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Supporting Information

Local Structure Analysis and Structure Mining for Design of Photocatalytic Metal Oxychloride Intergrowths

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Table S1: Elemental composition of the samples obtained experimentally by SEM-EDS.

	Ta 0%	**Ta 25%**	**Ta 50%**	**Ta 75%**	**Ta 100%**
Bi/Cl	0.48	0.43	0.38	0.32	0.23
(Ideal ratios)	0.5	0.44	0.38	0.31	0.25
Ta/Gd	-	0.32	0.8	2.45	-
(Ideal ratios)	-	0.33	1	3	-

Table S2: Lattice parameters obtained from PDF refinement for Bi_4TaO_8Cl phase.

	Ta 0%	**Ta 25%**	**Ta 50%**	**Ta 75%**	**Ta 100%**
a (Å)	-	5.5285	5.4835	5.4513	5.4478
b (Å)	-	5.4526	5.4616	5.4986	5.4985
c (Å)	-	28.5241	28.6917	28.8018	28.8076
Volume ($Å^3$)	-	859.8504	859.2786	863.3201	862.9238

Table S3: Lattice parameters obtained from PDF refinement for Bi_2GdO_4Cl phase.

	Ta 0%	**Ta 25%**	**Ta 50%**	**Ta 75%**	**Ta 100%**
a=b (Å)	3.8812	3.8857	3.8913	3.8851	-
c (Å)	8.9509	8.9558	8.9614	8.9917	-
Volume ($Å^3$)	134.8338	135.2206	135.6955	135.7207	-

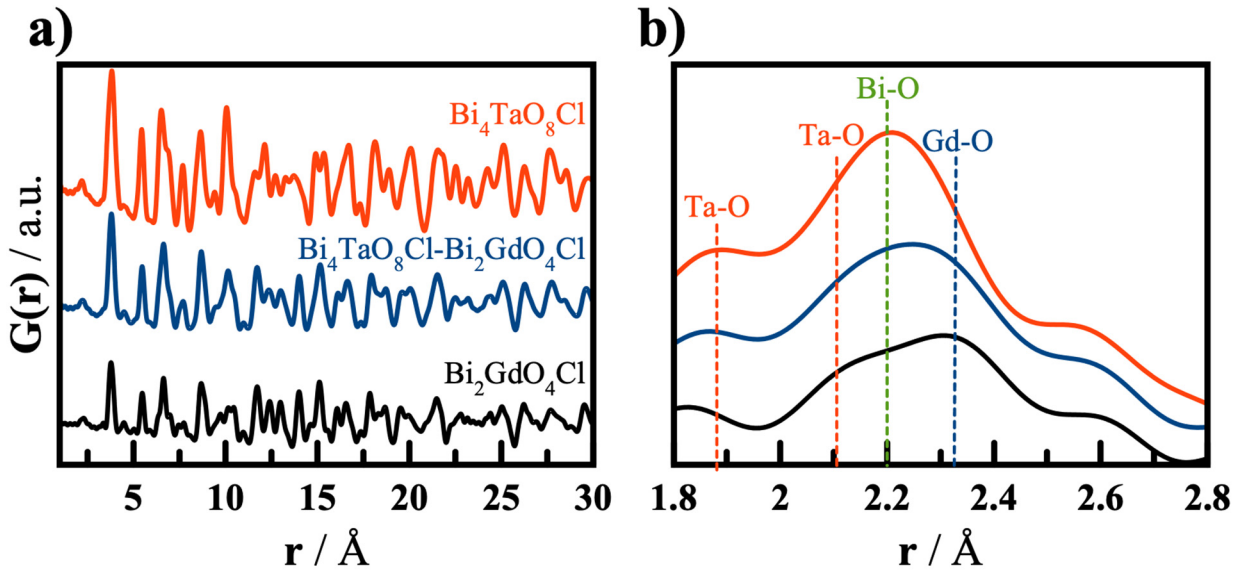

Figure S1: (a) PDFs of Ta 100% (red) and Ta 50% (blue) and Ta 0% (black) phases. (b) shows the local M-O environment of the parent phases, where both Ta-O, Gd-O and Bi-O can be observed.

Table S4: Refined atomic coordinates and isotropic thermal parameters of the pure Bi_2GdO_4Cl phase obtained from PDF refinements. Only the refined values are listed below. The atomic positions are constrained from the parent structure space group.

