Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2021

Structural diversities in centrosymmetric $La_8S_4Cl_8La_{12}S_8Cl_4[SbS_3]_8$ and non-centrosymmetric $Ln_{12}S_8Cl_8[SbS_3]_4$ (Ln = La and Ce): Syntheses, crystal and electronic structures, and optical properties

Hua-Jun Zhao,[†, ‖ *] Peng-Fei Liu,[‡, §] and Li-Ming Wu.[⊥*]

*E-mail for Hua-Jun Zhao: cszzl772002@yeah.net

*E-mail for Li-Ming Wu: wlm@bnu.edu.cn

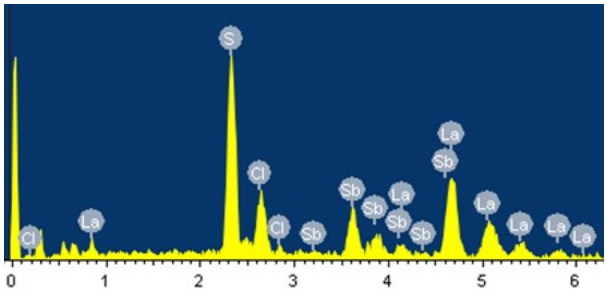

Figure S1. The EDX spectrum of $La_8S_4Cl_8La_{12}S_8Cl_4[SbS_3]_8$.

point-1

Element	Weight%	Atomic%
S K	18.36	41.57
Cl K	9.38	19.20
Sb L	19.87	11.85
La L	52.39	27.38
Totals	100.00	

point-2

Element	Weight%	Atomic%
S K	19.39	43.17
Cl K	9.31	18.74
Sb L	20.03	11.74
La L	51.28	26.35
Totals	100.00	

point-3

Element	Weight%	Atomic%
S K	19.24	43.30
Cl K	8.85	18.02
Sb L	17.99	10.67
La L	53.92	28.01
Totals	100.00	

point-4

Element	Weight%	Atomic%
S K	20.42	44.62
Cl K	9.43	18.64
Sb L	19.08	10.98
La L	51.07	25.76
Totals	100.00	

point-5

Element	Weight%	Atomic%
S K	20.39	44.65
Cl K	9.36	18.53
Sb L	18.12	10.45
La L	52.14	26.36
Totals	100.00	

The atomic percent obtained by EDX results and those based on the single crystal data.

Element	average EDX	standard deviations	crystal
S K	43.46	1.14	47.37
Cl K	18.63	0.38	15.79
Sb L	11.14	0.56	10.53
La L	26.77	0.81	26.32

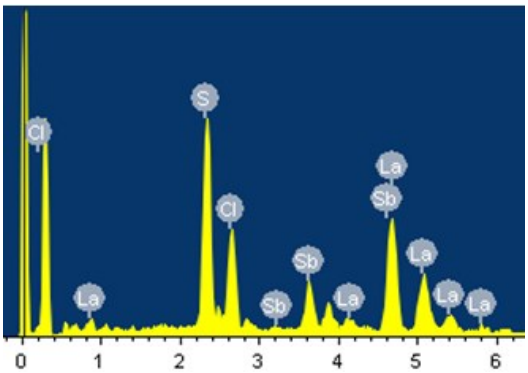

Figure S2. The EDX spectrum of $La_{12}S_8Cl_8[SbS_3]_4$.

point-1

Element	Weight%	Atomic%
S K	16.12	36.22
Cl K	12.74	25.89
Sb L	13.75	8.13
La L	57.39	29.76
Totals	100.00	

Point-2

Element	Weight%	Atomic%
S K	16.44	36.00
Cl K	14.02	27.76
Sb L	15.22	8.78
La L	54.32	27.46
Totals	100.00	

Point-3

Element	Weight%	Atomic%
S K	15.97	35.33
Cl K	13.87	27.75
Sb L	15.18	8.85
La L	54.98	28.08
Totals	100.00	

Point-4

Element	Weight%	Atomic%
S K	14.61	32.29
Cl K	15.42	30.84
Sb L	16.10	9.37
La L	53.87	27.49
Totals	100.00	

Point-5

Element	Weight%	Atomic%
S K	16.85	37.79
Cl K	11.89	24.12
Sb L	16.38	9.68
La L	54.89	28.42
Totals	100.00	

The atomic percent obtained by EDX results and those based on the single crystal data.

