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Supporting Information

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Supporting Information S1. Alexander Frebel *et al.*

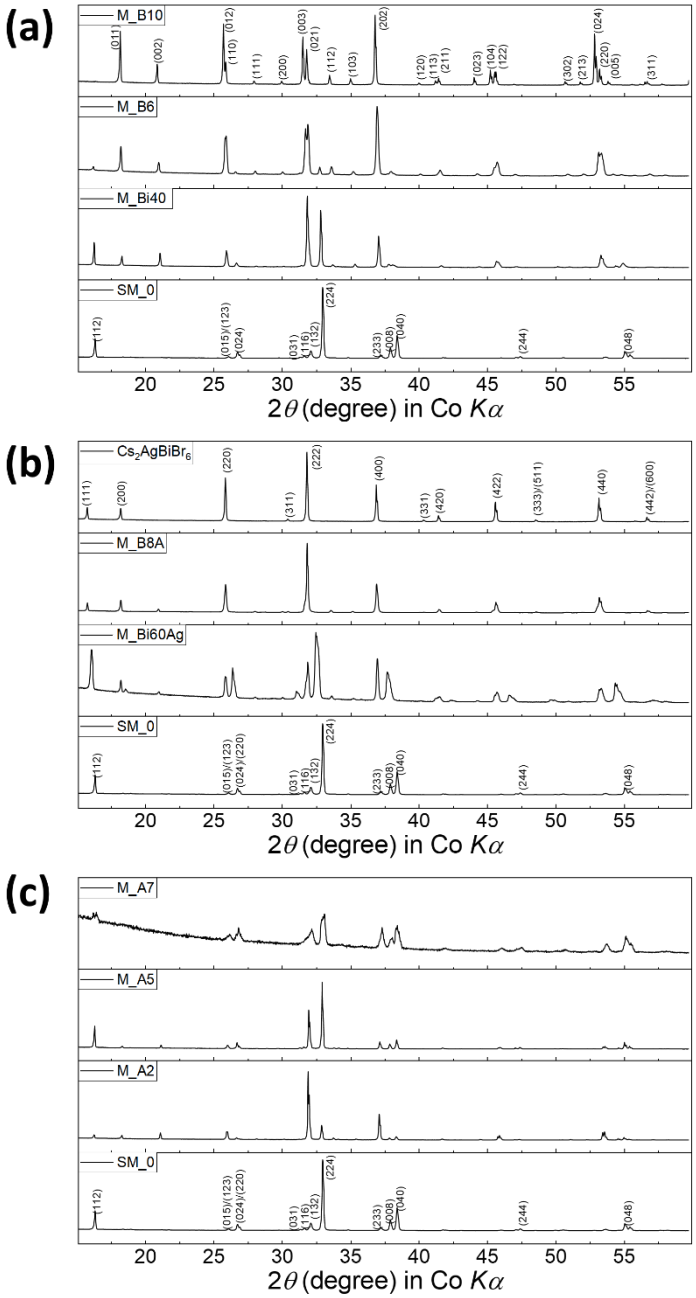

Figure S1. XRD patterns of the 3 substitution paths of Cs_2SbBr_6. **(a)** Bi substitution ending up in $Cs_3Bi_2Br_9$, **(b)** Bi+Ag substitution ending up in $Cs_2AgBiBr_6$, and **(c)** Ag substitution.

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Table S2. Unit cell parameters *a* and *b*, and tetragonality *c/a* derived from LeBail fits (space group: $I4_1/amd$).

	a (Å)	*c* (Å)	*c/a*
SM_0	10.845(5)	21.967(1)	2.025(4)
M_B4	10.905(3)	21.989(1)	2.016(3)
M_B6	10.904(4)	21.959(8)	2.013(8)
M_B6A	10.939(4)	21.941(0)	2.005(6)
M_A2	10.849(3)	21.972(3)	2.025(2)
M_A5	10.848(8)	21.970(7)	2.025(1)
M_A7	10.850(1)	21.956(1)	2.023(5)

