Supplementary Information (SI) for ChemComm.

Supporting Information

Three antimony-based organic-inorganic hybrid perovskites (1,4-3.2.2-H_2dabcn)SbX_5 (X = Cl, Br, l) show progressively decreasing phase transition temperatures and bandgaps

Ying Wei, Jie Zhou, Lin Zhou*, Zhenhong Wei*

School of Chemistry and Chemical Engineering, Nanchang University,
Nanchang, 330031, P. R. China

*Corresponding Author(s): weizh@ncu.edu.cn

Measurement Methods

Single-crystal and powder X-ray crystallography.

X-ray single-crystal diffraction experiments were performed utilizing a Rigaku Saturn 924 diffractometer, outfitted with Mo-Kα radiation (λ = 0.71073 Å). X-ray diffraction (XRD) analyses were executed employing a PANalytical X'Pert3 diffractometer, equipped with a Cu Kα X-ray source (λ = 1.5418 Å, 40 kV, 150 mA), with a scan rate set at 10° min^{-1} for the measurements.

Thermal analyses.

Differential scanning calorimetry (DSC) measurements were performed with a NETZSCH DSC 200F3 instrument. Crystalline samples underwent both heating and cooling processes at a consistent rate of 20 K min^{-1} under aluminum crucibles and nitrogen atmosphere.

SHG and dielectric measurements.

The second harmonic generation (SHG) was examined using INSTEC instruments. Complex dielectric permittivities were assessed utilizing the DMS-1000 dielectric temperature spectrum measuring system. Silver conductive paste was utilized to coat the surfaces of the samples, serving dual roles as the top and bottom electrodes.

Experimental

In the preparation, chemicals and solvents 1,4-3.2.2-H_2dabcn, antimony halide SbX_3 and the concentrated hydrohalic acid HX (X = Cl, Br and I) were purchased and used directly without additional purification.

Synthesis of (1,4-3.2.2-H_2dabcn)$SbCl_5$ (1): To a 10 mL concentrated HCl (45%, 1.8 g) aqueous solution of $SbCl_3$ (2.0 mmol, 0.56 g), solid 1, 4-3.2.2-dabcn (2.0 mmol, 0.24 g) was added. The mixture was heated to 50°C, and kept stirring for 1h. The resulting transparent solution is cooled to room temperature and slowly evaporated for 3 days to obtain massive white crystals. The crystals are separated by filtration and then dried under infrared light. Yield: 1.11 g, 42%. Anal. calculated for $C_7H_{15}Cl_5N_2Sb$: C, 19.73; H, 3.62; N, 6.64 Found: C, 19.62; H, 3.49; N, 6.55. IR (KBr, cm^{-1}): 3156(vs), 2958(w), 2923(w), 2875(w), 2601(w), 2504(w), 2448(w), 1641(vs), 1564(vs), 1430(vs), 1333(s), 1256(w), 1131(vs), 1041(s), 1003(s), 923(v), 878(w), 837(w), 774(vs), 719(m), 640(v), 517(m).

Synthesis of (1,4-3.2.2-H_2dabcn)$SbBr_5$ (2): To a 10 mL of concentrated HBr (40%, 2.1 g) aqueous solution of $SbBr_3$ (2.0 mmol, 0.64 g), solid 1,4-3.2.2-dabcn (2.0 mmol, 0.24 g) and heated to 50 °C with stirring for 1 h. The resulting clear solution was cooled to room temperature and slowly evaporated for 3 days to give white bulk crystals. The crystals were separated by filtration and subsequently dried under infrared light. Yield: 1.5 g, 50%. Anal. calculated for $C_7H_{15}Br_5N_2Sb$: C, 12.95; H, 2.33; N, 4.32 Found: C, 12.87; H, 2.46; N, 4.20. IR (KBr, cm^{-1}): 3149(vs), 2926(w), 2875(m), 2601(w), 2467(w), 2448(m), 1641(vs), 1503(s), 1430(vs), 1323(s), 1261(vs), 1013(s), 978(s), 923(s), 878(w), 837(vs), 774(m), 719(w), 640(vs), 510(w).