Element	average EDX	standard deviations	crystal
S K	35.53	1.81	45.45
Cl K	27.27	2.24	18.18
Sb L	8.96	0.53	9.09
La L	28.24	0.84	27.27

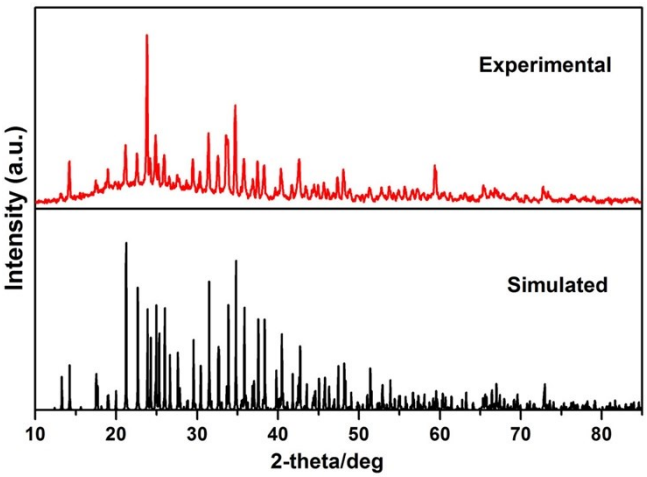

Figure S3. The experimental and simulated X-ray powder diffraction patterns of $La_8S_4Cl_8La_{12}S_8Cl_4[SbS_3]_8$. (Some peaks on the experimental patterns don't match those on the simulated ones are due to the effect of preferred orientation.)

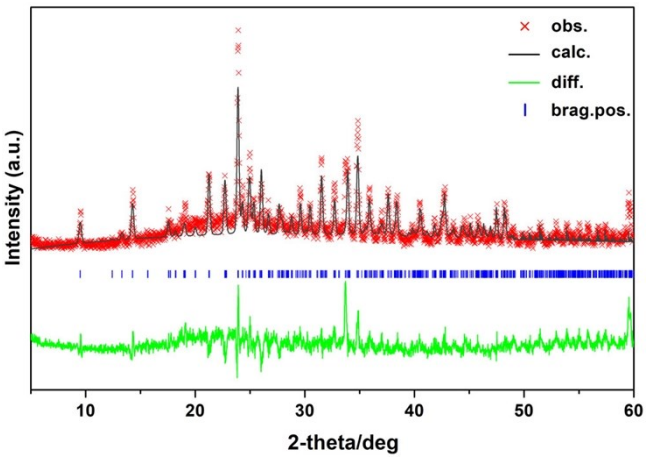

Figure S4. The powder XRD of $La_8S_4Cl_8La_{12}S_8Cl_4[SbS_3]_8$ with the observed (×) and calculated (black line) intensities, and the difference results (green line).