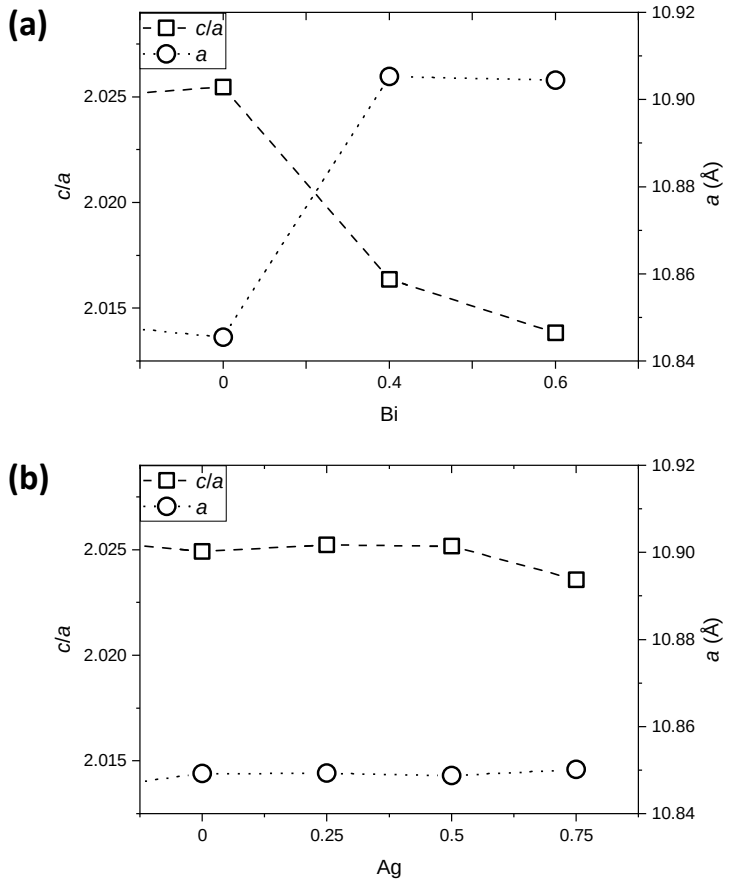

Figure S2. The by Le Bail fit determined lattice parameter *a* and the unit cell parameter ratio *c/a* of the **(a)** Bi substituted samples and **(b)** Ag substituted samples.

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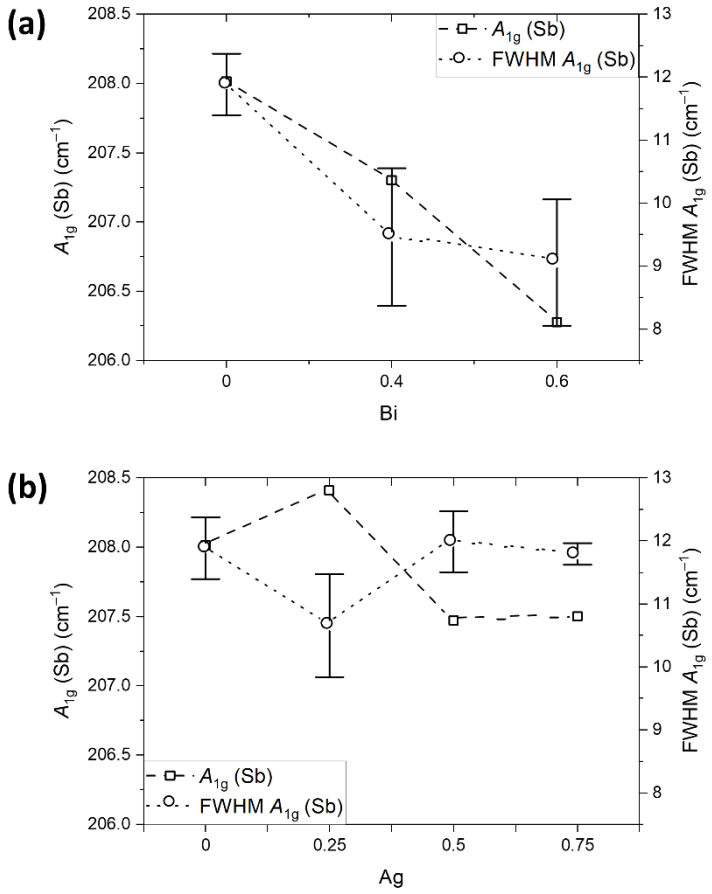

Figure S3. Average band position and broadening of the A_{1g} band of the Sb-Br bondings of the **(a)** Bi substituted samples and **(b)** Ag substituted samples. **(c)** Position and broadening of several crystals containing the Cs_2SbBr_6 and $Cs_3Sb_2Br_9$ phase.

