Supplementary Information

Lone-Pair-Induced Structural Ordering in the Mixed-Valent oD Metal-Halides $Rb_{23}Bi^{III}_{x}Sb^{III}_{7-x}Sb^{V}_{2}Cl_{54}$ ($0 \le x \le 7$)

Bogdan M. Benin,[†,‡,#] Kyle M. McCall,[†,‡,#] Michael Wörle,[†] Dominique Borgeaud,[†] Thomas Vonderach,[†] Kostiantyn Sakhatskyi,[†,‡] Sergii Yakunin,[†,‡] Detlef Günther,[†] Maksym V. Kovalenko*[,†,‡]

[†]Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1, CH-8093 Zürich, Switzerland

[‡]Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

# - these authors contributed equally

Table S1. Reported resistivities for mixed-valent $A_4M^{III}M^{V}X_{12}$ materials.

Composition	*R (Ωcm)*	*Ref.*
$Rb_{23}Bi^{III}_{7}Sb^{V}_{2}Cl_{54}$	1.0×10^{10}	This work
$Cs_4Sb^{III}Sb^{V}Cl_{12}$	2.74×10^{11}	[5]
$Rb_4Sb^{III}Sb^{V}Cl_{12}$	3.3×10^{12}	[5]
$Cs_4Bi^{III}Sb^{V}Cl_{12}$	6.06×10^{14}	[5]
$Cs_4In^{III}Sb^{V}Cl_{12}$	1.06×10^{15}	[5]
$(NH_4)_4Sb^{III}Sb^{V}Br_{12}$	1×10^{7}	[6]

Note S1: Detailed description of ICPMS experiment.

All the preparation steps were done gravimetrically using a Mettler Toledo AT400 balance. The solid samples (approximately 100 mg) were transferred into PTFE digestion vials. A mixture of concentrated HNO_3 (1 mL), ultrapure HCl (3 mL) and Ho recovery standard (1 mL of 1 mg L^{-1} stock solution) was then added to all digestion vials including the digestion blanks. A microwave-assisted digestion was carried out using a turboWave (MLS GmbH, Germany) microwave system. The samples were digested while holding a temperature of 240 °C (1200 W) at 120 bar for 20 minutes (after ramp-up time). After cooling to room temperature, the clear and colourless solutions were transferred into TPP 50 mL centrifuge tubes and diluted to 50 mL using ultrapure water. The sample solutions were further diluted by a factor of $5x10^5$ using an aqueous solution of 1% HNO_3 and 1% HCl. A stock solution of Ir (internal standard) was added in order to obtain a concentration of 2 µg L^{-1} in every sample.

The analysis was carried out using a sector-field inductively coupled plasma mass spectrometer (Element XR, ThermoFisher, Bremen, Germany). The solutions were introduced using a micro concentric nebulizer (200 µL min^{-1}, borosilicate glass, glass expansion) combined with a cyclonic spray chamber (borosilicate glass, glass expansion), quartz injector, torch with guard electrode, sampler and skimmer made of nickel. A 1 µg L^{-1} tuning solution containing Rb, In, Sb and Bi was used to obtain maximum signal intensities and a flat-top peak shape. The oxide formation ratio for CeO/Ce and UO/U was estimated to be as low as 3% and 5%, respectively. Further instrumental parameters were adjusted as follows: a nebulizer gas flow of 1.06 L min^{-1}, a Plasma gas flow of 16 L min^{-1}, an auxiliary gas flow of 1 L min^{-1}, and a power of 1350 W. The faraday, analogue, and counting detector modes were cross-calibrated using the Faraday-Cross Calibration sequence provided by the manufacturer.

The isotopes ^{85}Rb, ^{115}In, ^{121}Sb, ^{165}Ho, ^{209}Bi were measured in the low resolution ($m/\Delta m = 300$) mode using the e-scan mode. 6 runs and 6 passes were performed yielding a total measurement time of approximately 2 min per sample.

An external calibration was carried out. Six calibration solutions were measured containing 0, 0.2, 0.5, 1.5, 2.5, and 4 µg L^{-1} of Rb ICP reference standard; 0, 0.2, 0.5, 1.0, 1.5, and 2 µg L^{-1} of In, Sb and Bi ICP reference standards; and 0, 10, 20, 40, 60, and 80 ng L^{-1} of Ho ICP reference standard. A linear regression was conducted to fit the calibration curves.

The limits of detection (LODs) for Rb, In, Sb and Bi were determined to be 19.5 ng L^{-1}, 2.4 ng L^{-1}, 12.7 ng L^{-1} and 0.7 ng L^{-1}, respectively. In order to validate the method and exclude any matrix effects, some samples

were spiked with Rb, In, Sb, Bi ICP reference standards. A spike consisting of approximately 100% of the original content of the corresponding analyte in the sample was added. Recoveries between 94 to 109%

Table S2. Crystal data and structure refinement for $Rb_{23}Sb_9Cl_{54}$ at 293(2) K.

Empirical formula	$Rb_{23}Sb_9Cl_{54}$
Formula weight	4975.86
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Cmcm*
Unit cell dimensions	a = 22.3435(7) Å, α = 90° b = 12.9057(4) Å, β = 90° c = 37.0625(13) Å, γ = 90°
Volume	10687.3(6) Å^3
Z	4
Density (calculated)	3.093 g/cm^3
Absorption coefficient	14.016 mm^{-1}
F(000)	8912
Crystal size	0.075 x 0.07 x 0.02 mm^3
\q range for data collection	1.648 to 27.102°
Index ranges	-28<=h<=28, -16<=k<=16, -47<=l<=44
Reflections collected	56777
Independent reflections	6429 [R_{int} = 0.0971]
Completeness to θ = 25.242°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6429 / 0 / 217
Goodness-of-fit	1.191
Final R indices [I > 2\s(I)]	R_{obs} = 0.1322, wR_{obs} = 0.3133
R indices [all data]	R_{all} = 0.1521, wR_{all} = 0.3279
Largest diff. peak and hole	5.088 and -1.183 e·Å^{-3}
Twin law BASF coefficient	0.242(4)
Twin law matrix	[0.5, 1.5, 0; 0.5, -0.5, 0; 0, 0, -1]

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.1570P)^2+473.2945P]$ where $P=(Fo^2+2Fc^2)/3$

Table S3. Atomic coordinates (x10⁴) and equivalent isotropic displacement parameters (Å²x10³) for $Rb_{23}Sb_9Cl_{54}$ at 293(2) K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}*
Sb(1)	5000	9977(2)	7500	1	37(1)
Sb(2)	3341(1)	5008(2)	7500	1	37(1)
Sb(3)	3324(1)	1653(2)	5800(1)	1	41(1)
Sb(4)	5000	6683(2)	5716(1)	1	46(1)
Rb(1)	5000	13788(3)	8146(1)	1	47(1)
Rb(2)	5000	10230(4)	8819(2)	1	69(2)
Rb(3)	5000	6665(5)	7500	1	64(2)
Rb(4)	1443(1)	3106(2)	6850(1)	1	48(1)
Rb(5)	3333(2)	1664(3)	6906(1)	1	58(1)
Rb(6)	3207(2)	4852(3)	6178(1)	1	72(1)
Rb(7)	1735(2)	3400(3)	5397(1)	1	75(1)
Rb(8)	5000	3166(4)	5481(2)	1	74(2)
Cl(1)	5000	11323(8)	7999(3)	1	70(3)
Cl(2)	5000	8559(7)	8064(3)	1	58(2)
Cl(3)	3809(4)	9898(7)	7500	1	52(2)
Cl(4)	4048(3)	5708(5)	8059(2)	1	55(2)
Cl(5)	2783(4)	6817(7)	7500	1	53(2)
Cl(6)	3986(4)	3279(7)	7500	1	52(2)
Cl(7)	2674(3)	4343(7)	7002(2)	1	67(2)
Cl(8)	2382(3)	2343(6)	6222(2)	1	60(2)
Cl(9)	4145(3)	2739(7)	6230(2)	1	67(2)
Cl(10)	3454(4)	-88(6)	6223(2)	1	64(2)
Cl(11)	2544(3)	794(6)	5412(2)	1	60(2)
Cl(12)	3280(4)	3229(6)	5403(3)	1	71(2)
Cl(13)	4147(3)	915(6)	5411(2)	1	58(2)
Cl(14)	4255(5)	5943(11)	5350(3)	1	103(4)
Cl(15)	5000	5205(11)	6072(4)	1	117(7)
Cl(16)	5751(5)	7444(10)	6072(3)	1	106(4)
Cl(17)	5000	8175(11)	5351(4)	1	106(6)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Anisotropic displacement parameters (Å²x10³) for $Rb_{23}Sb_9Cl_{54}$ at 293(2) K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(1)	39(2)	28(2)	45(2)	0	0	0
Sb(2)	38(1)	30(2)	42(2)	-2(1)	0	0
Sb(3)	38(1)	34(1)	49(1)	2(1)	2(1)	-2(1)
Sb(4)	47(2)	38(2)	54(2)	0	0	-3(2)
Rb(1)	41(2)	36(2)	65(2)	0	0	2(2)
Rb(2)	55(2)	84(3)	70(3)	0	0	-3(2)
Rb(3)	65(3)	50(3)	77(3)	0	0	0
Rb(4)	43(2)	41(2)	61(2)	4(1)	3(1)	2(2)
Rb(5)	60(2)	59(2)	55(2)	5(2)	-1(2)	1(2)
Rb(6)	83(2)	63(2)	68(2)	18(2)	-3(2)	1(2)
Rb(7)	73(2)	70(2)	82(2)	-12(2)	1(2)	-1(2)
Rb(8)	89(3)	68(3)	66(2)	0	0	-1(2)
Cl(1)	96(8)	42(5)	72(7)	0	0	-10(5)
Cl(2)	52(5)	39(5)	84(7)	0	0	7(4)
Cl(3)	27(4)	55(5)	73(6)	-3(3)	0	0