Atoms	**x**	**y**	**z**	**u_{11}**	**u_{22}**	**u_{33}**
Bi	-	-	0.2835	0.0079	0.0065	0.0097
Bi	-	-	0.7165	0.0079	0.0065	0.0097
Gd	-	-	-	0.0071	0.0071	0.0071
O	-	-	-	0.0161	0.0160	0.1229
Cl	-	-	-	0.0282	0.0282	0.0282

Table S5: Refined atomic coordinates and isotropic thermal parameters of the Ta 25% phase in the intergrown sample obtained from PDF refinements. Only the refined values are listed below. The atomic positions are constrained from the parent structure space group.

Atoms	**x**	**y**	**z**	**u_{11}**	**u_{22}**	**u_{33}**
Ta	0.0319	0.2407	0.7551	-0.0015	-0.0015	-0.0015
Ta	0.5319	0.7593	0.2449	-0.0015	-0.0015	-0.0015

Ta	0.5319	0.7407	0.7449	-0.0015	-0.0015	-0.0015
Ta	0.0319	0.2593	0.2551	-0.0015	-0.0015	-0.0015
Bi	0.0349	0.7041	0.6573	0.0021	0.0071	0.0015
Bi	0.5349	0.2959	0.3427	0.0021	0.0071	0.0015
Bi	0.5349	0.2041	0.8427	0.0021	0.0071	0.0015
Bi	0.0349	0.7959	0.1573	0.0021	0.0071	0.0015
Bi	0.0409	0.2394	0.9324	0.0021	0.0071	0.0015
Bi	0.5409	0.7606	0.0676	0.0021	0.0071	0.0015
Bi	0.5409	0.7394	0.5676	0.0021	0.0071	0.0015
Bi	0.0409	0.2606	0.4324	0.0021	0.0071	0.0015
Bi	0.0574	0.7270	0.8378	0.0021	0.0071	0.0015
Bi	0.5574	0.2729	0.1622	0.0021	0.0071	0.0015
Bi	0.5574	0.2270	0.6622	0.0021	0.0071	0.0015
Bi	0.0574	0.7729	0.3378	0.0021	0.0071	0.0015
Bi	0.0497	0.2295	0.5681	0.0021	0.0071	0.0015
Bi	0.5497	0.7706	0.4319	0.0021	0.0071	0.0015
Bi	0.5497	0.7295	0.9319	0.0021	0.0071	0.0015
Bi	0.0496	0.2706	0.0681	0.0021	0.0071	0.0015
Cl	-	-	-	0.2119	0.2119	0.2119
O	-	-	-	0.4655	0.8944	0.0133
Bi	-	-	0.2846	0.0079	0.0079	0.0125
Bi	-	-	0.7155	0.0079	0.0079	0.0125
Gd	-	-	-	0.0065	0.0065	0.0065
O	-	-	-	0.0459	0.0458	0.0708
Cl	-	-	-	0.0247	0.0247	0.0247

Table S6: Refined atomic coordinates and isotropic thermal parameters of the Ta 50% phase in the intergrown sample obtained from PDF refinements. Only the refined values are listed below. The atomic positions are constrained from the parent structure space group.

Atoms	x	y	z	u_{11}	u_{22}	u_{33}
Ta	-0.0075	0.2407	0.7551	0.0047	0.0047	0.0047
Ta	0.4925	0.7593	0.2449	0.0047	0.0047	0.0047
Ta	0.4925	0.7407	0.7449	0.0047	0.0047	0.0047
Ta	-0.0075	0.2593	0.2551	0.0047	0.0047	0.0047
Bi	0.0336	0.7122	0.6543	0.0044	0.0089	0.0081
Bi	0.5336	0.2878	0.3457	0.0044	0.0089	0.0081
Bi	0.5336	0.2123	0.8457	0.0044	0.0089	0.0081
Bi	0.0336	0.7878	0.1543	0.0044	0.0089	0.0081
Bi	0.0154	0.2487	0.9319	0.0044	0.0089	0.0081
Bi	0.5154	0.7513	0.0680	0.0044	0.0089	0.0081
Bi	0.5154	0.7487	0.5680	0.0044	0.0089	0.0081
Bi	0.0154	0.2513	0.4319	0.0044	0.0089	0.0081
Bi	0.0461	0.7303	0.8399	0.0044	0.0089	0.0081
Bi	0.5461	0.2697	0.1600	0.0044	0.0089	0.0081
Bi	0.5461	0.2303	0.6600	0.0044	0.0089	0.0081
Bi	0.0461	0.7697	0.3399	0.0044	0.0089	0.0081
Bi	0.0219	0.2323	0.5676	0.0044	0.0089	0.0081
Bi	0.5219	0.7677	0.4324	0.0044	0.0089	0.0081
Bi	0.5219	0.7323	0.9324	0.0044	0.0089	0.0081
Bi	0.0219	0.2677	0.0676	0.0044	0.0089	0.0081
Cl	-	-	-	0.0308	0.0308	0.0308
O	-	-	-	-0.0066	0.2090	0.0211
Bi	-	-	0.2851	0.0076	0.0077	0.0131
Bi	-	-	0.7145	0.0076	0.0077	0.0131

