Supporting Information for

Structural Modification from Centrosymmetric $Rb_4Hg_2Ge_2S_8$ to Noncentrosymmetric $(Na_3Rb)Hg_2Ge_2S_8$: Mixed Alkali-metals Strategy for Infrared Nonlinear Optical Material Design

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1. Syntheses of $Rb_4Hg_2Ge_2S_8$.

The single crystals of $Rb_4Hg_2Ge_2S_8$ were prepared by high-temperature solid-state reaction of Na_2S (78 mg,), HgS (233 mg), GeS_2 (137 mg) and RbCl (500 mg), which was added as cation exchanger and flux. The mixture was thoroughly ground in an agate mortar and loaded into silica tubes. The silica tubes were sealed with oxy-hydrogen flame under a high vacuum of 10^{-3} Pa, and were then placed in a computer-controlled furnace. The following temperature control program was executed: heating from room temperature to 1073K in 10 hours, kept for 3 days, then cooling slowly to room temperature with a ramp rate of 3 K/h. Greenish transparent block crystals were obtained in approximately 50% yield based on Hg. We tried to synthesize the polycrystalline sample $Rb_4Hg_2Ge_2S_8$ by a similar strategy but failed.

2. Figure S1.

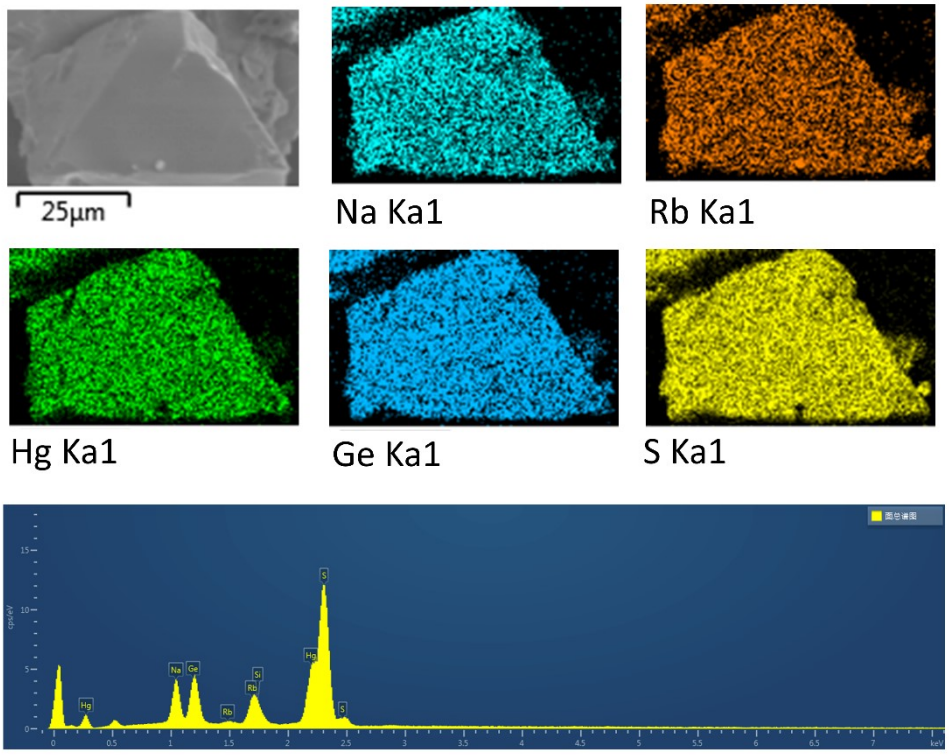

Figure S1. The SEM pictures and EDS results of $(Na_3Rb)Hg_2Ge_2S_8$.