Cl(4)	43(3)	48(3)	75(4)	0(3)	-8(3)	-4(3)
Cl(5)	53(5)	41(4)	66(6)	-1(4)	0	0
Cl(6)	50(4)	39(4)	67(6)	2(4)	0	0
Cl(7)	57(4)	79(5)	66(4)	-23(4)	-6(3)	-10(4)
Cl(8)	42(3)	64(4)	74(5)	7(3)	4(3)	-10(4)
Cl(9)	65(4)	71(5)	64(4)	-22(4)	-5(3)	-4(4)
Cl(10)	78(4)	43(3)	73(5)	-2(3)	5(4)	13(3)
Cl(11)	55(4)	66(4)	60(4)	2(3)	-12(3)	-9(4)
Cl(12)	99(6)	45(4)	70(5)	10(4)	-3(4)	18(4)
Cl(13)	47(3)	64(4)	64(4)	1(3)	13(3)	-9(3)
Cl(14)	109(8)	119(9)	81(6)	-42(7)	-23(5)	-17(6)
Cl(15)	220(20)	53(7)	79(10)	0	0	17(7)
Cl(16)	88(7)	129(9)	100(7)	-45(7)	-22(5)	-9(7)
Cl(17)	194(19)	49(7)	76(9)	0	0	19(6)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

Table S5. Selected bond lengths [Å] for $Rb_{23}Sb_9Cl_{54}$ at 293(2) K with estimated standard deviations in parentheses.

Label	Distances
Sb(1)-Cl(1)	2.537(11)
Sb(1)-Cl(2)	2.777(11)
Sb(1)-Cl(3)	2.664(8)
Sb(2)-Cl(4)	2.757(7)
Sb(2)-Cl(5)	2.647(10)
Sb(2)-Cl(6)	2.656(9)
Sb(2)-Cl(7)	2.521(7)
Sb(3)-Cl(8)	2.769(7)
Sb(3)-Cl(9)	2.803(7)
Sb(3)-Cl(10)	2.755(8)
Sb(3)-Cl(11)	2.518(7)
Sb(3)-Cl(12)	2.512(8)
Sb(3)-Cl(13)	2.524(7)
Sb(4)-Cl(14)	2.349(9)
Sb(4)-Cl(15)	2.319(14)
Sb(4)-Cl(16)	2.350(9)
Sb(4)-Cl(17)	2.352(13)

Table S6. Results from ICP-MS.

Formula[1]	Expected			Measured					
	Rb mass%	Sb mass%	Bi mass%	Rb mass%	Std.	Sb mass%	Std.	Bi mass%	Std.
$RbSbCl_6$	20.4	28.9	-	20.5	0.4	27.23	0.11	<LOD[2]	-
$Rb_{23}Bi_{6.62}Sb_{2.38}Cl_{54}$	35.4	5.2	24.9	35.2	0.7	4.08	0.03	24.7	0.6
$Rb_{23}Bi_7Sb_2Cl_{54}$	35.2	4.36	26.2	36	0.6	4.113	0.023	25	0.5
$Rb_{23}Sb_9Cl_{54}$	39.5	22	-	40.4	0.8	21.31	0.09	< LOD[2]	-

[1]From single-crystal X-ray diffraction.
[2]Limit-of-detection for Bi = 0.02%.

Table S7. Octahedral antimony sites in $Rb_{23}Sb^{III}_7Sb^{V}_2Cl_{54}$ (*Cmcm*).

Site label	*Wyckoff site*	*% Sb*	*Average bond length, (Å)*	*Distortion index Δd*	*Effective Coord. #*	*Angle variance*	*Bond valence sum*	*Distortion*	*Valence*
Sb1	4c	100	2.660	0.031	5.650	13.683	2.692	Disphenoidal	III
Sb2	8g	100	2.644	0.031	5.660	14.430	2.804	Disphenoidal	III
Sb3	16h	100	2.647	0.049	5.393	4.532	2.856	Trigonal	III
Sb4	8f	100	2.345	0.004	5.995	0.786	5.310	Undistorted	V

Values for bond lengths, the bond length distortion index Δd, angle variance, bond valence sums, and the effective coordination numbers calculated using the Vesta3 crystallography software.[3]

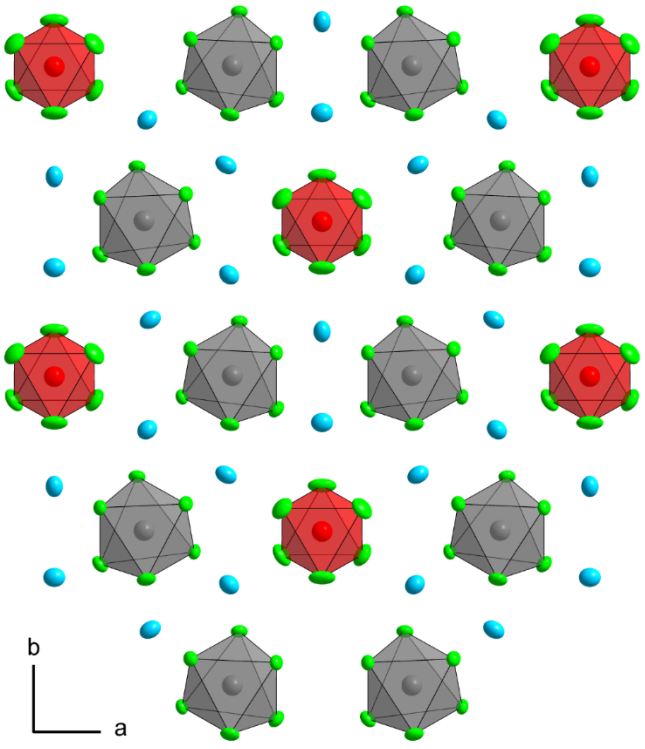

Figure S1. A view of the mixed-valent layer of $Rb_{23}Sb_9Cl_{54}$ along the c-axis.

