(2) |
| I | 16*l* | 0.15264(7) | x+1/2 | 0.35877(8) | 1.19(7) |
| **$TlPb_2BrI_4$** (*a* = 8.68754(7) Å, *c* = 15.2518(1) Å), V=1151.10(1) Å$^3$, $R_p$ = 7.83, $R_{wp}$ = 10.90 | | | | | |
| Tl | 4*a* | 0 | 0 | ¼ | 3.59(7) |
| Pb | 8*h* | 0.16458(6) | x+1/2 | 0 | 1.38(4) |
| Br | 4*c* | 0 | 0 | 0 | 0.7(1) |
| I | 16*l* | 0.15660(6) | x+1/2 | 0.35815(6) | 1.09(4) |
| **$TlPb_2Br_{1.5}I_{3.5}$**(*a* = 8.65986(5) Å, *c* = 15.18378(9) Å), V=138.68(1) Å$^3$, $R_p$ = 7.54, $R_{wp}$ = 9.99 | | | | | |
| Tl | 4*a* | 0 | 0 | ¼ | 2.26(6) |
| Pb | 8*h* | 0.16396(5) | x+1/2 | 0 | 0.83(4) |
| Br | 4*c* | 0 | 0 | 0 | 1.06(3) |
| 0.12(2)Br + 0.88(2) I | 16*l* | 0.15794(6) | x+1/2 | 0.35853(6) | 1.15(6) |
| **$TlPb_2Br_2I_3$**(*a* = 8.62492(5) Å, *c* = 15.06791(9) Å), V=1102.13(1) Å$^3$, $R_p$ = 7.19, $R_{wp}$ = 9.59 | | | | | |
| Tl | 4*a* | 0 | 0 | ¼ | 2.71(5) |
| Pb | 8*h* | 0.16380(5) | x+1/2 | 0 | 1.55(4) |
| Br | 4*c* | 0 | 0 | 0 | 1.07(2) |
| 0.26(2) Br + 0.74(2) I | 16*l* | 0.15766(6) | x+1/2 | 0.35838(6) | 1.45(5) |
| **$TlPb_2Br_{2.5}I_{2.5}$**(*a* = 8.58906(5) Å, *c* = 14.9397(1) Å), V=1102.13(1) Å$^3$, $R_p$ =6.14, $R_{wp}$ = 7.89 | | | | | |
| Tl | 4*a* | 0 | 0 | ¼ | 2.96(5) |
| Pb | 8*h* | 0.16652(5) | x+1/2 | 0 | 1.25(3) |
| Br | 4*c* | 0 | 0 | 0 | 1.37(3) |
| 0.38(1) Br + 0.62(1)I | 16*l* | 0.15630(6) | x+1/2 | 0.3589(6) | 1.44(4) |
| **$TlPb_2Br_3I_2$** (*a* = 8.55483(8) Å, *c* = 14.8026(1) Å), V=1083.33(2) Å$^3$, $R_p$ = 8.60, $R_{wp}$ = 11.08 | | | | | |
| Tl | 4*a* | 0 | 0 | ¼ | 2.21(2) |
| Pb | 8*h* | 0.17238(9) | x+1/2 | 0 | 1.34(3) |
| Br | 4*c* | 0 | 0 | 0 | 1.02(5) |
| 0.51(2) Br + 0.49(2) I | 16*l* | 0.14782(8) | x+1/2 | 0.3577(1) | 1.38(6) |
| **$TlPb_2Br_{3.5}I_{1.5}$** (*a* = 8.51785(2) Å, *c* = 14.6573(1) Å), V=1063.44(1) Å$^3$, $R_p$ = 6.71, $R_{wp}$ = 8.62 | | | | | |
| Tl | 4*a* | 0 | 0 | ¼ | 2.41(3) |
| Pb | 8*h* | 0.16685(5) | x+1/2 | 0 | 0.98(4) |
| Br | 4*c* | 0 | 0 | 0 | 1.52(3) |
| 0.69(1) Br + 0.31(1) I | 16*l* | 0.15472(6) | x+1/2 | 0.35860(6) | 1.41(6) |

**Table S4.** Crystallographic data for the $TlPb_2BrI_4$ compound.

| Property | Characteritic |
|---|---|
| Space group | *I* 4/*m c m* (№ 140) |
| Unit cell dimensions | *a* = 8.7041(3) Å |
| | *c* = 15.2692(6) Å |
| Cell volume | 1156.8(2) Å$^3$ |
| Density, calculated | 6.9255(8) g/cm$^3$ |
| Pearson code | *tI*32 |
| Wyckoff sequence | *lhca* |
| Radiation and wavelength | CuKα, 1.54185 Å |
| Two-theta and sinT/l (max) | 100.02 and 0.497 |
| $R_I$ | 0.0581 |
| $R_P$ | 0.1459 |