Synthesis of (1,4-3.2.2-H_2dabcn)SbI_5 (3): To a 10 mL of concentrated HI (55%, 1.7 g) aqueous solution of SbI_3 (2.0 mmol, 0.98 g), 10 mL of hypo phosphorous acid (55%, 1.5 g) and solid 1,4-3.2.2-dabcn (2.0 mmol, 0.24 g) were added successively. The reaction was heated to 100 °C and kept stirring for 1 h. The resulting clear solution was cooled to room temperature and slowly evaporated for 3 days to obtain black bulk crystals. The crystals were separated by filtration and subsequently dried under infrared light. Yield: 1.6 g, 36%. Anal. calculated for $C_7H_{15}I_5N_2Sb$: C, 9.15; H, 1.71; N, 3.17 Found: C, 9.48; H,1.65; N, 3.25. IR (KBr, cm^{-1}): 3475(w), 3156(m) 2958(w), 2601(w), 2504(w), 2448(m), 1641(vs), 1564(w), 1430(w), 1333(vs), 1041(vs), 923(w), 878(w), 837(w), 640(w), 520(vs).

Computational Methods.

All calculations using density functional theory (DFT) were carried out using the Vienna Ab initio simulation package (VASP).[1] The generalized gradient approximation of the Perdew−Burke−Ernzerhof (PBE) parametrization with the projector-augmented wave (PAW) method was performed for the exchange and correlation functional.[2] For all elements, including Sb, I, C, N and H, ultrasoft pseudopotentials were used. The kinetic energy cutoff of 420 eV and a 2 × 2 × 1 Monkhorst–Pack k-point mesh for the wave function basis set were employed. The energy convergence criterion is set as 1.0×10^{-5} eV for structural relaxations. Finally, data processing and graphical plotting were performed using Vaspkit and Origin software.

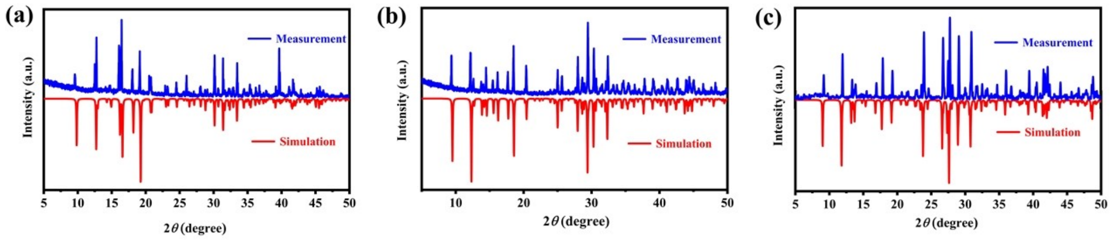

Fig. S1. Powder X-ray diffractograms of compounds **1−3**.

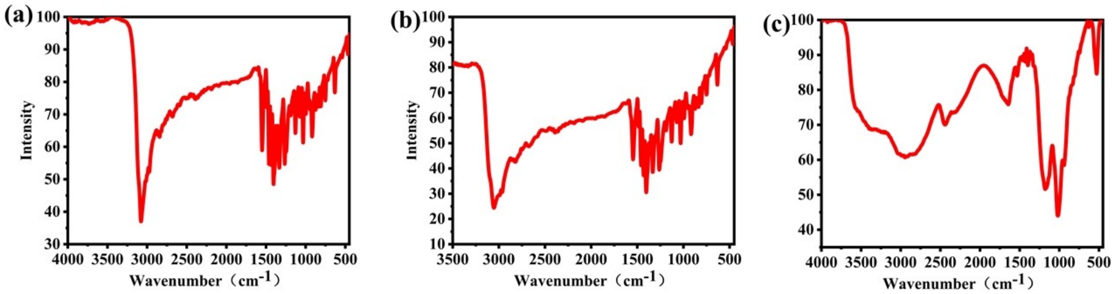

Fig. S2. Infrared spectra of solid compounds **1−3** in KBr particles recorded at room temperature.