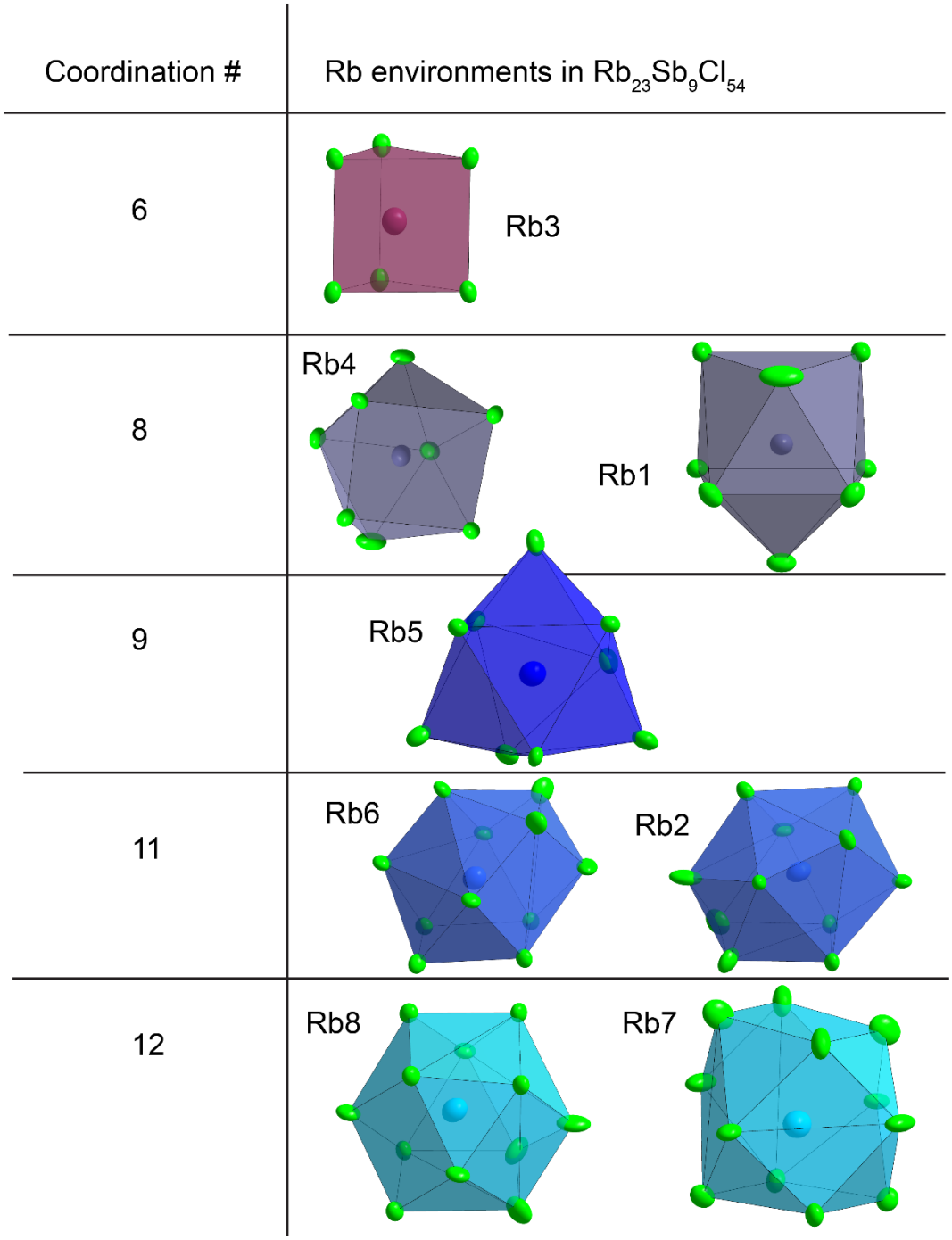

Figure S2. Rb^+ environments in $Rb_{23}Sb_9Cl_{54}$ colored differently according to coordination number. These colors are applied to the Rb environments in Figure S3.

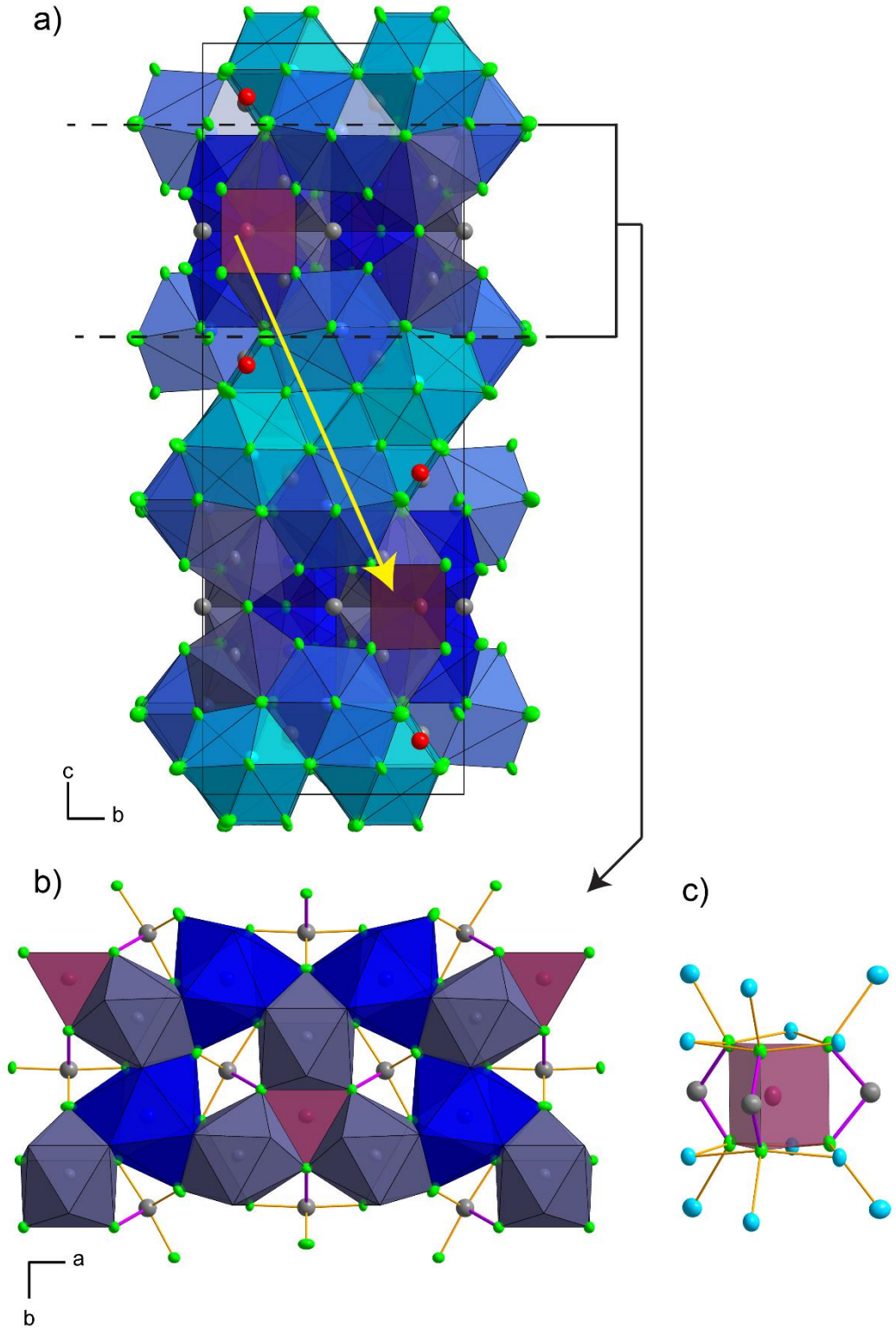

Figure S3. a) The unit cell of $Rb_{23}Sb_9Cl_{54}$ as viewed along the a-axis with Rb-polyhedra colored according to their coordination numbers (indicated in Figure S2). The yellow arrow demonstrates the structure directing effect of the 6-coordinate Rb cation (Rb3). b) A slab of the unit cell (indicated by bracket in subfigure a) viewed along the c-axis, with purple bonds pointing along the direction of the lone pair. c) The first and second coordination sphere of Rb3.

Table S8. Summary of $Rb_{23}Sb_9Cl_{54}$ Rb coordination environments.

Site label	*Wyckoff site*	*Avg. bond length (Å)*	*Min. (Å)*	*Max. (Å)*	*Distortion index Δd*	*Effective Coord. #*	*Coord. #*	*Coord. Lone Pairs*	*Slab location*
Rb1	8f	3.315	3.228	3.427	0.015	7.904	8	-	I-II space
Rb2	8f	3.682	3.350	4.062	0.057	9.032	11	-	
Rb3	4c	3.216	=	=	0.000	6.000	6	3 (slab II)	II cent
Rb4	16h	3.322	3.230	3.401	0.015	7.909	8	-	II edge
Rb5	16h	3.507	3.333	3.775	0.050	8.046	9	1 (slab I/III)	II edge
Rb6	16h	3.692	3.341	4.110	0.061	8.752	11	-	I edge
Rb7	16h	3.672	3.459	3.892	0.032	11.214	12	-	I-I' space
Rb8	8f	3.650	3.416	3.981	0.052	10.359	12	-	I-I' space

Values for bond lengths, the bond length distortion index Δd and the effective coordination numbers calculated using the Vesta3 crystallography software.[3]