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Supporting Information S4. In order to show a relation between the oxidation state of Sb, both the position and broadening of A_{1g} bands of both possible structures Cs_2SbBr_6 (M_0 black) and $Cs_3Sb_2Br_6$ (M_0 yellow) together with the Bi substituted samples are summarized in **Figure S4**. It can be shown that due to the dominance of Sb^{3+} the A_{1g} band is shifted towards higher wavenumber. Additionally, the FWHM is reduced. The sample M_0 black representing the Cs_2SbBr_6 structure have the band placed at lower wavenumber and show compared to the other samples the highest broadening, due to the coexistence of two different oxidation states. By Bi substitution the wavenumber of the A_{1g} band is further reduced and the broadening shows in the samples without Ag a lower value. A plausible reason for the shift to lower wavenumber is the larger ion size of Bi^{3+} compared to Sb^{3+}.[17,20]

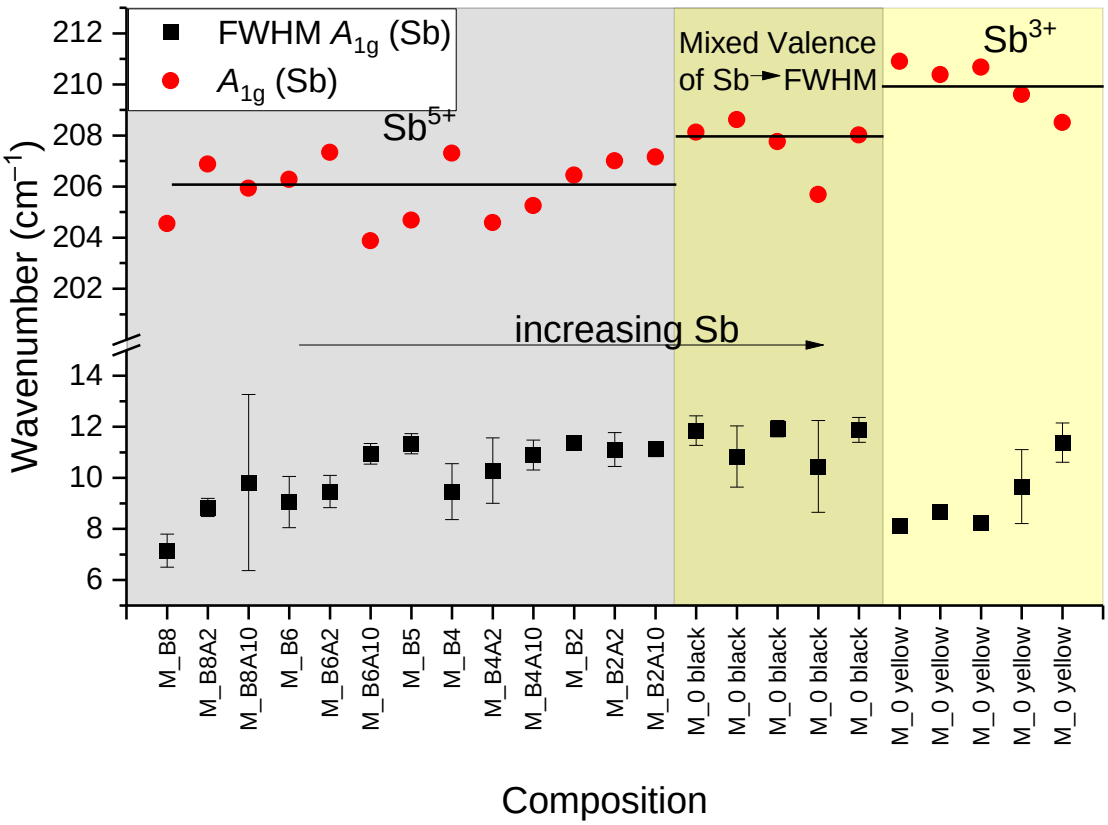

Figure S4. Position and broadening of the A_{1g} band of the Sb-Br bonds of crystals containing the Cs_2SbBr_6 and $Cs_3Sb_2Br_9$ phase.