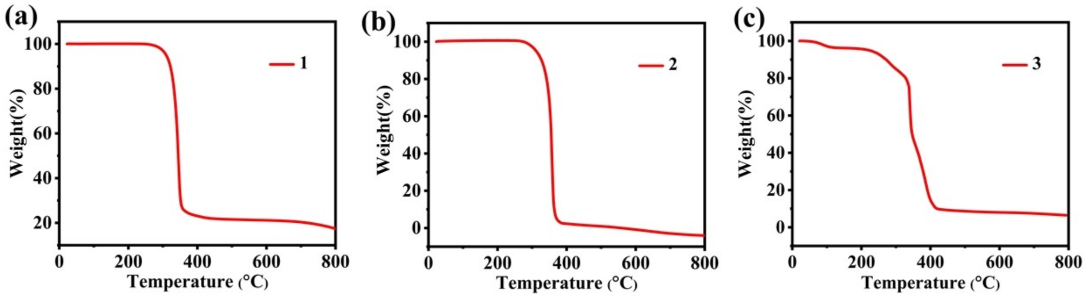

Fig. S3. TGA of **1** (a), **2** (b) and **3** (c).

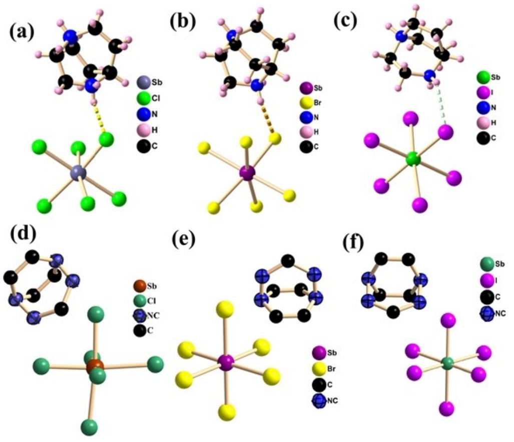

Fig. S4. Molecular structures of **1−3** at LTP (a-c) and HTP (d-f).

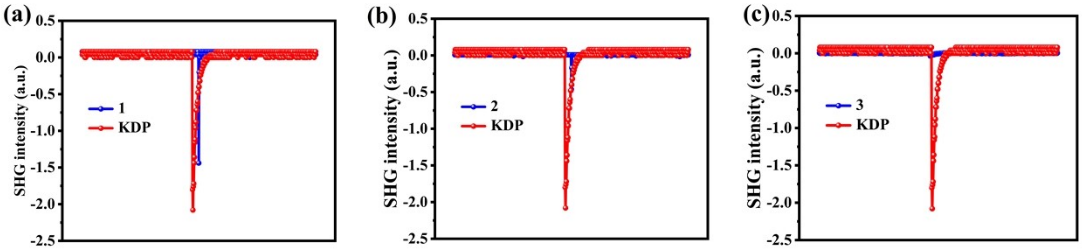

Fig. S5 The plots of the SHG signal intensity of compounds **1** (a), **2** (b) and **3** (c) against the reference sample KDP at room temperature.

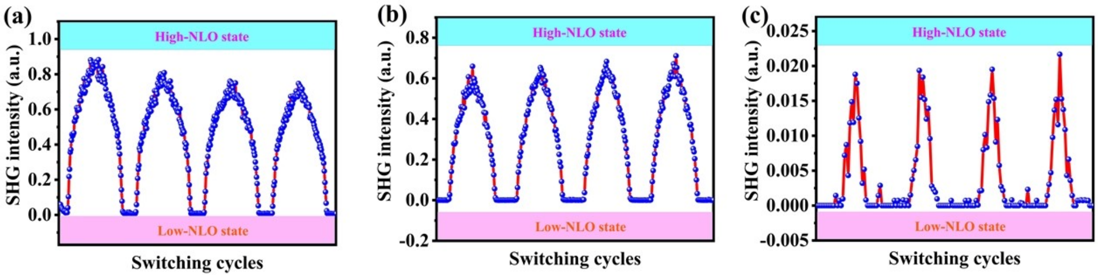

Fig. S6. The SHG cycles of compounds **1** (a), **2** (b) and **3** (c).

Table S1. Crystal data and structure refinement for **1−3** at 298 K.