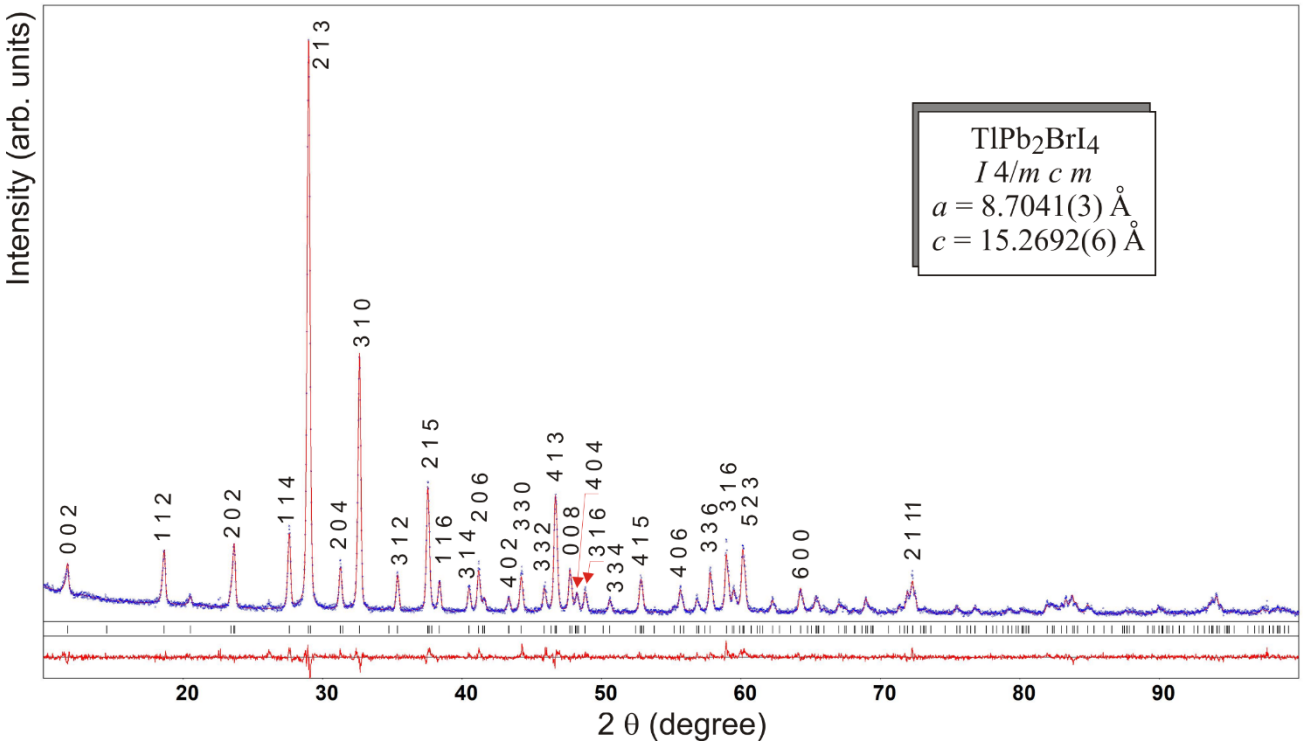


**Figure S4.** Experimental and theoretical diffraction patterns of the $TlPb_2BrI_4$ compound and their difference.

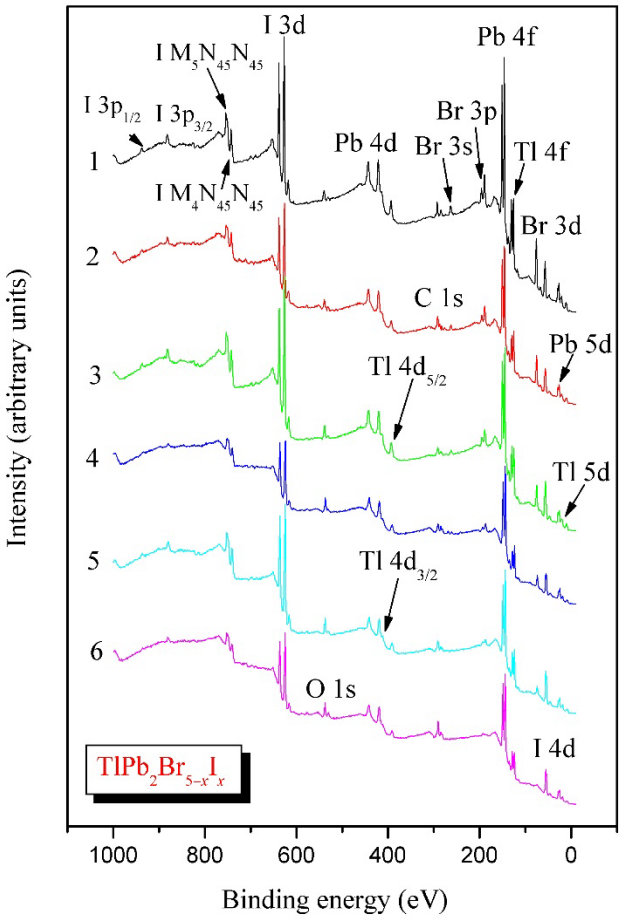


**Figure S5.** Survey XPS spectra measured for the $TlPb_2Br_{5-x}I_x$ solid solutions: 1 – $TlPb_2Br_3I_2$, 2 – $TlPb_2Br_{2.5}I_{2.5}$, 3 – $TlPb_2Br_2I_3$, 4 – $TlPb_2Br_{1.5}I_{3.5}$, 5 – $TlPb_2BrI_4$, 6 – $TlPb_2Br_{0.5}I_{4.5}$.