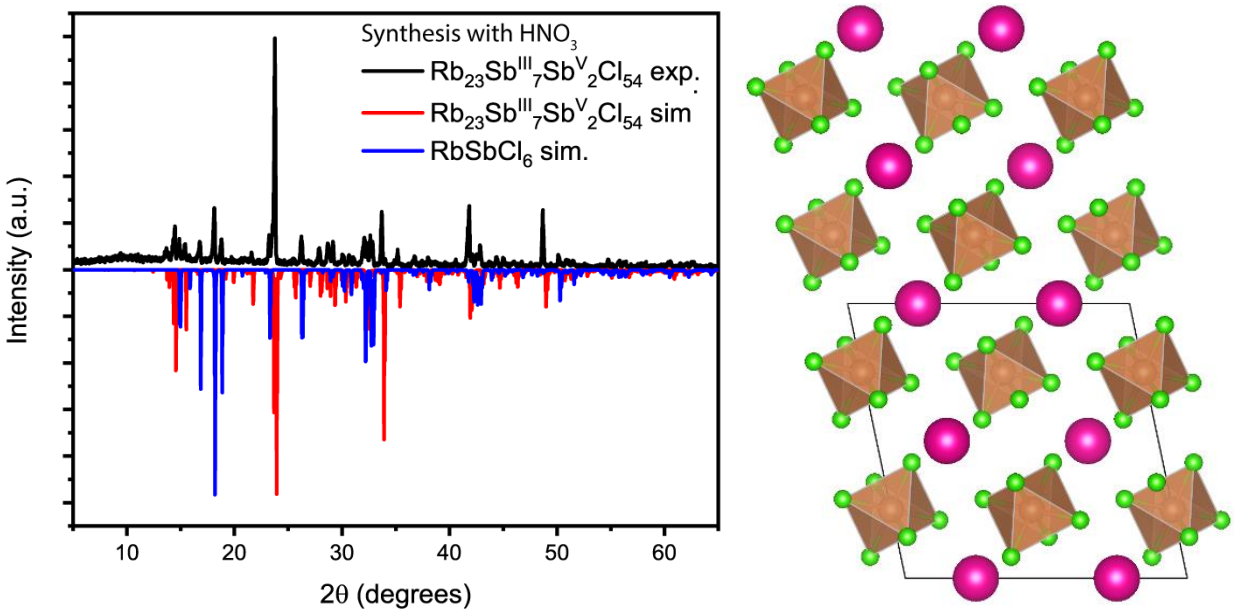

Figure S4. PXRD of material synthesized with HNO_3 as the oxidant; Crystal structure of $RbSbCl_6$.

Table S9. Crystal data and structure refinement for $RbSbCl_6$ at 293(2) K

Empirical formula	$RbSbCl_6$
Formula weight	419.92
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	a = 12.0736(4) Å, α = 90° b = 6.3321(2) Å, β = 101.905(3)° c = 12.1366(3) Å, γ = 90°
Volume	907.90(5) Å^3
Z	4
Density (calculated)	3.072 g/cm^3
Absorption coefficient	10.040 mm^{-1}
F(000)	760
Crystal size	0.291 x 0.212 x 0.103 mm^3
θ range for data collection	3.431 to 31.495°
Index ranges	-14<=h<=17, -9<=k<=6, -17<=l<=17
Reflections collected	5049
Independent reflections	1504 [R_{int} = 0.0275]
Completeness to θ = 25.242°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1504 / 0 / 39
Goodness-of-fit	1.043
Final R indices [I > 2σ(I)]	R_{obs} = 0.0347, wR_{obs} = 0.0907
R indices [all data]	R_{all} = 0.0397, wR_{all} = 0.0954
Largest diff. peak and hole	3.230 and -1.062 e·Å^{-3}

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0647P)^2+1.3476P]$ where $P=(Fo^2+2Fc^2)/3$

Table S10. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for $RbSbCl_6$ at 293(2) K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}^*
Sb(01)	7500	7500	5000	1	22(1)
Rb(02)	5000	8903(1)	7500	1	48(1)
Cl(03)	7118(1)	5846(2)	6632(1)	1	37(1)
Cl(04)	8491(1)	4452(2)	4623(1)	1	35(1)
Cl(05)	5787(1)	6142(2)	3910(1)	1	38(1)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S11. Anisotropic displacement parameters (Å^{2}x10^3) for $RbSbCl_6$ at 293(2) K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(01)	23(1)	23(1)	21(1)	-1(1)	5(1)	-1(1)
Rb(02)	48(1)	49(1)	48(1)	0	13(1)	0
Cl(03)	46(1)	38(1)	30(1)	-2(1)	16(1)	7(1)
Cl(04)	39(1)	29(1)	40(1)	6(1)	12(1)	-4(1)
Cl(05)	29(1)	40(1)	41(1)	-6(1)	-1(1)	-7(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

Table S12. Select bond lengths [Å] for $RbSbCl_6$ at 293(2) K with estimated standard deviations in parentheses.

Label	Distances
Sb(01)-Cl(03)	2.3681(8)
Sb(01)-Cl(04)	2.3643(9)
Sb(01)-Cl(05)	2.3744(8)

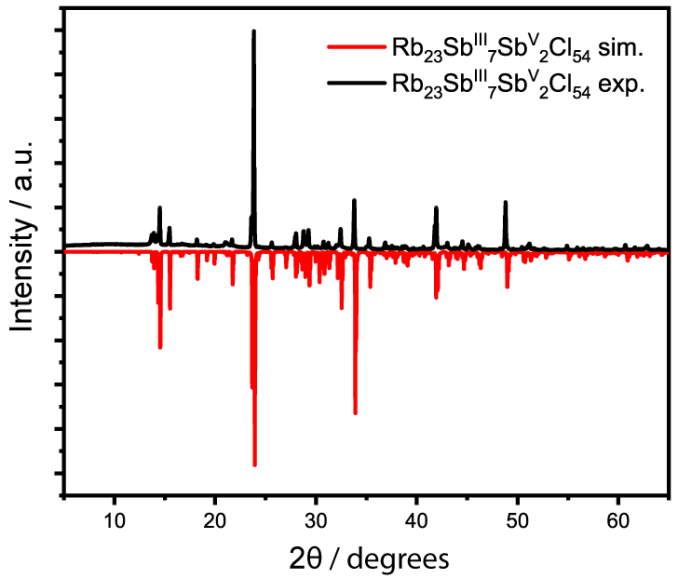

Figure S5. PXRD of $Rb_{23}Sb_9Cl_{54}$ prepared with H_2O_2.

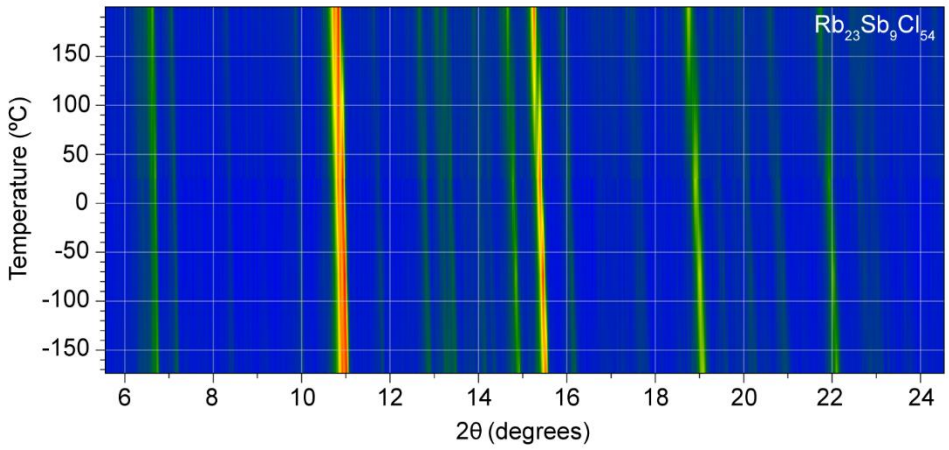

Figure S6. Temperature dependent PXRD measured from -150 °C to 150 °C.

Table S13. Crystal data and structure refinement for $Rb_{23}Bi_{2.50}Sb_{6.50}Cl_{54}$ at 293(2) K.