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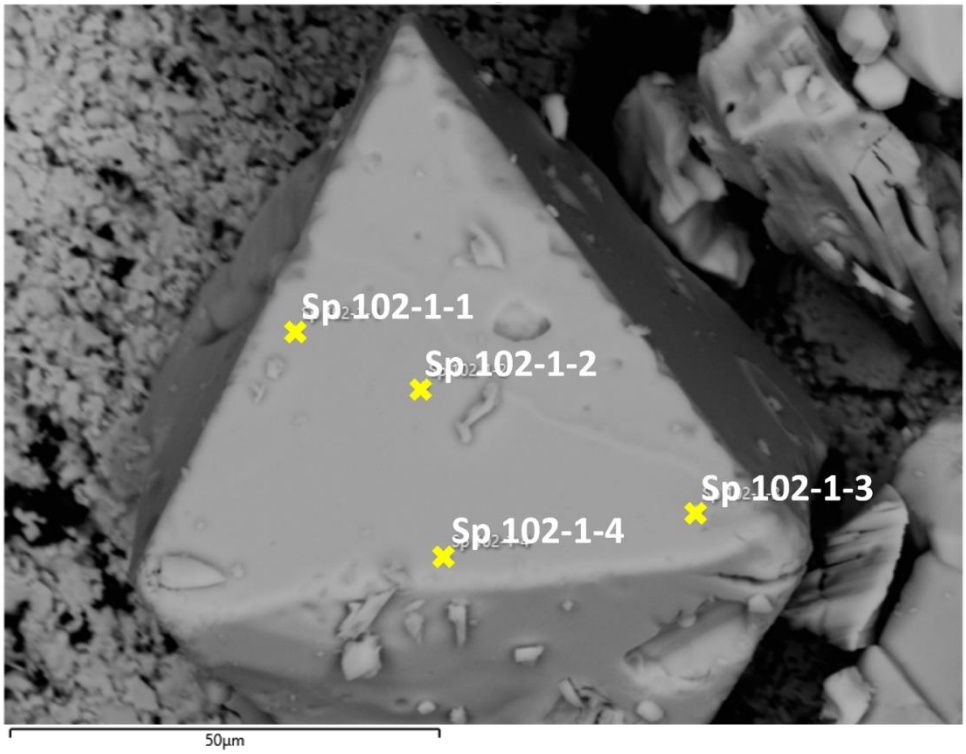
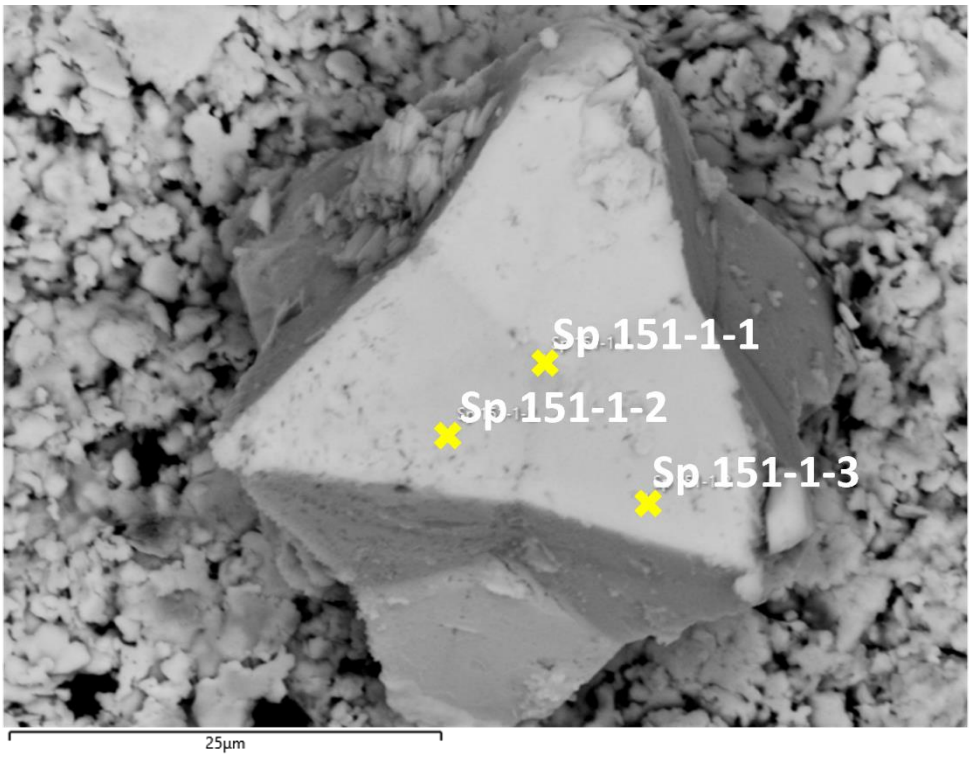
Additional SEM and EDX measurements.