3. Figure S2.

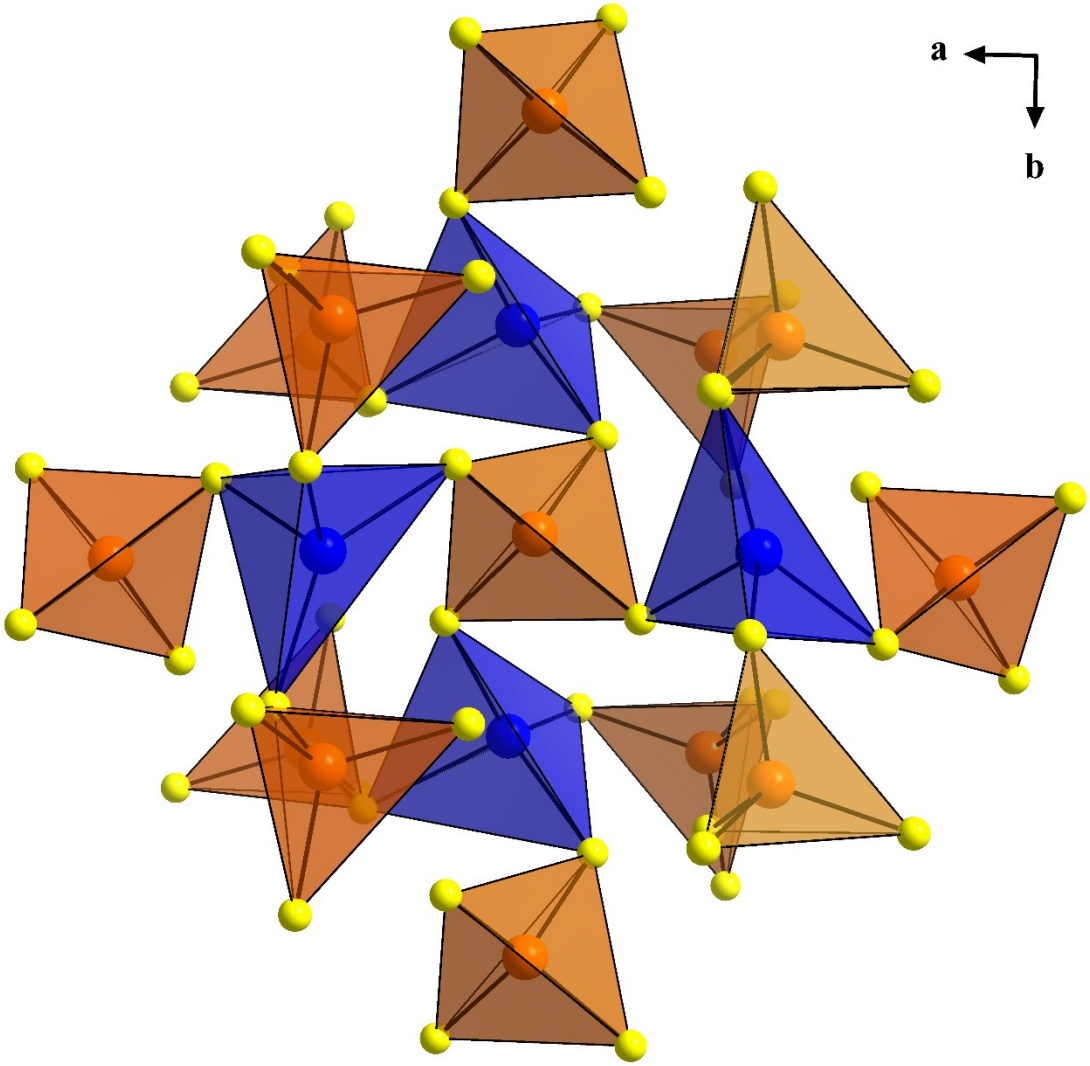

Figure S2. 3D covalent framework structure $[HgGeS_4]^{2-}$ of $(Na_3Rb)Hg_2Ge_2S_8$.