Empirical formula	$Rb_{23}Bi_{2.50}Sb_{6.50}Cl_{54}$
Formula weight	5194.28
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	*R*32
Unit cell dimensions	a = 12.95670(10) Å, α = 90° b = 12.95670(10) Å, β = 90° c = 111.7130(14) Å, γ = 120°
Volume	16241.4(3) Å^3
Z	6
Density (calculated)	3.186 g/cm^3
Absorption coefficient	17.266 mm^{-1}
F(000)	13848
Crystal size	0.351 x 0.103 x 0.03 mm^3
θ range for data collection	1.641 to 32.577°
Index ranges	-19<=h<=19, -19<=k<=19, -168<=l<=168
Reflections collected	291748
Independent reflections	13184 [R_{int} = 0.1364]
Completeness to θ = 25.242°	99.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13184 / 0 / 345
Goodness-of-fit	1.095
Final R indices [I > 2σ(I)]	R_{obs} = 0.0582, wR_{obs} = 0.1029
R indices [all data]	R_{all} = 0.0808, wR_{all} = 0.1111
Largest diff. peak and hole	1.963 and -3.740 e·Å^{-3}

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0192P)^2+481.0651P]$ where $P=(Fo^2+2Fc^2)/3$

Table S14. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for $Rb_{23}Bi_{2.50}Sb_{6.50}Cl_{54}$ at 293(2) K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}*
Bi(1)	10009(1)	6666.67	6666.67	0.551(9)	19(1)
Sb(1)	10009(1)	6666.67	6666.67	0.449(9)	19(1)
Bi(2)	10000	10000	6102(1)	0.255(10)	22(1)
Sb(2)	10000	10000	6102(1)	0.745(10)	22(1)
Bi(3)	6666.67	3333.33	6102(1)	0.280(10)	22(1)
Sb(3)	6666.67	3333.33	6102(1)	0.720(10)	22(1)
Bi(4)	6684(1)	6666(1)	5574(1)	0.076(7)	35(1)
Sb(4)	6684(1)	6666(1)	5574(1)	0.924(7)	35(1)
Sb(5)	3333.33	6666.67	6068(1)	1	28(1)
Bi(6)	3333(1)	3333(1)	5000	0.604(10)	29(1)
Sb(6)	3333(1)	3333(1)	5000	0.396(10)	29(1)
Rb(1)	13333.33	6666.67	6666.67	1	35(1)
Rb(2)	6666.67	3333.33	6864(1)	1	35(1)
Rb(3)	6666.67	3333.33	6469(1)	1	34(1)
Rb(4)	6219(1)	6667(1)	6449(1)	1	21(1)
Rb(5)	9718(2)	6664(2)	6224(1)	1	45(1)
Rb(6)	6834(2)	6661(2)	5975(1)	1	64(1)
Rb(7)	10000	10000	5705(1)	1	75(2)
Rb(8)	6666.67	3333.33	5706(1)	1	72(1)
Rb(9)	3333.33	6666.67	5669(1)	1	76(2)
Rb(10)	9984(3)	6666(3)	5443(1)	1	103(2)

Rb(11)	9554(4)	9555(4)	5218(1)	0.3333	48(2)
Rb(12)	6663(2)	6668(2)	5198(1)	0.6667	54(1)
Rb(13)	6661(5)	3775(4)	5219(1)	0.3333	48(2)
Rb(14)	6667(7)	6667(7)	5000	0.3333	68(2)
Rb(15)	6664(5)	3781(4)	4783(1)	0.3333	47(2)
Cl(1)	8914(3)	4263(2)	6667(1)	1	26(1)
Cl(2)	11438(3)	6666(3)	6852(1)	1	26(1)
Cl(3)	8662(3)	6666(4)	6494(1)	1	42(1)
Cl(4)	8095(3)	8385(3)	6242(1)	1	36(1)
Cl(5)	9902(4)	8339(4)	5968(1)	1	45(1)
Cl(6)	6387(3)	4956(3)	6243(1)	1	35(1)
Cl(7)	6753(4)	1764(4)	5968(1)	1	45(1)
Cl(8)	4810(6)	6663(7)	6186(1)	1	95(2)
Cl(9)	1870(6)	6662(8)	5946(1)	1	98(2)
Cl(10)	5113(6)	5088(6)	5702(1)	1	75(2)
Cl(11)	6684(5)	8237(6)	5704(1)	1	74(2)
Cl(12)	8268(5)	6670(5)	5699(1)	1	70(2)
Cl(13)	4977(8)	6658(10)	5436(1)	1	144(4)
Cl(14)	6687(9)	4982(7)	5438(1)	1	130(3)
Cl(15)	8363(8)	8347(8)	5438(1)	1	129(3)
Cl(16)	8534(11)	6666(11)	5182(2)	0.3333	55(3)
Cl(17)	7999(14)	10003(16)	5170(2)	0.3333	72(4)
Cl(18)	6663(12)	8549(12)	5184(2)	0.3333	60(3)
Cl(19)	5334(14)	8670(14)	5169(2)	0.3333	68(4)
Cl(20)	4780(12)	4792(12)	5182(2)	0.3333	58(3)
Cl(21)	4663(15)	3323(18)	5169(2)	0.3333	76(5)
Cl(22)	5730(13)	4427(11)	4999(1)	0.3333	53(3)
Cl(23)	7622(13)	5363(12)	4999(2)	0.3333	53(3)
Cl(24)	7955(12)	8908(12)	5000(1)	0.3333	53(3)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S15. Anisotropic displacement parameters ($Å^2x10^3$) for $Rb_{23}Bi_{2.50}Sb_{6.50}Cl_{54}$ at 293(2) K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi(1)	16(1)	18(1)	24(1)	9(1)	0(1)	0(1)
Sb(1)	16(1)	18(1)	24(1)	9(1)	0(1)	0(1)
Bi(2)	24(1)	24(1)	19(1)	12(1)	0	0
Sb(2)	24(1)	24(1)	19(1)	12(1)	0	0
Bi(3)	24(1)	24(1)	17(1)	12(1)	0	0
Sb(3)	24(1)	24(1)	17(1)	12(1)	0	0
Bi(4)	28(1)	29(1)	49(1)	14(1)	1(1)	0(1)
Sb(4)	28(1)	29(1)	49(1)	14(1)	1(1)	0(1)
Sb(5)	33(1)	33(1)	18(1)	16(1)	0	0
Bi(6)	31(1)	31(1)	24(1)	15(1)	0(1)	0(1)
Sb(6)	31(1)	31(1)	24(1)	15(1)	0(1)	0(1)
Rb(1)	33(1)	33(1)	38(2)	16(1)	0	0
Rb(2)	40(1)	40(1)	26(1)	20(1)	0	0
Rb(3)	38(1)	38(1)	25(1)	19(1)	0	0
Rb(4)	19(1)	21(1)	25(1)	10(1)	2(1)	0(1)
Rb(5)	55(1)	28(1)	39(1)	12(1)	-2(1)	1(1)
Rb(6)	47(1)	67(2)	85(2)	35(1)	4(1)	-1(1)
Rb(7)	86(2)	86(2)	53(2)	43(1)	0	0
Rb(8)	85(2)	85(2)	45(2)	42(1)	0	0

Rb(9)	99(2)	99(2)	31(2)	49(1)	0	0
Rb(10)	115(2)	140(3)	63(2)	71(2)	-2(2)	-2(2)
Rb(11)	43(3)	49(3)	48(2)	21(2)	-5(2)	-9(2)
Rb(12)	59(2)	60(2)	44(2)	31(2)	2(1)	0(1)
Rb(13)	48(2)	49(3)	50(2)	26(3)	1(2)	4(2)
Rb(14)	72(4)	72(4)	63(5)	38(5)	-2(2)	2(2)
Rb(15)	47(2)	47(3)	50(2)	25(3)	2(2)	-5(2)
Cl(1)	26(2)	18(2)	31(2)	8(2)	0(2)	0(1)
Cl(2)	25(2)	25(2)	28(2)	12(2)	-7(2)	1(2)
Cl(3)	36(2)	75(3)	30(2)	39(2)	-6(2)	0(2)
Cl(4)	32(2)	35(2)	29(2)	8(2)	12(2)	14(2)
Cl(5)	58(2)	40(2)	36(2)	23(2)	-1(2)	-12(2)
Cl(6)	53(2)	33(2)	28(2)	28(2)	-1(2)	-14(2)
Cl(7)	60(2)	48(2)	38(2)	35(2)	2(2)	-9(2)
Cl(8)	87(4)	189(7)	42(2)	93(4)	-29(2)	4(3)
Cl(9)	85(4)	187(8)	55(3)	92(5)	-22(3)	-4(4)
Cl(10)	62(3)	65(3)	73(3)	15(3)	27(3)	24(3)
Cl(11)	98(4)	63(3)	72(3)	49(3)	2(3)	-23(3)
Cl(12)	58(3)	104(4)	60(2)	49(3)	-21(2)	2(3)
Cl(13)	111(6)	207(11)	150(8)	106(7)	48(6)	8(7)
Cl(14)	174(9)	88(5)	154(7)	85(6)	9(6)	19(5)
Cl(15)	95(6)	90(6)	146(7)	5(4)	-20(5)	-22(5)
Cl(16)	44(7)	41(6)	74(8)	16(5)	10(6)	-3(6)
Cl(17)	53(8)	96(12)	76(10)	45(9)	0(7)	-2(9)
Cl(18)	47(7)	50(8)	79(9)	22(6)	3(6)	6(6)
Cl(19)	55(8)	61(9)	70(9)	17(7)	12(7)	14(7)
Cl(20)	45(7)	54(8)	82(9)	30(7)	-4(6)	-10(7)
Cl(21)	60(9)	108(14)	85(11)	61(10)	4(8)	9(10)
Cl(22)	47(7)	53(7)	50(6)	18(6)	-1(6)	2(5)
Cl(23)	49(7)	57(7)	58(6)	29(6)	-1(6)	-1(5)
Cl(24)	60(7)	53(7)	52(6)	33(7)	-6(5)	-3(5)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

Note S2. Site relations between $Rb_{23}Sb^{III}_{7}Sb^{V}_{2}Cl_{54}$ (*Cmcm*) and $Rb_{23}Bi^{III}_{x}Sb^{III}_{7-x}Sb^{V}_{2}Cl_{54}$ (*R*32) structures:

Sb1 & Sb2 (*Cmcm*) => Bi/Sb1 & disordered Bi6/Sb6 (*R*32)
Sb3 (*Cmcm*) => Bi2/Sb2, Bi3/Sb3, and a portion of mixed III-V site Bi4/Sb4 (*R*32)
Sb4 (*Cmcm*) => Sb5 & a portion of mixed III-V site Bi4/Sb4 (*R*32)

Table S16. Octahedral bismuth and antimony sites in $Rb_{23}Bi^{III}_{2.50}Sb^{III}_{4.50}Sb^{V}_{2}Cl_{54}$ (x = 2.50, *R*32).