Gd	-	-	-	0.0067	0.0067	0.0067
O	-	-	-	0.0197	0.0863	0.1317
Cl	-	-	-	0.0247	0.0247	0.0247

Table S7: Refined atomic coordinates and isotropic thermal parameters of the Ta 75% phase in the intergrown sample obtained from PDF refinements. Only the refined values are listed below. The atomic positions are constrained from the parent structure space group.

Atoms	**x**	**y**	**z**	$\mathbf{u_{11}}$	$\mathbf{u_{22}}$	$\mathbf{u_{33}}$
Ta	0.0129	0.2556	0.7519	0.0043	0.0043	0.0043
Ta	0.5129	0.7444	0.2480	0.0043	0.0043	0.0043
Ta	0.5129	0.7556	0.7480	0.0043	0.0043	0.0043
Ta	0.0129	0.2444	0.2519	0.0043	0.0043	0.0043
Bi	0.0328	0.6941	0.6566	0.0070	0.0077	0.0101
Bi	0.5328	0.3059	0.3434	0.0070	0.0077	0.0101
Bi	0.5328	0.1941	0.8434	0.0070	0.0077	0.0101
Bi	0.0328	0.8059	0.1566	0.0070	0.0077	0.0101
Bi	0.0174	0.2421	0.9324	0.0070	0.0077	0.0101
Bi	0.5174	0.7579	0.0677	0.0070	0.0077	0.0101
Bi	0.5174	0.7421	0.5677	0.0070	0.0077	0.0101
Bi	0.0174	0.2579	0.4324	0.0070	0.0077	0.0101
Bi	0.0613	0.7237	0.8419	0.0070	0.0077	0.0101
Bi	0.5613	0.2763	0.1580	0.0070	0.0077	0.0101
Bi	0.5613	0.2237	0.6580	0.0070	0.0077	0.0101
Bi	0.0613	0.7763	0.3419	0.0070	0.0077	0.0101
Bi	0.0342	0.2449	0.5678	0.0070	0.0077	0.0101
Bi	0.5342	0.7551	0.4322	0.0070	0.0077	0.0101
Bi	0.5342	0.7449	0.9322	0.0070	0.0077	0.0101

Bi	0.0342	0.2551	0.0678	0.0070	0.0077	0.0101
Cl	-	-	-	0.0461	0.0461	0.0461
O	-	-	-	0.0036	0.2491	0.0052
Bi	-	-	0.2833	0.0082	0.0071	0.0099
Bi	-	-	0.7167	0.0082	0.0071	0.0099
Gd	-	-	-	0.0070	0.0070	0.0070
O	-	-	-	0.0974	0.0123	0.0644
Cl	-	-	-	0.0165	0.0165	0.0165

Table S8: Refined atomic coordinates and isotropic thermal parameters of the pure Bi_4TaO_8Cl phase obtained from PDF refinements. Only the refined values are listed below. The atomic positions are constrained from the parent structure space group.

Atoms	**x**	**y**	**z**	**u_{11}**	**u_{22}**	**u_{33}**
Ta	0.0223	0.2583	0.7527	0.0039	0.0039	0.0039
Ta	0.5223	0.7418	0.2473	0.0039	0.0039	0.0039
Ta	0.5223	0.7583	0.7473	0.0039	0.0039	0.0039
Ta	0.0223	0.2418	0.2527	0.0039	0.0039	0.0039
Bi	0.0318	0.6923	0.6566	0.0068	0.0078	0.0081
Bi	0.5318	0.3077	0.3435	0.0068	0.0078	0.0081
Bi	0.5318	0.1923	0.8435	0.0068	0.0078	0.0081
Bi	0.0318	0.8077	0.1566	0.0068	0.0078	0.0081
Bi	0.0287	0.2423	0.9323	0.0068	0.0078	0.0081
Bi	0.5287	0.7577	0.0676	0.0068	0.0078	0.0081
Bi	0.5287	0.7423	0.5677	0.0068	0.0078	0.0081
Bi	0.0287	0.2577	0.4323	0.0068	0.0078	0.0081
Bi	0.0702	0.7146	0.8408	0.0068	0.0078	0.0081
Bi	0.5703	0.2854	0.1592	0.0068	0.0078	0.0081
Bi	0.5703	0.2146	0.6592	0.0068	0.0078	0.0081