4. **Figure S3.**

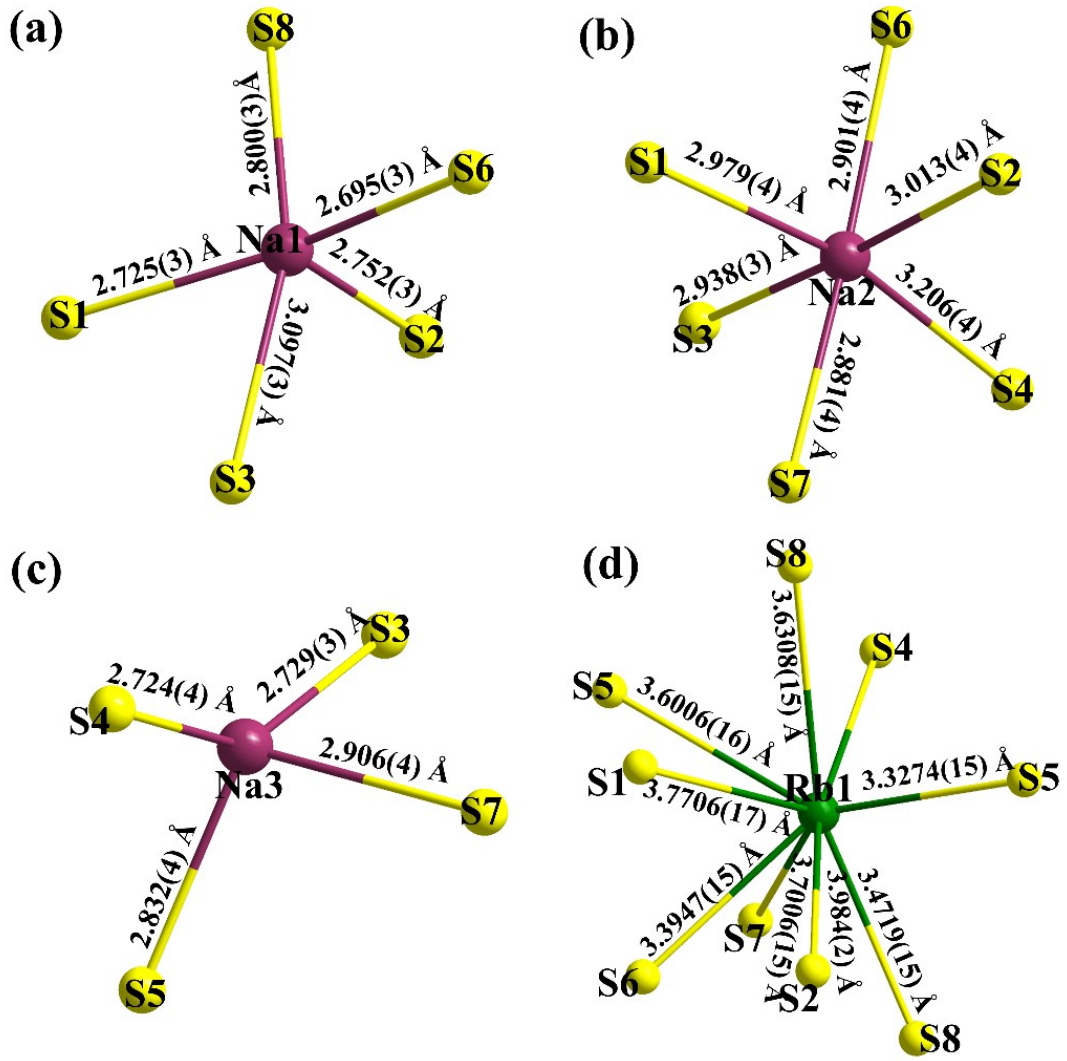

Figure S3. (a) the coordination environments of Na1 atoms, (b) Na2 atoms, (c) Na3 atoms and (d) Rb1 atoms in $(Na_3Rb)Hg_2Ge_2S_8$.