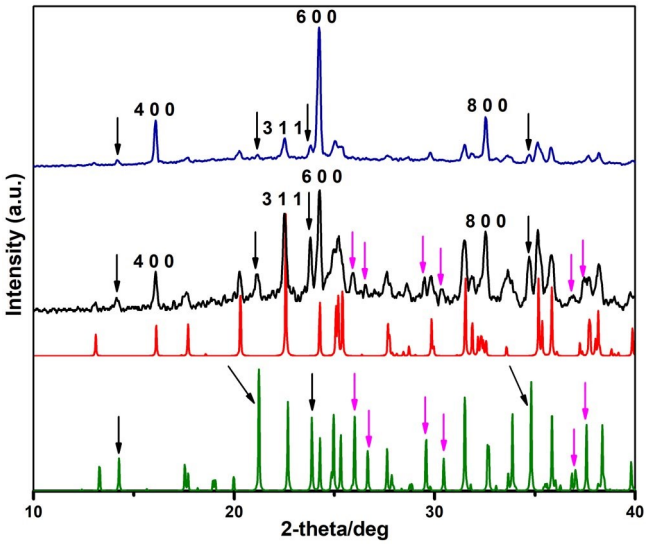

Figure S5. The experimental X-ray powder diffraction patterns of $La_{12}S_8Cl_8[SbS_3]_4$ obtained in different temperature: 800 ℃ (blue) and 750 ℃ (black) and simulated X-ray powder diffraction patterns of $La_{12}S_8Cl_8[SbS_3]_4$ (red) and $La_8S_4Cl_8La_{12}S_8Cl_4[SbS_3]_8$ (green). The peaks marked with arrows are due to the coexistence of $La_8S_4Cl_8La_{12}S_8Cl_4[SbS_3]_8$. Note that when the temperature was increased to 800℃, six peaks marked with pink arrows disappeared and the intensities of four peaks marked with black arrows signifficantly decreased, indicating the percentage of the $La_8S_4Cl_8La_{12}S_8Cl_4[SbS_3]_8$ impurity are reduce dramatically. However, the experimental densities of 4 0 0, 6 0 0, and 8 0 0 increased, especially the density of 6 0 0 is nearly four times that of 3 1 1 which is the peak with the highest intensity in simulated powder XRD pattern of $La_{12}S_8Cl_8[SbS_3]_4$ (red), which can be attributed to the effect of preferred orientation.)

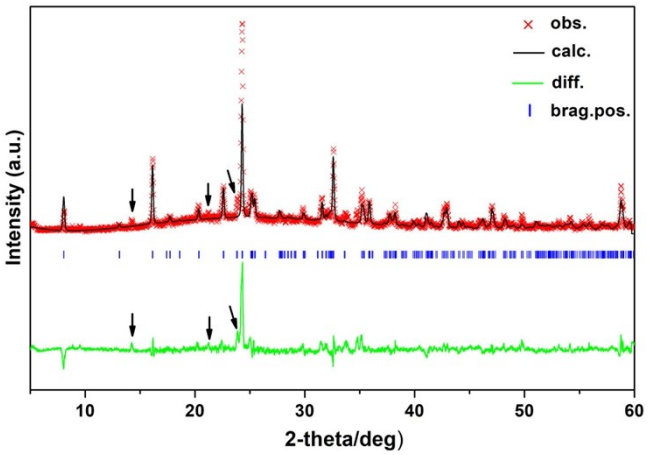

Figure S6. The powder XRD of $La_{12}S_8Cl_8[SbS_3]_4$ with the observed (×) and calculated (black line) intensities, and the difference results (green line). Peaks marked with black arrows are due to the minor impurity.

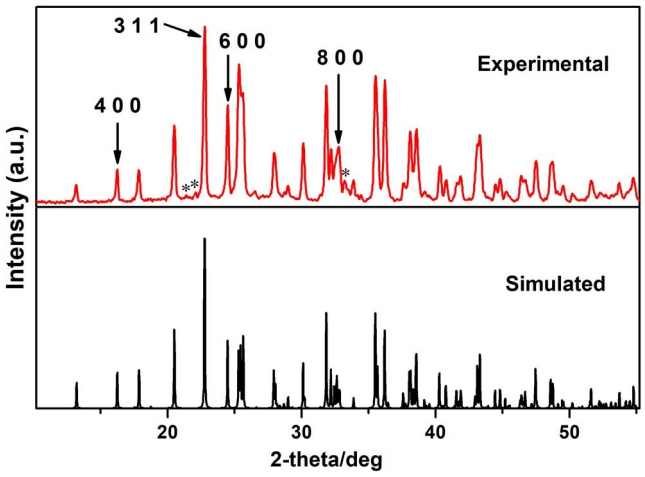

Figure S7. The experimental and simulated X-ray powder diffraction patterns of $Ce_{12}S_8Cl_8[SbS_3]_4$. The peaks marked with asterisks are due to small amounts of unknown impurities. (Note that densities of 4 0 0, 6 0 0, 8 0 0, and 311 in experimental powder XRD pattern compare well with the simulated ones, which indicate the absence of preferred orientation in this compound.)