Site label	*Wyckoff site*	*% Sb*	*Average bond length, (Å)*	*Distortion index Δd*	*Effective Coord. #*	*Angle variance*	*Valence*
Bi1/Sb1	9d	44.9	2.694	0.022	5.833	16.444	III
Bi2/Sb2	6c	74.5	2.678	0.042	5.576	5.434	III
Bi3/Sb3	6c	72.0	2.679	0.041	5.592	5.641	III
Bi4/Sb4*	18f	92.4	2.580	0.033	5.724	0.377	Mixed III,V
Sb5	6c	100	2.331	0.000	6.000	0.276	V
Bi6/Sb6**	9e	39.6	2.673	0.028	5.717**	Disordered	III

*mixed III-V, reflected by very large thermal parameters near disordered layer
**rotationally disordered (3-fold), coord # divided by 3
Values for bond lengths, the bond length distortion index Δd, angle variance, and the effective coordination numbers calculated using the Vesta3 crystallography software.[3]

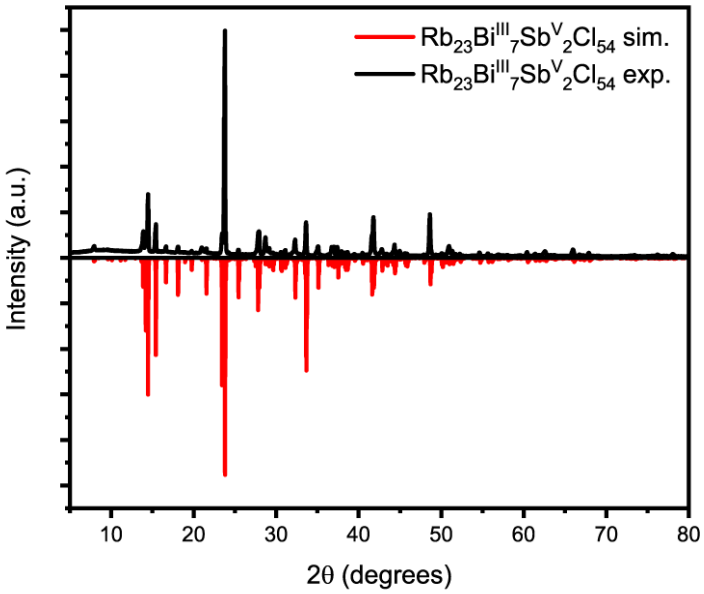

Figure S7. PXRD of $Rb_{23}Bi_{6.97}Sb_{2.03}Cl_{54}$.

Table S17. Crystal data and structure refinement for $Rb_{23}Bi_{6.62}Sb_{2.38}Cl_{54}$ at 298 K.

Empirical formula	$Rb_{23}Bi_{6.62}Sb_{2.38}Cl_{54}$
Formula weight	5553.61
Temperature	298 K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	*R*32
Unit cell dimensions	a = 12.9752(6) Å, α = 90° b = 12.9752(6) Å, β = 90° c = 112.438(8) Å, γ = 120°
Volume	16393.5(18) $Å^3$
Z	6
Density (calculated)	3.375 g/cm^3
Absorption coefficient	22.719 mm^{-1}
F(000)	14640
Crystal size	0.27 x 0.24 x 0.05 mm^3
θ range for data collection	1.630 to 31.525°
Index ranges	-18<=h<=18, -18<=k<=19, -160<=l<=156
Reflections collected	62871
Independent reflections	11380 [R_{int} = 0.0973]
Completeness to θ = 25.242°	99.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11380 / 0 / 341
Goodness-of-fit	1.072
Final R indices [I > 2σ(I)]	R_{obs} = 0.0864, wR_{obs} = 0.2231
R indices [all data]	R_{all} = 0.1204, wR_{all} = 0.2438
Largest diff. peak and hole	6.069 and -3.405 $e·Å^{-3}$

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0973P)^2+1152.5934P]$ where $P=(Fo^2+2Fc^2)/3$

Table S18. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters ($Å^2$x10^3) for $Rb_{23}Bi_{6.62}Sb_{2.38}Cl_{54}$ at 298 K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}*
Bi(1)	10002(1)	6666.67	6666.67	1	30(1)
Bi(2)	10000	10000	6102(1)	1	33(1)
Bi(3)	6666.67	3333.33	6102(1)	1	32(1)
Bi(4)	6679(2)	6668(2)	5569(1)	0.541(15)	48(1)
Sb(4)	6679(2)	6668(2)	5569(1)	0.459(15)	48(1)
Sb(5)	3333.33	6666.67	6067(1)	1	40(1)
Bi(6)	3332(2)	3332(2)	5000	1	48(1)
Rb(1)	13333.33	6666.67	6666.67	1	39(2)
Rb(2)	6666.67	3333.33	6860(1)	1	42(1)
Rb(3)	6666.67	3333.33	6472(1)	1	42(1)
Rb(4)	6222(2)	6669(2)	6449(1)	1	30(1)
Rb(5)	9737(3)	6668(3)	6221(1)	1	56(1)
Rb(6)	6864(3)	6666(3)	5969(1)	1	81(2)
Rb(7)	10000	10000	5710(1)	1	92(2)
Rb(8)	6666.67	3333.33	5710(1)	1	93(2)
Rb(9)	3333.33	6666.67	5670(1)	1	88(2)
Rb(10)	9971(6)	6665(6)	5442(1)	1	118(2)
Rb(11)	9584(13)	9544(10)	5216(1)	0.3333	66(3)
Rb(12)	6660(5)	6676(6)	5197(1)	0.6667	75(2)
Rb(13)	6670(13)	3776(10)	5216(1)	0.3333	61(3)