5. Figure S4.

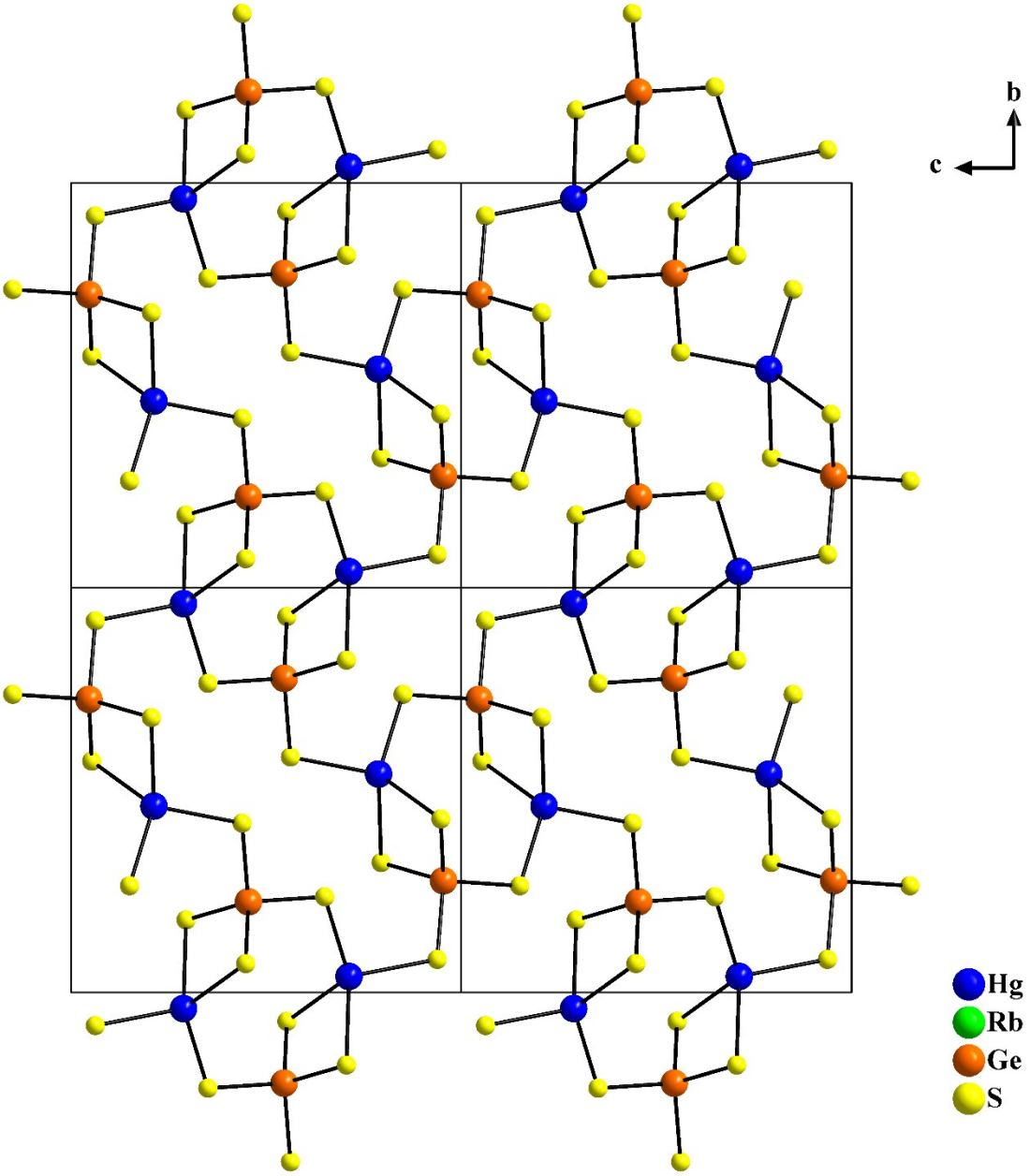

Figure S4. 2D layered structure $\{[HgGeS_4]^{2-}\}_\infty$ in the bc plane of $Rb_4Hg_2Ge_2S_8$.

6. **Table S1** Atomic coordinates, equivalent isotropic displacement parameters and bond valence sums (BVS) for $Rb_4Hg_2Ge_2S_8$.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq} (Å^2) [a]	BVS
Hg1	4e	-0.12548(2)	0.95919(2)	0.28943(2)	0.02627(7)	2.04
Ge1	4e	0.14265(5)	0.77624(4)	0.5462(4)	0.01402(9)	4.10
Rb1	4e	0.12779(5)	0.48431(4)	0.26205(4)	0.02614(10)	1.20
Rb2	4e	0.63657(5)	0.72637(4)	0.50102(4)	0.02795(10)	0.93
S1	4e	0.02136(13)	0.76424(10)	0.35068(10)	0.0227(2)	–2.11
S2	4e	−0.03318(12)	0.82081(9)	0.7046(10)	0.0195(2)	–1.97
S3	4e	0.32719(12)	0.92881(9)	0.5536(10)	0.019(2)	–2.12
S4	4e	0.25032(13)	0.58284(9)	0.56304(10)	0.0214(2)	–2.05