Empirical formula	$C_7H_{15}Cl_5N_2Sb$	$C_7H_{16}Br_5N_2Sb$	$C_7H_{16}I_5N_2Sb$
Formula weight	427.23	649.52	884.47
Temperature/K	298.0	298.0	298.0
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P\mathrm{na}2_1$
a/Å	8.5619(2)	8.7842(3)	14.8591(5)
b/Å	11.9096(2)	12.4619(3)	13.0389(4)
c/Å	13.6606(4)	13.8984(5)	9.1663(2)
α/°	90.00	90	90
β/°	90.00	90	90
γ/°	90.00	90	90
Volume/Å^3	1392.96(6)	1521.43(8)	1775.94(9)
Z	4	4	4
ρ_{calc}g/cm^3	2.032	2.836	3.308
μ/mm^{-1}	2.912	14.920	10.226
F(000)	832.0	1192.0	1552.0
Crystal size/mm^3	0.06 × 0.05 × 0.04	0.05 × 0.04 × 0.03	0.04 × 0.03 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.54 to 56.58	4.39 to 56.59	4.156 to 56.6
Index ranges	$-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$	$-11 \leq h \leq 11$, $-14 \leq k \leq 16$, $-18 \leq l \leq 16$	$-19 \leq h \leq 19$, $-17 \leq k \leq 17$, $-11 \leq l \leq 12$
Reflections collected	38687	22998	40103
Independent reflections	3462 [R_{int} = 0.0716, R_{sigma} = 0.0280]	3771 [R_{int} = 0.0731, R_{sigma} = 0.0509]	4291 [R_{int} = 0.0626, R_{sigma} = 0.0359]
Data/restraints/parameters	3462/137/136	3771/64/137	4291/11/138
Goodness-of-fit on F^2	1.043	1.063	1.060
Final R indexes [I≥2σ (I)]	R_1 = 0.0292, wR_2 = 0.0721	R_1 = 0.0323, wR2 = 0.0709	R_1 = 0.0377, wR_2 = 0.0978
Final R indexes [all data]	R_1 = 0.0317, wR_2 = 0.0736	R_1 = 0.0397, wR_2 = 0.0752	R_1 = 0.0393, wR_2 = 0.0989
Largest diff. peak/hole / e Å^{-3}	1.84/-1.12	1.00/-0.95	1.87/-1.57
Flack parameter	-0.02(3)	0.020(15)	0.44(12)

Table S2. Crystal data and structure refinement for **1−3** at high temperature.

Empirical formula	$C_7H_{14}Cl_5N_2Sb$	$C_7H_{14}Br_5N_2Sb$	$C_7H_{14}I_5N_2Sb$
Formula weight	425.21	647.46	882.46
Temperature/K	468.00(10)	420.02(10)	364.98(10)
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*
a/Å	13.9507(9)	14.1887(13)	14.8988(7)
b/Å	8.5795(5)	8.8334(7)	9.1960(4)
c/Å	11.9950(7)	12.4471(10)	13.1209(6)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å^3	1435.68(15)	1560.1(2)	1797.68(14)
Z	4	4	4
ρ_{calc}g/cm^3	1.967	2.757	3.261
μ/mm^{-1}	2.825	14.550	10.102
F(000)	824.0	1184.0	1544.0
Crystal size/mm^3	0.04 × 0.03 × 0.02	0.04 × 0.03 × 0.02	0.04 × 0.03 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	5.838 to 61.8	6.342 to 61.978	6.062 to 61.976
Index ranges	-18 ⩽ h ⩽ 20, -11 ⩽ k ⩽ 12, -16 ⩽ l ⩽ 17	-17 ⩽ h ⩽ 20, -11 ⩽ k ⩽ 12, -15 ⩽ l ⩽ 18	-16 ≤ h ≤ 21, -10 ≤ k ≤ 13, -14 ≤ l ≤ 19
Reflections collected	9287	9727	11525
Independent reflections	1958 [R_{int} = 0.0431, R_{sigma} = 0.0358]	2019 [R_{int} = 0.1196, R_{sigma} = 0.0798]	2349 [R_{int} = 0.0278, R_{sigma} = 0.0220]
Data/restraints/parameters	1958/78/77	2019/78/76	2349/78/77
Goodness-of-fit on F^2	1.070	1.059	1.050
Final R indexes [I⩾2σ (I)]	R_1 = 0.0508, wR_2 = 0.1472	R_1 = 0.0602, wR_2 = 0.1576	R_1 = 0.0424, wR_2 = 0.1058
Final R indexes [all data]	R_1 = 0.0708, wR_2 = 0.1605	R_1 = 0.0852, wR_2 = 0.1741	R_1 = 0.0524, wR_2 = 0.1123
Largest diff. peak/hole / e Å^{-3}	0.95/-0.76	1.30/-1.18	1.63/-1.30

Table S3. Hydrogen bond lengths [Å] and bond angles [°] of **1** at 298 K.