Bi	0.0702	0.7854	0.3408	0.0068	0.0078	0.0081
Bi	0.0413	0.2429	0.5670	0.0068	0.0078	0.0081
Bi	0.5413	0.7572	0.4329	0.0068	0.0078	0.0081
Bi	0.5413	0.7429	0.9329	0.0068	0.0078	0.0081
Bi	0.0413	0.2572	0.0670	0.0068	0.0078	0.0081
Cl	-	-	-	0.0255	0.0255	0.0255
O	-	-	-	0.0091	0.0412	0.0268

Table S9: Selected bond distances in the Ta 75%, Ta 50% and Ta 25% samples

	Ta 0%	**Ta 25%**	**Ta 50%**	**Ta 75%**	**Ta 100%**
a: Ta-O / Å	-	1.762	1.882	1.880	1.850
b: Ta-O / Å	-	2.199	2.091	2.093	2.123
c: Ta-Ta / Å	-	3.893	3.873	3.873	3.873
a': Gd-O / Å	2.396	2.398	2.401	3.401	-
b': Gd-Gd / Å	3.881	3.886	3.891	3.885	-

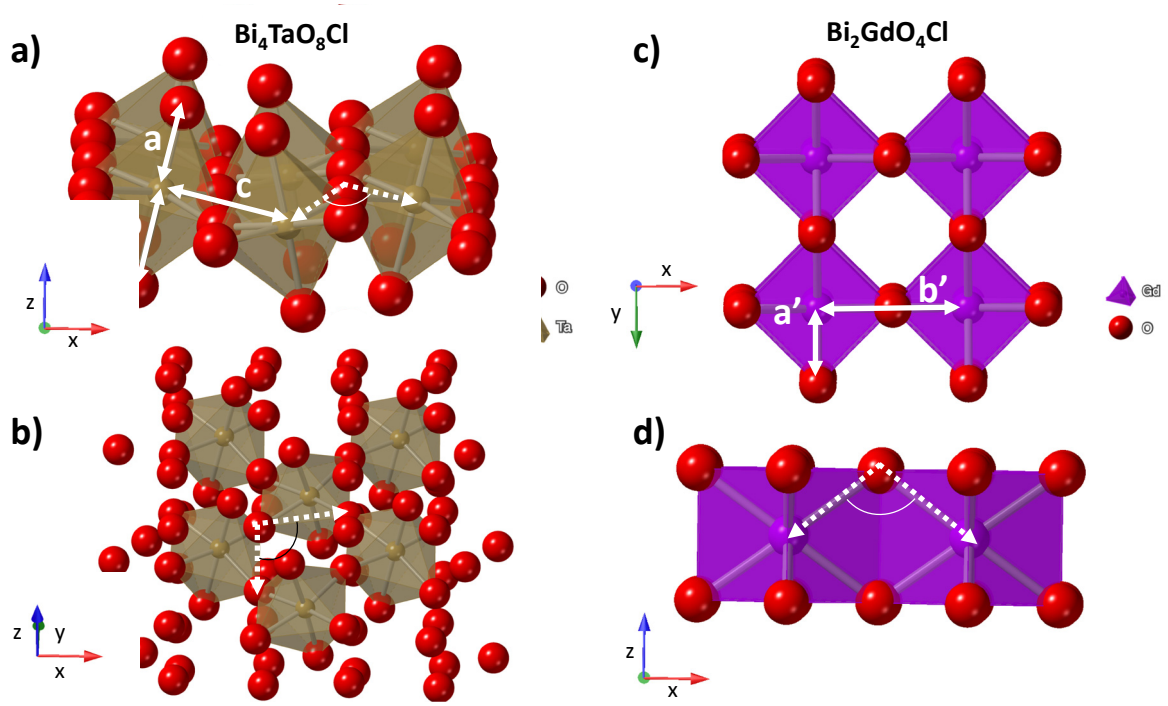

Figure S2: Bond distances and angles in (a-b) Bi_4TaO_8Cl and (c-d) Bi_2GdO_4Cl. (b) display the angle used to calculate the octahedral tilting in Bi_4TaO_8Cl.