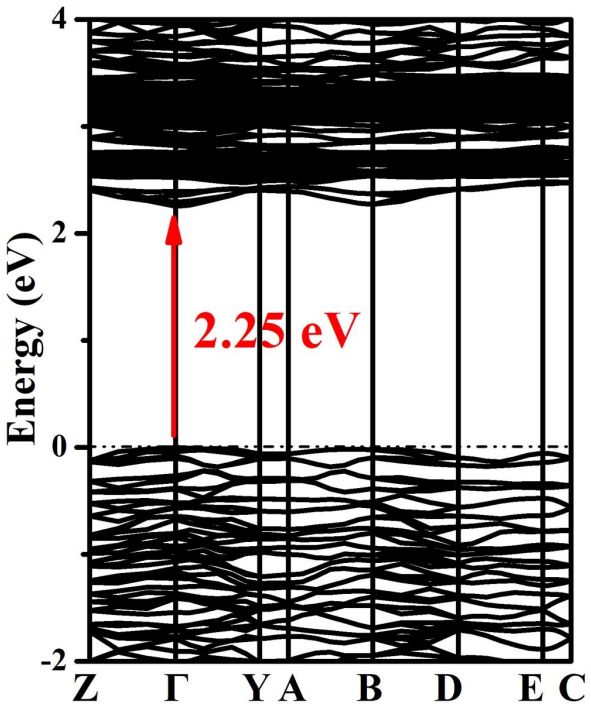

Figure S8. Full band structures of $La_{12}S_8Cl_8[SbS_3]_4$.

Table S1. Atomic coordinates and equivalent isotropic displacement parameters of $La_8S_4Cl_8La_{12}S_8Cl_4[SbS_3]_8$

atom	symmetry	x	y	z	U(eq)	BVS
La1	*8e*	0.20491(6)	0.71875(6)	0.16116(2)	0.01092(17)	2.940
La2	*4d*	0.21051(9)	0.30591(9)	0.2500	0.00906(19)	2.970
La3	*8e*	0.28479(6)	0.45859(6)	0.04198(2)	0.00987(17)	2.985
Sb1	*8e*	0.30501(7)	0.16931(7)	0.13208(2)	0.01102(18)	3.110
S1	*8e*	0.0586(3)	0.0186(2)	0.20352(5)	0.0105(4)	2.008
S2	*4c*	0.5516(4)	0.2500	0	0.0097(5)	2.164
S3	*8e*	0.4247(3)	0.3774(3)	0.17868(5)	0.0111(4)	2.149
S4	*8e*	0.0754(3)	0.3979(3)	0.11183(5)	0.0110(4)	2.071
S5	*8e*	0.5597(3)	0.2507(3)	0.09140(5)	0.0116(4)	2.019
Cl1	*4d*	0.6211(5)	0.1695(4)	0.2500	0.0208(6)	0.784
Cl2	*8e*	0.1120(3)	0.0918(3)	0.03501(5)	0.0177(4)	0.866

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

Table S2. Atomic coordinates and equivalent isotropic displacement parameters of $La_{12}S_8Cl_8[SbS_3]_4$.

atom	symmetry	x	y	z	U(eq)	BVS
La1	*4a*	0.77527(3)	0.70317(8)	0.97434(7)	0.00989(14)	2.982
La2	*4a*	0.92858(2)	0.70979(9)	0.62823(6)	0.00815(13)	2.965
La3	*4a*	0.57335(3)	0.78612(9)	0.61699(6)	0.00895(14)	2.982
Sb1	*4a*	0.72811(3)	0.80597(10)	0.40387(9)	0.01337(16)	3.033
S1	*4a*	0.84795(14)	0.4447(4)	0.8070(4)	0.0093(5)	1.997
S2	*4a*	0.50334(14)	0.9483(3)	0.8750(4)	0.0089(4)	2.170
S3	*4a*	069247(12)	0.5757(4)	0.6146(4)	0.0103(6)	2.079
S4	*4a*	0.65856(13)	0.9387(4)	0.9513(4)	0.0107(6)	2.000
S5	*4a*	0.80826(13)	0.9278(4)	0.6496(4)	0.0104(6)	2.067
Cl1	*4a*	0.93751(14)	0.8876(4)	0.9999(4	0.0187(6)	0.787
Cl2	*4a*	0.55981(12)	0.3940(4)	0.7467(4)	0.0179(6)	0.864

Table S3. Atomic coordinates and equivalent isotropic displacement parameters of $Ce_{12}S_8Cl_8[SbS_3]_4$.