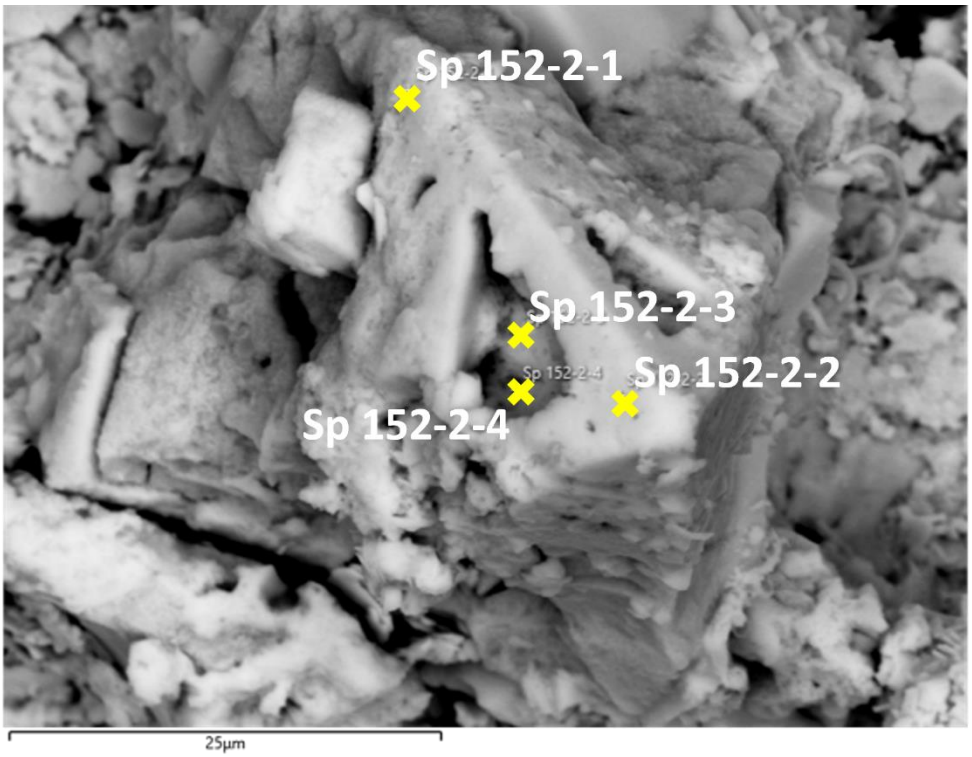
Spectrum Label	Sp 102-1-1	Sp 102-1-2	Sp 102-1-3	Sp 102-1-4
Cs	22.24	22.29	22.72	22.45
Sb	11.41	11.35	11.71	11.51
Bi	0	0	0	0
Ag	0	0	0.21	0
Br	66.35	66.35	65.37	66.05

Figure S5(a) SEM and EDX measurement of sample M_0. Atomic ratios are given in the table.