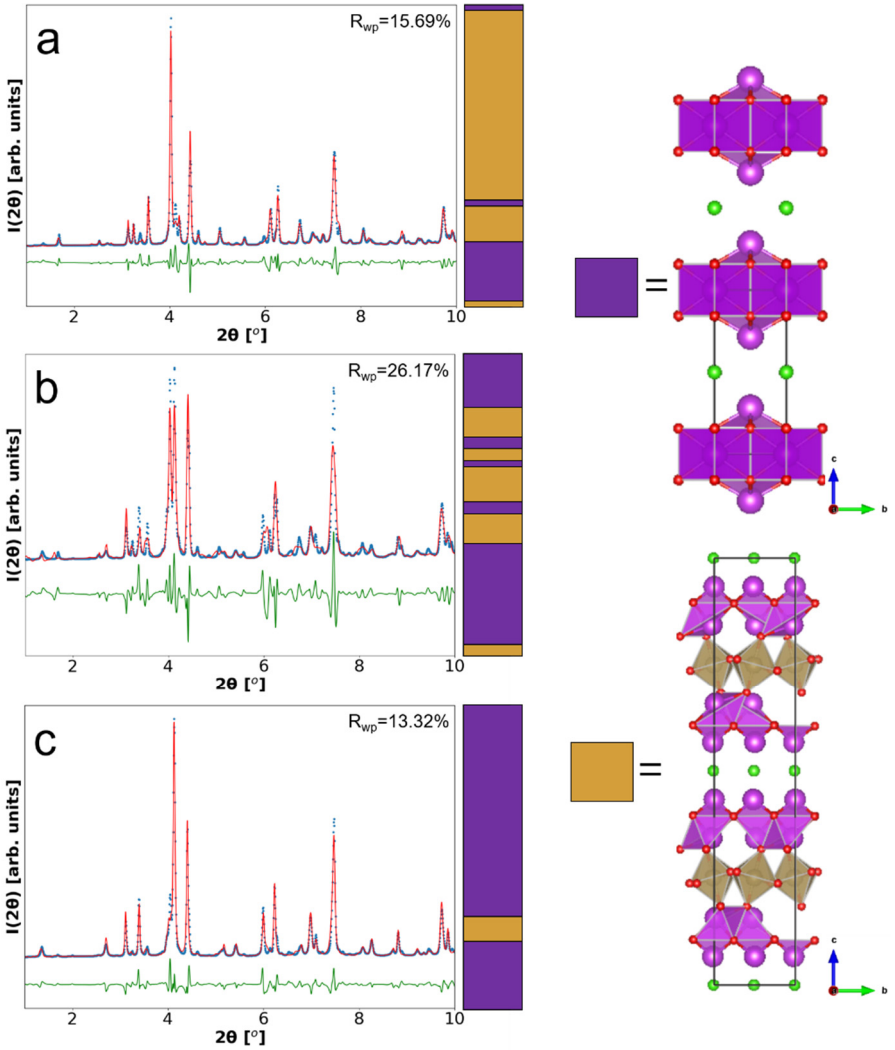

Figure S3: Rietveld refinement of the best fit for structure mining of Ta 75% (a), Ta 50% (b) and Ta 25% (c) with experimental data in dotted blue, refined model in red and difference curve in green. The structure of the corresponding superstructure is schematized on the right-side of the plot, with purple bocks corresponding to Gd-domains and brown ones to Ta-domains.