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

7. **Table S2** Atomic coordinates, equivalent isotropic displacement parameters and bond valence sums (BVS) for $(Na_3Rb)Hg_2Ge_2S_8$.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq} (Å^2) [a]	BVS
Hg1	4a	0.22816(2)	0.95221(4)	0.49736(2)	0.02681(7)	2.15
Hg2	4a	0.48729(2)	0.50932(4)	0.73545(2)	0.02708(7)	2.15
Ge1	4a	0.25481(6)	0.46081(10)	0.36626(3)	0.01228(13)	4.16
Ge2	4a	0.47576(5)	0.99170(8)	0.61673(3)	0.01205(13)	4.04
Na1	4a	0.47381(18)	0.5037(4)	0.47367(18)	0.0297(7)	1.26
Na2	4a	0.5100(3)	0.9965(5)	0.37045(19)	0.0379(9)	0.92
Na3	4a	0.3671(3)	−0.0475(5)	0.2613(2)	0.0472(10)	1.01
Rb1	4a	0.23051(5)	0.4120(11)	0.61936(4)	0.03025(16)	0.91
S1	4a	0.33262(11)	0.2228(2)	0.4316(8)	0.0246(3)	–2.06
S2	4a	0.15076(11)	0.6722(2)	0.4235(10)	0.0312(4)	–2.09
S3	4a	0.38022(10)	0.6532(2)	0.32619(8)	0.0215(3)	–2.05
S4	4a	0.16107(11)	0.3035(2)	0.28389(8)	0.0242(3)	–2.13
S5	4a	0.31459(9)	0.8900(2)	0.61824(8)	0.0209(3)	–2.08
S6	4a	0.5533(10)	0.8602(2)	0.51982(7)	0.0174(3)	–2.11
S7	4a	0.53783(10)	0.8685(2)	0.7229(7)	0.0196(3)	–2.06
S8	4a	0.5027(11)	1.32109(19)	0.61202(8)	0.0206(3)	–2.03

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

8. Table S3 Selected band distances (Å) and band angles (°) for $Rb_4Hg_2Ge_2S_8$.

Hg1–S1	2.4609(10)	Rb1–S3^{2}	3.3600(11)
Hg1–S2^{5}	2.6601(10)	Rb1–S3^{12}	3.2944(11)
Hg1–S3^{5}	2.5835(10)	Rb1–S4	3.3878(11)
Hg1–S4^{2}	2.5551(10)	Rb1–S4^{6}	3.6298(12)
Ge1–S1	2.2245(11)	Rb2–S1^{7}	3.6924(11)
Ge1–S2	2.2122(10)	Rb2–S1^{10}	3.5116(12)
Ge1–S3	2.2036(10)	Rb2–S2^{10}	3.5307(11)
Ge1–S4	2.2304(10)	Rb2–S2^{11}	3.3554(11)
Rb1–S1	3.2141(11)	Rb2–S3	3.3468(10)
Rb1–S1^{12}	3.8591(12)	Rb2–S3^{9}	3.6997(11)
Rb1–S2^{6}	3.3338(11)	Rb2–S4	3.5459(12)
Rb1–S2^{11}	3.4920(11)	Rb2–S4^{8}	3.4588(11)
S3^{5}—Hg1—S2^{5}	83.91(3)	S3—Ge1—S2	105.11(4)
S4^{2}—Hg1—S3^{5}	112.98(3)	S3—Ge1—S4	113.68(4)
S4^{2}—Hg1—S2^{5}	111.25(3)	S3—Ge1—S1	111.80(4)
S1—Hg1—S3^{5}	122.33(3)	S2—Ge1—S4	113.17(4)
S1—Hg1—S2^{5}	119.47(3)	S2—Ge1—S1	112.44(4)
S1—Hg1—S4^{2}	105.85(3)	S1—Ge1—S4	100.90(4)

Symmetry codes: (1)-1+*X*, +*Y*, +*Z*; (2)-1/2+*X*, 3/2-*Y*, -1/2+*Z*; (3)1/2-*X*, 1/2+*Y*, 1/2-*Z*; (4)-1/2-*X*, 1/2+*Y*, 1/2-*Z*; (5)-*X*, 2-*Y*, 1-*Z*; (6)-*X*, 1-*Y*, 1-*Z*; (7)1+*X*, +*Y*, +*Z*; (8)1/2+*X*, 3/2-*Y*, 1/2+*Z*; (9)1-*X*, 1-*Y*, 1-*Z*; (10)1-*X*, 2-*Y*, 1-*Z*; (11)1/2+*X*, 3/2-*Y*, -1/2+*Z*; (12)1/2-*X*, -1/2+*Y*, 1/2-*Z*; (13)-1/2+*X*, 3/2-*Y*, 1/2+*Z*.