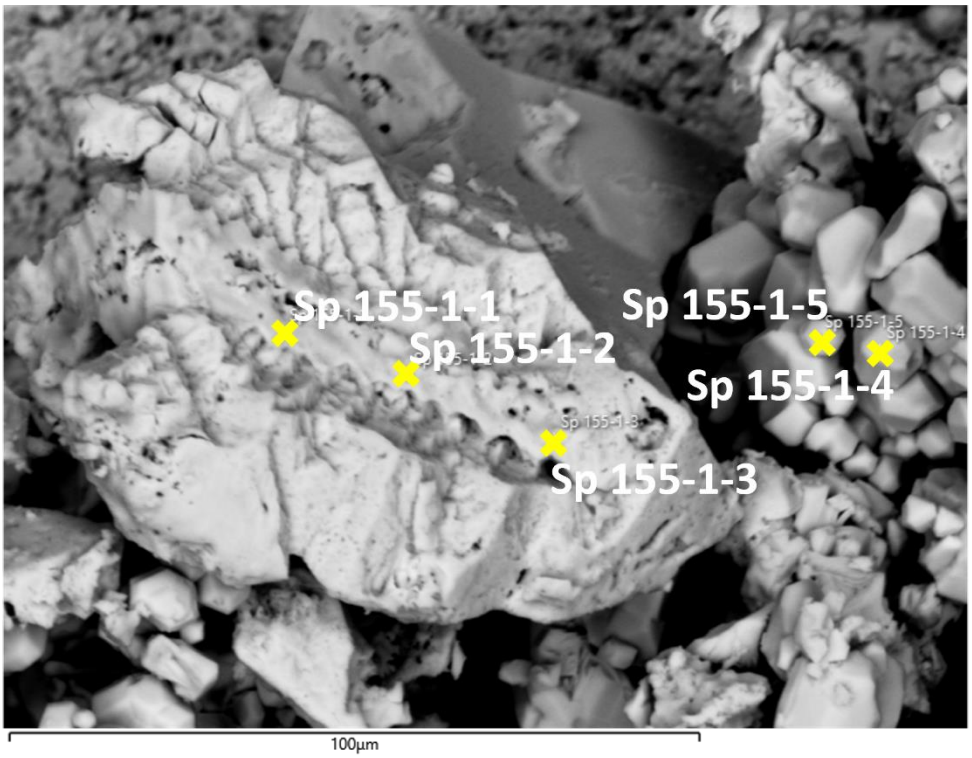
Spectrum Label	Sp 151-1-1	Sp 151-1-2	Sp 151-1-3
Cs	21.76	22.39	25.05
Sb	5.07	5.56	6.16
Bi	5.98	6.65	6.15
Ag	1.3	2.4	2.52
Br	65.89	63.01	60.13

Figure S5(b) SEM and EDX measurement of sample M_B6A2. Atomic ratios are given in the table.



Spectrum Label	Sp 152-2-1	Sp 152-2-2	Sp 152-2-3	Sp 152-2-4
Cs	35.13	26.48	27.88	29.28
Sb	13.13	7.24	5.9	5.85
Bi	8.93	5.17	9.4	9.35
Ag	1.88	0.77	0.45	0.42
Br	40.92	60.31	56.38	55.1

Figure S5(c) SEM and EDX measurement of sample M_B6A. Atomic ratios are given in the table.



Spectrum Label	Sp 155-1-1	Sp 155-1-2	Sp 155-1-3	Sp 155-1-4	Sp 155-1-5
Cs	16.62	21	20.6	21.59	21.53
Sb	4.91	6.31	6.35	11.28	11.23
Bi	4.96	4.96	5.09	3.32	3.55
Ag	0.83	1.14	1.68	0.36	0.63
Br	72.67	66.59	66.29	63.46	63.06

Figure S5(d) SEM and EDX measurement of sample M_B4A. Atomic ratios are given in the table.