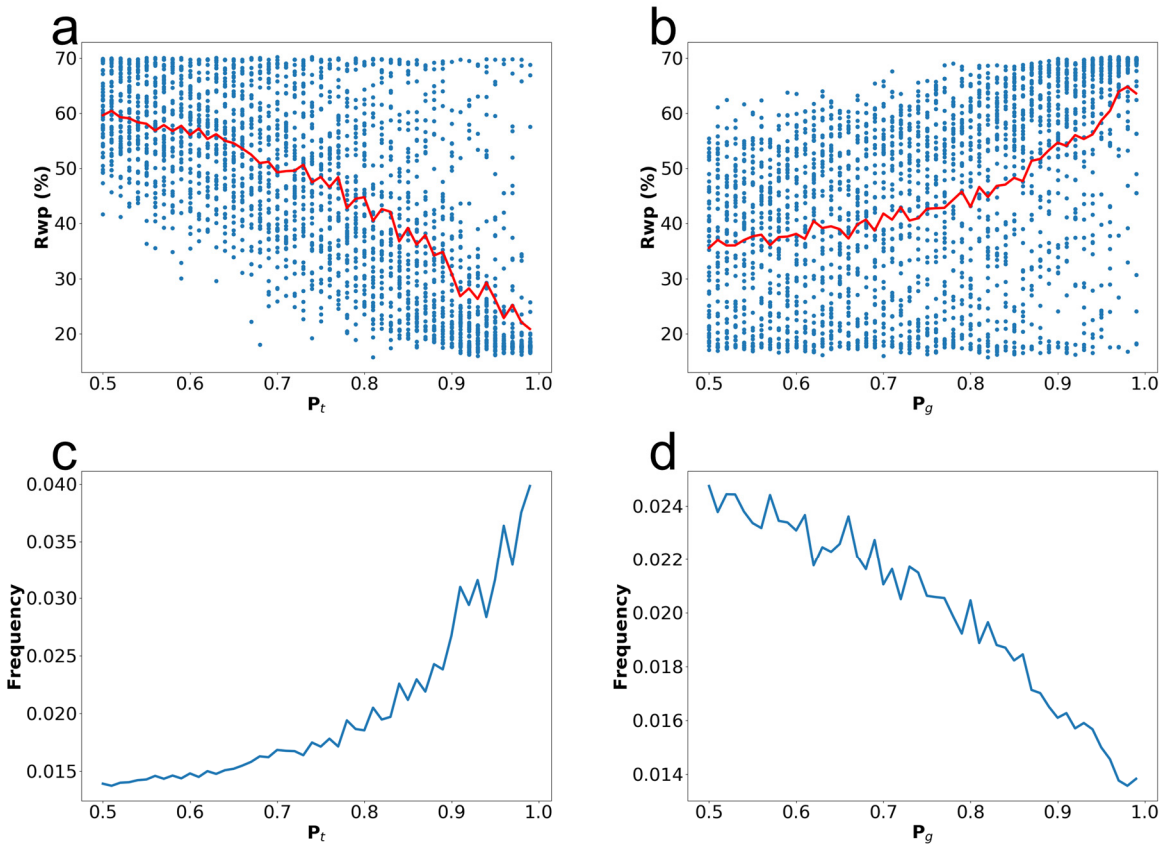

Figure S4: R_{wp} value of the Rietveld refinements of Ta 75% plotted as a function of the P_t (a) and P_g (b) values of each supercell. Probability distribution of the stacking probabilities P_t (c) and P_g (d).