D-H…A	D-H [Å]	H…A[Å]	D…A[Å]	D-H…A[°]
N007-H007…Cl02A[1]	0.91	2.48	3.238 (4)	141
N00G-H00N…Cl05A[2]	0.90	2.61	3.441(11)	153
N00G-H000…Cl04A[2]	0.90	2.67	3.247(8)	123

Table S4. Hydrogen bond lengths [Å] and bond angles [°] of **2** at 298 K.

D-H…A	D-H [Å]	H…A[Å]	D…A[Å]	D-H…A[°]
N007-H007…Br05A[1]	0.98	2.87	3.538 (6)	126
N007-H007…Br02A[1]	0.98	2.68	3.474(6)	138
N00D-H00K…Br04A[1]	0. 89	2.66	3.506(12)	160
N00D-H03…Br05A[1]	0. 89	2.68	3.308(9)	129

Table S5. Hydrogen bond lengths [Å] and bond angles [°] of **3** at 298 K.

D-H…A	D-H [Å]	H…A[Å]	D…A[Å]	D-H…A[°]
N1-H1…I5A[1]	0.98	2.95	3.686 (12)	133
N2-H2C…I3A[2]	0.89	3.01	3.836(18)	156
N2-H2D…I5A[2]	0.89	2.91	3.526(16)	128

Table S6. Bond Lengths and Angles for **1** at 298 K.

Sb01—Cl02	2.7596(13)	Sb01—Cl05	2.6905(19)
Sb01—Cl03	2.4407(13)	Sb01—Cl06	2.5839(17)
Sb01—Cl04	2.5099(13)	Cl03—Sb1—Cl02	87.30(5)
Cl03—Sb1—Cl04	88.40(6)	Cl03—Sb1—Cl05	89.05(5)
Cl04—Sb1—Cl02	89.33(7)	Cl04—Sb1—Cl05	174.40(5)
Cl04—Sb1—Cl06	90.50(5)	Cl05—Sb1—Cl02	88.57(6)
Cl06—Sb1—Cl02	93.01(5)	Cl06—Sb1—Cl05	87.79(5)

Table S7. Bond Lengths and Angles for **1** at 468 K.

Sb7—Cl8	2.758(3)	Sb7—Cl9	2.518(3)
Sb7—Cl10^{1}	2.526(2)	Sb7—Cl10	2.526(2)
Sb7—Cl1	2.8263(3)	Sb7—Cl1^{2}	2.8263(3)
Cl8—Sb7—Cl1^{1}	92.08(4)	Cl8—Sb7—Cl1	92.08(4)
Cl9—Sb7—Cl8	179.63(10)	Cl9—Sb7—Cl10	89.73(9)
Cl9—Sb7—Cl10^{2}	88.15(6)	Cl9—Sb7—Cl1^{1}	88.15(6)
Cl9—Sb7—Cl1	90.01(7)	Cl10^{2}—Sb7—Cl8	90.01(7)
Cl10—Sb7—Cl8	88.71(11)	Cl10—Sb7—Cl10^{2}	88.71(11)
Cl10^{2}—Sb7—Cl1^{1}	174.53(5)	Cl10—Sb7—Cl1^{1}	86.24(5)
Cl10—Sb7—Cl1	174.53(5)	Cl10^{2}—Sb7—Cl1	86.24(5)
Cl1—Sb7—Cl1^{1}	98.734(15)		

Table S8. Bond Lengths and Angles for **2** at 298 K.

Sb01—Br02	2.9025(10)	Sb01—Br03	2.6714(9
Sb01—Br04	2.7588(9)	Sb01—Br05	2.6799(10)
Sb01—Br06^{1}	2.9905(11)	Sb01—Br06	2.8508(11)
Br02—Sb01—Br06^{1}	94.04(3)	Br03—Sb01—Br02	91.46(3)
Br03—Sb01—Br04	89.75(3)	Br03—Sb01—Br05	88.45(3)
Br03—Sb01—Br06^{1}	171.87(4)	Br03—Sb01—Br06	88.68(4)
Br04—Sb01—Br02	92.95(3)	Br04—Sb01—Br06	178.30(4)
Br04—Sb01—Br06^{1}	83.99(3)	Br05—Sb01—Br02	175.23(3)
Br05—Sb01—Br04	91.82(3)	Br05—Sb01—Br06^{1}	86.57(3)
Br05—Sb01—Br06	87.47(3)	Br06—Sb01—Br02	87.76(3)
Br06—Sb01—Br06^{1}	97.511(13)		

Table S9. Bond Lengths and Angles for **2** at 420 K.