9. Table S4 Selected band distances (Å) and band angles (°) for $(Na_3Rb)Hg_2Ge_2S_8$.

Hg1–S1^5	2.5410(14)	Na1^5–S8	2.800(3)
Hg1–S2	2.4896(15)	Na2^2–S1	2.979(4)
Hg1–S5	2.4973(14)	Na2^6–S2	3.013(4)
Hg1–S6^6	2.6408(13)	Na2–S3	2.938(3)
Hg2–S3^3	2.6207(14)	Na2^7–S4	3.206(4)
Hg2–S4^4	2.5304(14)	Na2–S6	2.901(4)
Hg2–S7	2.4595(13)	Na2^8–S7	2.881(4)
Hg2–S8^2	2.5588(13)	Na3^5–S3	2.729(3)
Ge1–S1	2.2097(15)	Na3–S4	2.724(4)
Ge1–S2	2.2067(15)	Na3^9–S5	2.832(4)
Ge1–S3	2.2005(15)	Na3^3–S7	2.906(4)
Ge1–S4	2.1921(15)	Rb1–S1	3.7706(17)
Ge2–S5	2.2232(14)	Rb1–S2	3.984(2)
Ge2–S6	2.2037(14)	Rb1–S4^4	3.4614(17)
Ge2–S7	2.2372(14)	Rb1–S5^2	3.6006(16)
Ge2–S8	2.1923(14)	Rb1–S5	3.3274(15)
Na1–S1	2.725(3)	Rb1–S6^7	3.3947(15)
Na1^7–S2	2.752(3)	Rb1–S7^7	3.7006(15)
Na1–S3	3.097(3)	Rb1–S8^2	3.6308(15)
Na1–S6	2.695(3)	Rb1–S8^6	3.4719(15)
S5—Hg1—S6^6	109.78(4)	S3—Ge1—S1	103.55(6)
S5—Hg1—S1^5	106.11(4)	S3—Ge1—S2	105.00(6)
S1^5—Hg1—S6^6	102.55(4)	S4—Ge1—S3	117.95(6)
S2—Hg1—S6^6	94.03(5)	S4—Ge1—S1	106.91(6)
S2—Hg1—S5	122.35(5)	S4—Ge1—S2	105.41(6)
S2—Hg1—S1^5	119.09(6)	S2—Ge1—S1	118.75(7)
S7—Hg2—S8^2	111.15(4)	S6—Ge2—S7	111.81(5)
S7—Hg2—S3^3	105.55(4)	S6—Ge2—S5	109.50(6)
S7—Hg2—S4^4	138.78(5)	S5—Ge2—S7	103.25(6)
S8^2—Hg2—S3^3	107.26(4)	S8—Ge2—S7	109.32(6)
S4^4—Hg2—S8^2	96.04(4)	S8—Ge2—S6	106.29(6)
S4^4—Hg2—S3^3	94.54(5)	S8—Ge2—S5	116.79(6)

Symmetry codes: (1) -1/2+*X*,1-*Y*, +*Z*; (2) +*X*,1+*Y*, +*Z*; (3) 1-*X*, 1-*Y*, 1/2+*Z*; (4) 3/2-*X*, +*Y*, 1/2+*Z*; (5) +*X*, -1+*Y*, +*Z*; (6) 1/2+*X*, -*Y*, +*Z*; (7) 1/2+*X*, 1-*Y*, +*Z*; (8) 1-*X*, -*Y*, 1/2+*Z*; (9) -1/2+*X*, -*Y*, +*Z*; (10) 3/2-*X*, -1+*Y*, 1/2+*Z*; (11) 1-*X*, 1-*Y*, -1/2+*Z*; (12) 3/2-*X*, +*Y*, -1/2+*Z*; (13) 3/2-*X*, 1+*Y*, -1/2+*Z*; (14) 1-*X*, -Y, -1/2+*Z*.