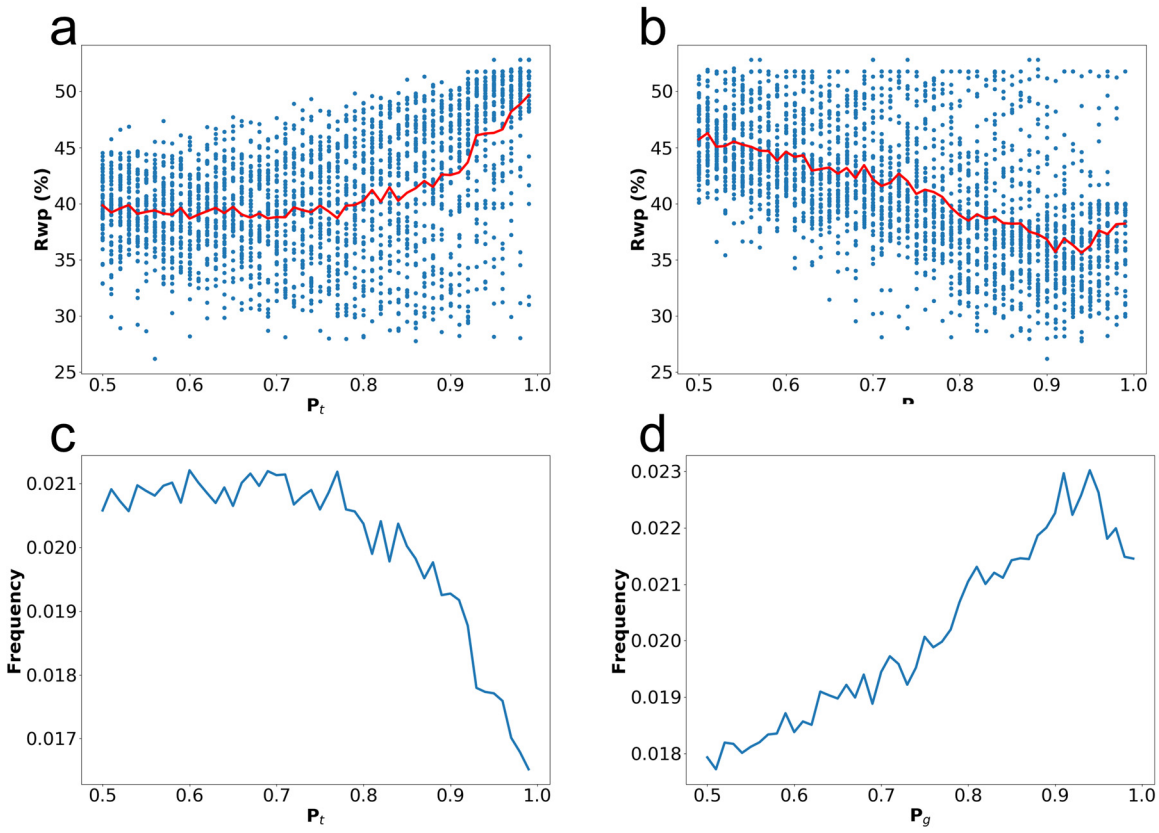

Figure S5: R_{wp} value of the Rietveld refinements of Ta 50% plotted as a function of the P_t (a) and P_g (b) values of each supercell. Probability distribution of the stacking probabilities P_t (c) and P_g (d).

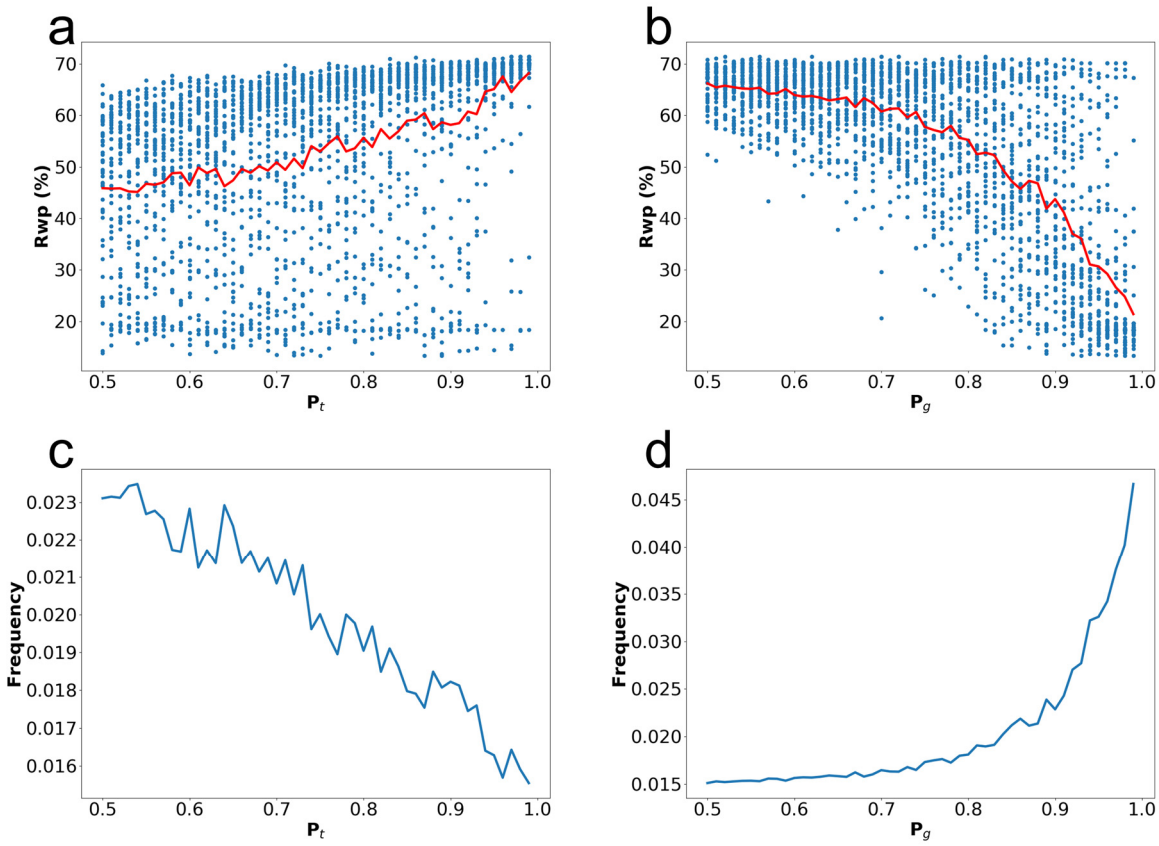

Figure S6: R_{wp} value of the Rietveld refinements of Ta 25% plotted as a function of the P_t (a) and P_g (b) values of each supercell. Probability distribution of the stacking probabilities P_t (c) and P_g (d).