Rb(14)	6670(15)	6670(15)	5000	0.3333	90(6)
Rb(15)	3781(11)	6668(13)	5216(1)	0.3333	63(3)
Cl(1)	8921(6)	4251(5)	6667(1)	1	38(2)
Cl(2)	11446(5)	6667(5)	6485(1)	1	34(2)
Cl(3)	8667(7)	6676(8)	6492(1)	1	53(2)
Cl(4)	8113(6)	8387(6)	6244(1)	1	45(2)
Cl(5)	9938(8)	8321(8)	5967(1)	1	58(2)
Cl(6)	6392(6)	4948(6)	6244(1)	1	47(2)
Cl(7)	4988(8)	3267(9)	5966(1)	1	62(2)
Cl(8)	4805(10)	6661(14)	6187(1)	1	95(4)
Cl(9)	3344(16)	5237(12)	5947(2)	1	111(5)
Cl(10)	5053(12)	5048(13)	5701(1)	1	87(3)
Cl(11)	6678(11)	8278(13)	5701(1)	1	86(3)
Cl(12)	8299(12)	6667(11)	5699(1)	1	80(3)
Cl(13)	4977(17)	6660(20)	5428(2)	1	145(7)
Cl(14)	6690(20)	4981(17)	5428(2)	1	150(8)
Cl(15)	8379(17)	8373(17)	5429(2)	1	143(7)
Cl(16)	8530(30)	6630(30)	5182(2)	0.3333	70(8)
Cl(17)	8650(30)	5290(30)	5178(3)	0.3333	81(10)
Cl(18)	6660(30)	8540(30)	5184(2)	0.3333	67(7)
Cl(19)	8020(30)	10040(30)	5178(2)	0.3333	79(10)
Cl(20)	8870(30)	7950(30)	4999(2)	0.3333	65(6)
Cl(21)	4770(30)	4760(30)	5184(2)	0.3333	62(7)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S19. Anisotropic displacement parameters ($Å^2x10^3$) for $Rb_{23}Bi_{6.62}Sb_{2.38}Cl_{54}$ at 298 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi(1)	16(1)	18(1)	57(1)	9(1)	0(1)	0(1)
Bi(2)	30(1)	30(1)	37(1)	15(1)	0	0
Bi(3)	30(1)	30(1)	37(1)	15(1)	0	0
Bi(4)	45(1)	46(1)	54(2)	23(1)	1(1)	1(1)
Sb(4)	45(1)	46(1)	54(2)	23(1)	1(1)	1(1)
Sb(5)	48(1)	48(1)	25(2)	24(1)	0	0
Bi(6)	61(1)	61(1)	24(1)	31(1)	0(1)	0(1)
Rb(1)	29(2)	29(2)	59(3)	14(1)	0	0
Rb(2)	39(2)	39(2)	47(2)	19(1)	0	0
Rb(3)	39(2)	39(2)	49(2)	19(1)	0	0
Rb(4)	22(1)	26(1)	43(2)	12(1)	2(1)	0(1)
Rb(5)	59(2)	34(2)	66(2)	17(2)	-3(2)	2(2)
Rb(6)	59(2)	86(3)	109(4)	43(2)	6(2)	0(2)
Rb(7)	101(4)	101(4)	75(4)	51(2)	0	0
Rb(8)	105(4)	105(4)	68(4)	53(2)	0	0
Rb(9)	106(4)	106(4)	52(3)	53(2)	0	0
Rb(10)	134(5)	169(6)	58(3)	82(4)	0(3)	-1(3)
Rb(11)	83(12)	67(8)	48(4)	37(6)	-6(5)	-3(4)
Rb(12)	90(4)	100(5)	37(2)	49(4)	2(2)	0(2)
Rb(13)	63(6)	66(8)	53(4)	32(7)	-5(5)	-2(4)
Rb(14)	106(11)	106(11)	49(8)	47(12)	-8(5)	8(5)
Rb(15)	75(9)	63(6)	49(4)	33(8)	2(4)	1(5)
Cl(1)	33(3)	21(2)	55(3)	10(2)	-3(3)	1(2)
Cl(2)	24(3)	27(2)	50(3)	12(2)	8(2)	1(2)
Cl(3)	40(3)	80(5)	54(4)	40(4)	-10(3)	3(4)

Cl(4)	31(3)	38(3)	56(4)	10(2)	12(3)	15(3)
Cl(5)	73(5)	46(4)	63(5)	36(4)	-3(4)	-18(4)
Cl(6)	52(4)	38(3)	61(4)	30(3)	-3(3)	-17(3)
Cl(7)	46(4)	76(5)	64(5)	31(4)	-16(4)	-2(4)
Cl(8)	79(7)	177(12)	53(5)	82(8)	-24(5)	2(6)
Cl(9)	201(15)	91(9)	83(7)	105(10)	4(8)	-20(6)
Cl(10)	79(7)	97(9)	68(5)	32(6)	17(6)	15(6)
Cl(11)	106(8)	88(8)	70(5)	53(7)	3(5)	-24(6)
Cl(12)	79(7)	104(8)	69(5)	54(7)	-20(6)	0(5)
Cl(13)	131(14)	250(20)	101(10)	128(16)	29(9)	2(12)
Cl(14)	230(20)	119(13)	131(13)	113(16)	2(13)	11(10)
Cl(15)	128(14)	125(14)	102(10)	8(10)	0(10)	-8(9)
Cl(16)	80(20)	74(17)	35(11)	28(15)	0(11)	-1(10)
Cl(17)	80(20)	63(17)	65(18)	7(15)	-7(14)	-8(13)
Cl(18)	69(17)	70(18)	51(13)	28(14)	-3(11)	-4(12)
Cl(19)	76(19)	140(30)	47(14)	70(20)	14(13)	-6(16)
Cl(20)	80(17)	88(19)	45(10)	56(17)	4(12)	2(11)
Cl(21)	80(19)	67(17)	41(11)	38(16)	-3(11)	-1(10)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

Table S20. Selected bond lengths [Å] for $Rb_{23}Bi_{6.62}Sb_{2.38}Cl_{54}$ at 298 K with estimated standard deviations in parentheses.

Label	Distances
Bi(1)-Cl(1)	2.719(5)
Bi(1)-Cl(2)	2.775(6)
Bi(1)-Cl(3)	2.622(7)
Bi(2)-Cl(4)	2.788(7)
Bi(2)-Cl(5)	2.625(8)
Bi(3)-Cl(6)	2.791(6)
Bi(3)-Cl(7)	2.626(9)
Bi(4)-Cl(10)	2.577(13)
Bi(4)-Cl(11)	2.566(12)
Bi(4)-Cl(12)	2.560(11)
Bi(4)-Cl(13)	2.714(19)
Bi(4)-Cl(14)	2.703(19)
Bi(4)-Cl(15)	2.712(18)
Sb(4)-Cl(10)	2.577(13)
Sb(4)-Cl(11)	2.566(12)
Sb(4)-Cl(12)	2.560(11)
Sb(4)-Cl(13)	2.714(19)
Sb(4)-Cl(14)	2.703(19)
Sb(4)-Cl(15)	2.712(18)
Sb(5)-Cl(8)	2.342(8)
Sb(5)-Cl(9)	2.301(10)
Bi(6)-Cl(17)#6	2.68(3)
Bi(6)-Cl(19)#10	2.64(3)
Bi(6)-Cl(20)#6	2.71(3)
Bi(6)-Cl(22)#10	2.70(3)
Bi(6)-Cl(23)	2.75(3)
Bi(6)-Cl(24)	2.64(3)

Symmetry transformations used to generate equivalent atoms:
(1) x-y+2/3,-y+1/3,-z+1/3 (2) y+2/3,x+1/3,-z+1/3 (3) -x+y+1,-x+2,z (4) -y+2,x-y+1,z (5) -x+y+1,-x+1,z (6) -y+1,x-y,z (7) -y+1,x-y+1,z (8) -x+y,-x+1,z (9) x-y,-y+1,-z+1 (10) -x+1,-x+y,-z+1 (11) y,x,-z+1 (12) x-y+2/3,-y+1/3,-z+1/3 (13) -x+2/3,-x+y+1/3,-z+1/3 (14) -x+y+2,-x+2,z (15) y+2/3,x+1/3,-z+1/3 (16) -x+2/3,-x+y+1/3,-z+1/3 (17) -y+2,x-y,z (18) y+2/3,x+1/3,-z+1/3 (19) -x+2/3,-x+y+1/3,-z+1/3 (20) -x+2,-x+y+1,-z+1 (21) x-y+1,-y+1,-z+1 (22) x-1,y,z (23) -x+1,-x+y+1,-z+1

Table S21. Octahedral bismuth and antimony sites in $Rb_{23}Bi^{III}_{6.62}Sb^{III}_{0.38}Sb^{V}_{2}Cl_{54}$ (x = 6.62, *R*32).

Site label	*Wyckoff site*	*% Sb*	*Average bond length, (Å)*	*Distortion index Δd*	*Effective Coord. #*	*Angle variance*	*Valence*
Bi1	9d	0	2.7057	0.020	5.870	17.280	III
Bi2	6c	0	2.706	0.030	5.788	6.474	III
Bi3	6c	0	2.709	0.030	5.781	6.194	III
Bi4/Sb4*	18f	45.9	2.638	0.027	5.830	0.155	Mixed III,V
Sb5	6c	100	2.322	0.009	5.984	0.480	V
Bi6**	9e	0	2.720	0.019	5.893**	Disordered	III

*mixed III-V, reflected by very large thermal parameters near disordered layer
**rotationally disordered (3-fold), coord # divided by 3
Values for bond lengths, the bond length distortion index Δd, angle variance, and the effective coordination numbers calculated using the Vesta3 crystallography software.[3]

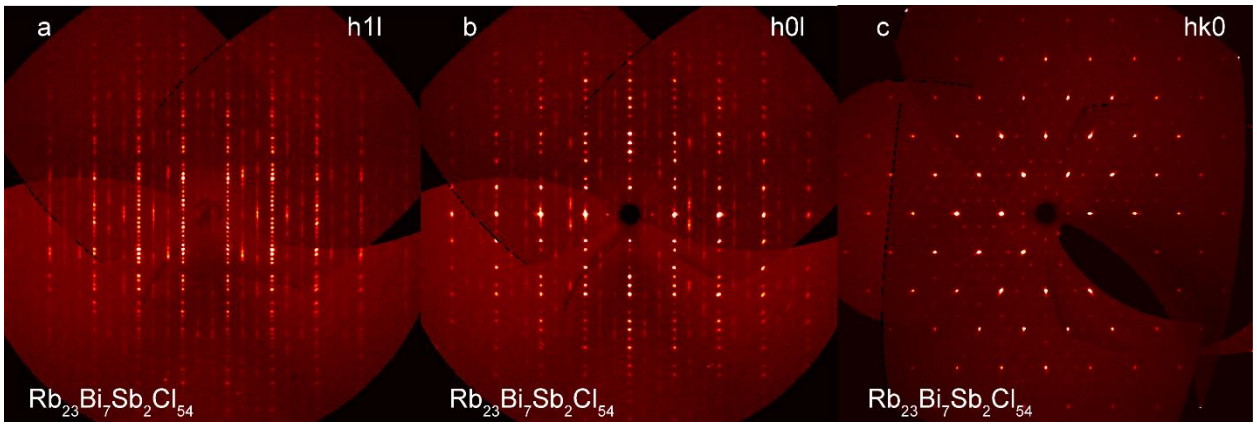

Figure S8. Unwrapped images from the diffraction experiment for $Rb_{23}Bi_7Sb_2Cl_{54}$. Panels a and b demonstrate the presence of diffuse scattering indicative of disorder in the structure.