Sb01—Br02	2.9185(17)	Sb01—Br03	2.7061(12)
Sb01—Br03^{1}	2.7061(12)	Sb01—Br04	2.6730(17)
Sb01—Br05^{2}	2.9357(5)	Sb01—Br05	2.9357(5)
Br02—Sb01—Br05	90.21(2)	Br02—Sb01—Br05^{1}	90.21(2)
Br03^{2}—Sb01—Br02	91.74(4)	Br03—Sb01—Br02	91.74(4)
Br03—Sb01—Br03^{2}	88.97(6)	Br03^{2}—Sb01—Br05^{1}	175.30(3)
Br03—Sb01—Br05^{1}	86.70(3)	Br03—Sb01—Br05	175.30(3)
Br03^{2}—Sb01—Br05	86.70(3)	Br04—Sb01—Br02	177.20(6)
Br04—Sb01—Br03	90.25(5)	Br04—Sb01—Br02	90.25(5)
Br04—Sb01—Br05^{1}	87.95(4)	Br04—Sb01—Br05	87.95(4)
Br05—Sb01—Br05^{1}	97.57(2)		

Table S10. Bond Lengths and Angles for **3** at 298 K.

Sb1—I1	3.0035(11)	Sb1—I2	2.8850(10)
Sb1—I3	2.8914(12)	Sb1—I4	3.0158(13)
Sb1—I4^{1}	3.1923(14)	Sb1—I5	3.1681(10)
I1—Sb1—I4^{1}	84.60(4)	I1—Sb1—I4	178.77(4)
I1—Sb1—I5	94.07(3)	I2—Sb1—I1	89.57(4)
I2—Sb1—I3	92.20(4)	I2—Sb1—I4	89.19(4)
I2—Sb1—I4^{1}	87.57(4)	I2—Sb1—I5	173.77(4)
I3—Sb1—I1	90.22(3)	I3—Sb1—I4	89.75(4)
I3—Sb1—I4^{1}	174.82(4)	I3—Sb1—I5	92.84(3)
I4—Sb1—I4^{1}	95.426(17)	I4—Sb1—I5	87.16(3)
I5—Sb1—I4^{1}	87.74(3)		

Symmetry codes:^{1}1-x,1/2+y,1-z

Table S11. Bond Lengths and Angles for **3** at 365 K.

Sb2—I3	3.1688(9)	Sb2—I4	2.9460(7)
Sb2—I4^{1}	2.9460(7)	Sb2—I5	2.8913(10)
Sb2—I1	3.1061(4)	Sb2—I1^{2}	3.1061(4)
I4^{1}—Sb2—I3	93.44(2)	I4—Sb2—I3	93.44(2)
I4—Sb2—I4^{1}	89.63(3)	I4^{1}—Sb2—I1	176.79(2)
I4—Sb2—I1	87.427(13)	I4—Sb2—I1^{2}	176.79(2)
I4^{1}—Sb2—I1^{2}	87.427(13)	I5—Sb2—I3	173.87(4)
I5—Sb2—I4^{1}	90.91(3)	I5—Sb2—I4	90.91(3)
I5—Sb2—I1	87.86(2)	I5—Sb2—I1^{2}	87.86(2)
I1—Sb2—I3	88.019(16)	I1^{2}—Sb2—I3	88.019(16)
I1^{2}—Sb2—I1	95.487(16)		

Symmetry codes: ^{1} +x, 3/2- y, +z; ^{2}1- x,1/2+ y,1- z;

[1] G. Kresse and J. Furthmuller, *Phys. Rev. B* **1996**, *54*, 11169-11186.

[2] a) P. E. Blochl, *Phys. Rev. B* **1994**, *50*, 17953-17979; b) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys.* **1997**, *78*, 1396-1396.