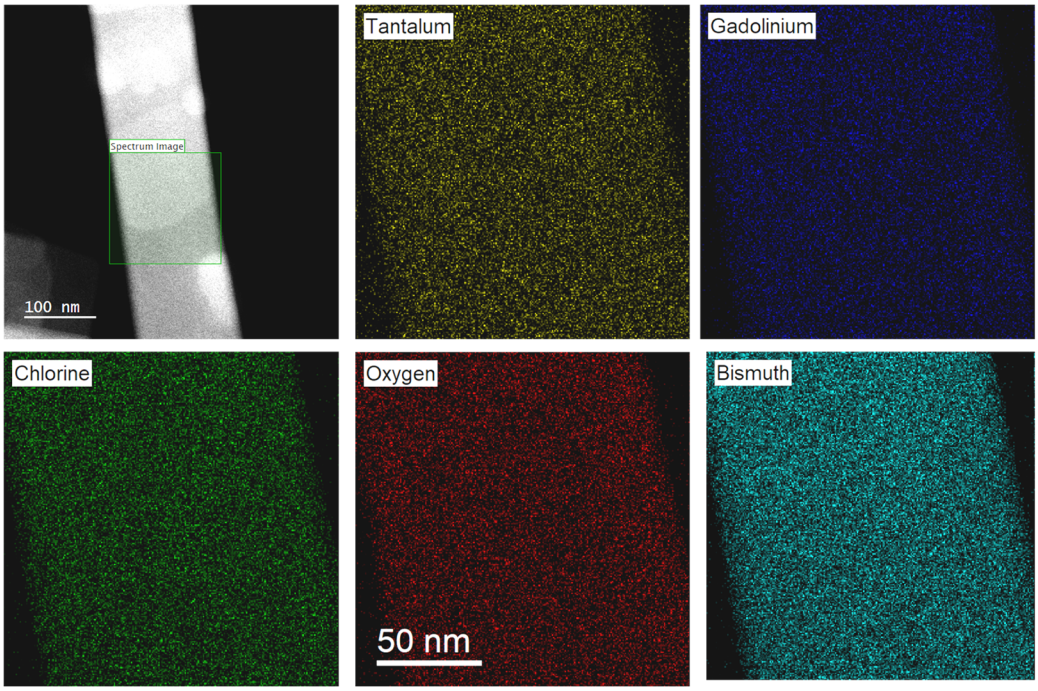

Figure S7: Scanning Transmission Electron Microscopy-Energy Dispersive X-ray Spectroscopy mapping of Ta 50% intergrowth.

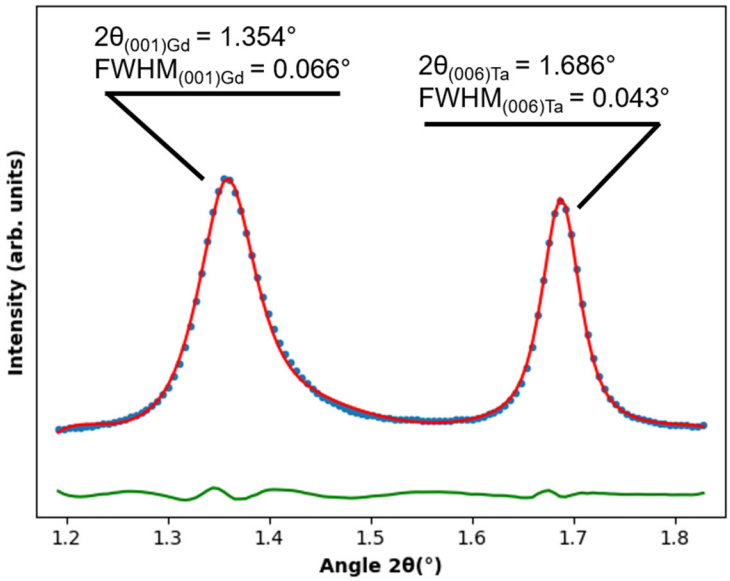

Figure S8: Example of fitting of Pseudo-Voigt functions on individual Bragg peaks for building the Williamson-Hall plots. Here the (001) peak of the Gd-phase and (006) peak of the Ta-phase in the XRD pattern of sample Ta 50% are shown as an example. The blue dots correspond to the experimental data, the red curve to the model and the green curve to the difference curve.

Table S10: R^2 factor from linear regression performed on each crystallographic plane families on the Williamson-Hall plots.

Sample	Ta-domain (00l)	Ta-domain (01l)	Ta-domain (11l)	Gd-domain (00l)	Gd-domain (01l)	Gd-domain (11l)
Ta 75%	0.663	0.040	0.228	0.746	0.611	0.928
Ta 50%	0.216	0.620	0.188	0.001	0.290	0.268
Ta 25%	0.317	0.692	0.017	0.076	0.835	0.139