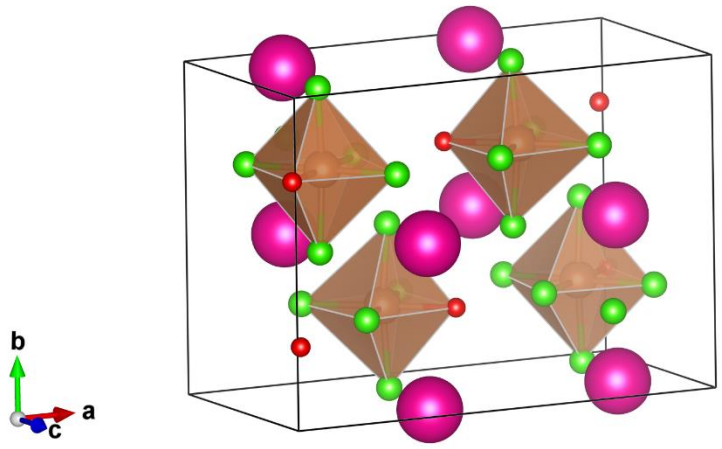

Figure S9. Unit cell of Rb_2SbCl_5O.

Table S22. Crystal data and structure refinement for Rb_2SbCl_5O at 300 K.

Empirical formula	Rb_2SbCl_5O
Formula weight	485.94
Temperature	300 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pnma*
Unit cell dimensions	a = 14.0332(6) Å, α = 90° b = 10.1091(4) Å, β = 90° c = 7.2292(3) Å, γ = 90°
Volume	1025.56(7) $Å^3$
Z	4
Density (calculated)	3.147 g/cm^3
Absorption coefficient	13.356 mm^{-1}
F(000)	872
Crystal size	0.22 x 0.18 x 0.03 mm^3
θ range for data collection	2.903 to 31.520°
Index ranges	-20<=h<=20, -14<=k<=14, -10<=l<=10
Reflections collected	11208
Independent reflections	1694 [R_{int} = 0.0415]
Completeness to θ = 25.242°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1694 / 0 / 49
Goodness-of-fit	1.171
Final R indices [I > 2σ(I)]	R_{obs} = 0.0389, wR_{obs} = 0.0896
R indices [all data]	R_{all} = 0.0443, wR_{all} = 0.0930
Largest diff. peak and hole	1.503 and -0.908 e·$Å^{-3}$

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0408P)^2+3.5645P]$ where $P=(Fo^2+2Fc^2)/3$

Table S23. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters ($Å^2$x10^3) for Rb_2SbCl_5O at 300 K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}*
Sb(01)	6146(1)	7500	6911(1)	1	23(1)
Rb(02)	6444(1)	5008(1)	1557(1)	1	37(1)
Cl(03)	7525(2)	7500	9041(2)	1	28(1)
Cl(04)	7227(2)	7500	4226(2)	1	36(1)
Cl(05)	6037(1)	5037(1)	6795(2)	1	34(1)
Cl(06)	5026(2)	7500	9570(2)	1	34(1)
O(07)	4905(4)	7500	4928(8)	1	40(2)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S24. Anisotropic displacement parameters ($Å^2$x10^3) for Rb_2SbCl_5O at 300 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(01)	23(1)	20(1)	26(1)	0	-2(1)	0
Rb(02)	36(1)	35(1)	40(1)	-1(1)	-5(1)	4(1)
Cl(03)	26(1)	33(1)	27(1)	0	-6(1)	0

Cl(04)	40(1)	43(1)	25(1)	0	8(1)	0
Cl(05)	40(1)	18(1)	45(1)	0(1)	-9(1)	-3(1)
Cl(06)	29(1)	34(1)	38(1)	0	10(1)	0
O(07)	36(3)	28(2)	57(3)	0	-26(3)	0

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

Table S25. Bond lengths [Å] for Rb_2SbCl_5O at 300 K with estimated standard deviations in parentheses.

Label	Distances
Sb(01)-Cl(03)	2.4727(15)
Sb(01)-Cl(04)	2.4632(17)
Sb(01)-Cl(05)#5	2.4956(11)
Sb(01)-Cl(05)	2.4956(11)
Sb(01)-Cl(06)	2.4836(16)
Sb(01)-O(07)	2.255(5)

Symmetry transformations used to generate equivalent atoms:
(1) -x+3/2,-y+1,z+1/2 (2) -x+3/2,y+1/2,z+1/2 (3) x,y,z+1 (4) x,-y+3/2,z+1 (5) x,-y+3/2,z (6) -x+3/2,-y+1,z-1/2 (7) x,y,z-1 (8) -x+1,-y+1,-z+1 (9) -x+1,y+1/2,-z+1

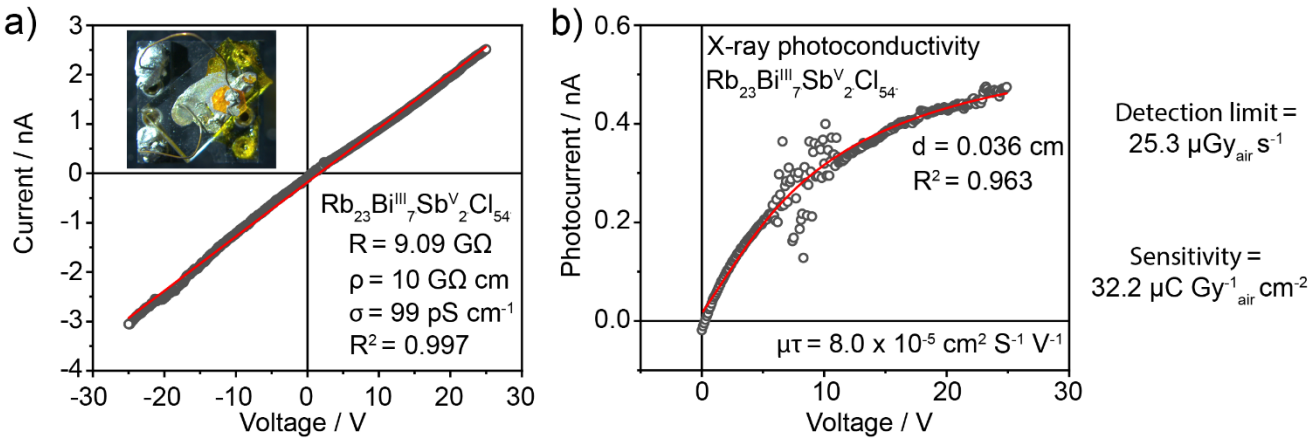

Figure S10. Electrical properties. a) I-V characterization of $Rb_{23}Bi_7Sb_2Cl_{54}$; inset: image of device with orange crystal, b) X-ray photoconductivity (with dark current subtracted) measured on a crystal with thickness d = 0.036 cm. Detection limit and sensitivity are reported at an applied voltage of 40 kV.

References

[1] G. M. Sheldrick, *Acta Crystallogr A* **2008**, *64*, 112-122.
[2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.
[3] K. Momma, F. Izumi, *J. Appl. Crystallogr.* **2011**, *44*, 1272-1276.
[4] H. Putz, K. Brandenburg, *Crystal Impact-GbR, Kreuzherrenstr* **2006**, *102*, 53227.
[5] L. Atkinson, P. Day, *J. Chem. Soc. A* **1969**, 2432-2436.
[6] M. L. Hackert, S. L. Lawton, R. A. Jacobson, *Proc. Iowa Acad. Sci.* **1968**, *75*.