atom	symmetry	x	y	z	U(eq)	BVS
Ce1	*4a*	0.16330(3)	0.29747(8)	0.02663(10)	0.01278(18)	3.021
Ce2	*4a*	0.00943(3)	0.28947(8)	0.37059(8)	0.00852(17)	3.010
Ce3	*4a*	0.36448(3)	0.21400(8)	0.38380(8)	0.00885(17)	3.038
Sb1	*4a*	0.20969(4)	0.19288(10)	0.59877(12)	0.0127(2)	3.067
S1	*4a*	0.09005(15)	0.5558(4)	0.1924(5)	0.0096(5)	2.005
S2	*4a*	0.43483(15)	0.0525(3)	0.1253(5)	0.0084(5)	2.187
S3	*4a*	0.24571(13)	0.4242(4)	0.3856(5)	0.0106(6)	2.133
S4	*4a*	0.28018(14)	0.0625(4)	0.0492(4)	0.0099(6)	2.050
S5	*4a*	0.12933(14)	0.0721(4)	0.3496(5)	0.0101(6)	2.097
Cl1	*4a*	-0.00003(15)	0.1118(4)	0.0000(5)	0.0175(6)	0.809
Cl2	*4a*	0.37796(14)	0.6071(4)	0.2541(5)	0.0168(6)	0.869

Table S4. Selected bond lengths (Å) of $La_8S_4Cl_8La_{12}S_8Cl_4[SbS_3]_8$.

La1-S1	2.841(2)
La1-S1	2.8607(19)
La1-S3	2.947(2)
La1-S3	2.9753(19)
La1-S4	3.0022(19)
La1-S4	3.0829(19)
La1-S5	3.101(2)
La2-Cl1	2.867(3)
La2-S1	2.8983(19)
La2-S1	2.8984(19)
La2-S1 ×2	2.999(2)
La2-Cl1	3.085(3)
La2-S3 ×2	3.1058(19)
La3-S2	2.8559(12)
La3-S2	2.8795(19)
La3-Cl2	2.912(2)
La3-Cl2	2.996(2)
La3-S5	2.9982(19)
La3-S4	3.0300(19)
La3-S5	3.073(2)
La3-Cl2	3.141(2)
Sb1-S4	2.4343(19)
Sb1-S5	2.435(2)
Sb1-S3	2.4412(19)

Table S5. Selected bond lengths (Å) of $La_{12}S_8Cl_8[SbS_3]_4$.

La1-S1	2.834(3)
La1-S1	2.860(3)
La1-S5	2.947(3)
La1-S3	2.984(3)
La1- S5	3.004(3)
La1- S3	3.059(3)
La1- S4	3.072(3)
La2-S2	2.875(3)
La2-S2	2.900(3)
La2-S1	2.901(3)
La2-Cl1	2.924(3)
La2-Cl1	3.017(3)
La2-S1	3.020(3)
La2-S5	3.118(3)
La2-Cl2	3.191(3)
La3-S2	2.841(3)
La3-S2	2.852(3)
La3-Cl2	2.916(3)
La3-Cl2	2.964(3)
La3-S4	3.012(3)
La3-S3	3.045(3)
La3-S4	3.087(3)
La3-Cl1	3.251(3)
Sb1-S3	2.440(3)
Sb1-S4	2.441(3)
Sb1-S5	2.457(3)

Table S6. Selected bond lengths (Å) of $Ce_{12}S_8Cl_8[SbS_3]_4$.

Ce1-S1	2.808(3)
Ce1-S1	2.846(4)
Ce1-S5	2.932(3)
Ce1-S3	2.950(3)
Ce1-S5	2.975(3)
Ce1-S3	3.023(4)
Ce1-S4	3.046(3)
Ce2-S2	2.851(3)
Ce2-S2	2.874(3)
Ce2-S1	2.879(4)
Ce2-Cl1	2.887(3)
Ce2-Cl1	2.984(3)
Ce2-S1	2.994(3)
Ce2-S5	3.079(3)
Ce2-Cl2	3.162(3)
Ce3-S2	2.818(3)
Ce3-S2	2.833(3)
Ce3-Cl2	2.884(3)
Ce3-Cl2	2.943(3)
Ce3-S4	2.974(3)
Ce3-S3	3.011(3)
Ce3-S4	3.049(3)
Ce3-Cl1	3.217(3)
Sb1-S3	2.436(3)
Sb1-S4	2.437(3)
Sb1-S5	2.452(3)