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A Series of $Rb_4Ln_2(P_2S_6)(PS_4)_2$ (Ln = La, Ce, Pr, Nd, Sm, Gd) Rare Earth Thiophosphates with Two Distinct Thiophosphate Units $[P^{V}S_4]^{3-}$ and $[P^{IV}_2S_6]^{4-}$

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1. $Rb_4Ce_2(P_2S_6)(PS_4)_2$ PXRD pattern

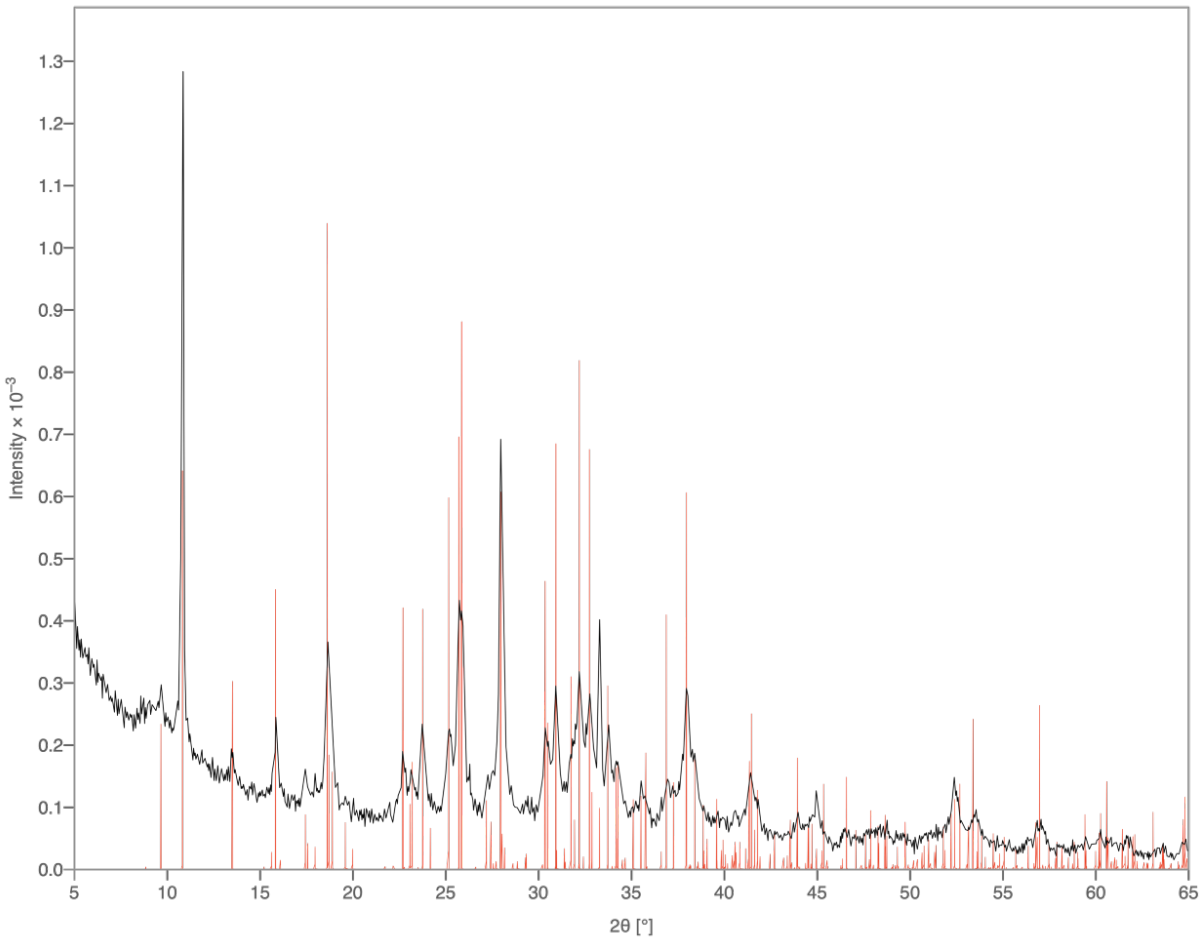

Fig S1. Experimental (black) and calculated (red) PXRD patterns of Rb_4Ce_2 $(P_2S_6)(PS_4)_2$.

2. $Rb_4Sm_2(P_2S_6)(PS_4)_2$ PXRD pattern

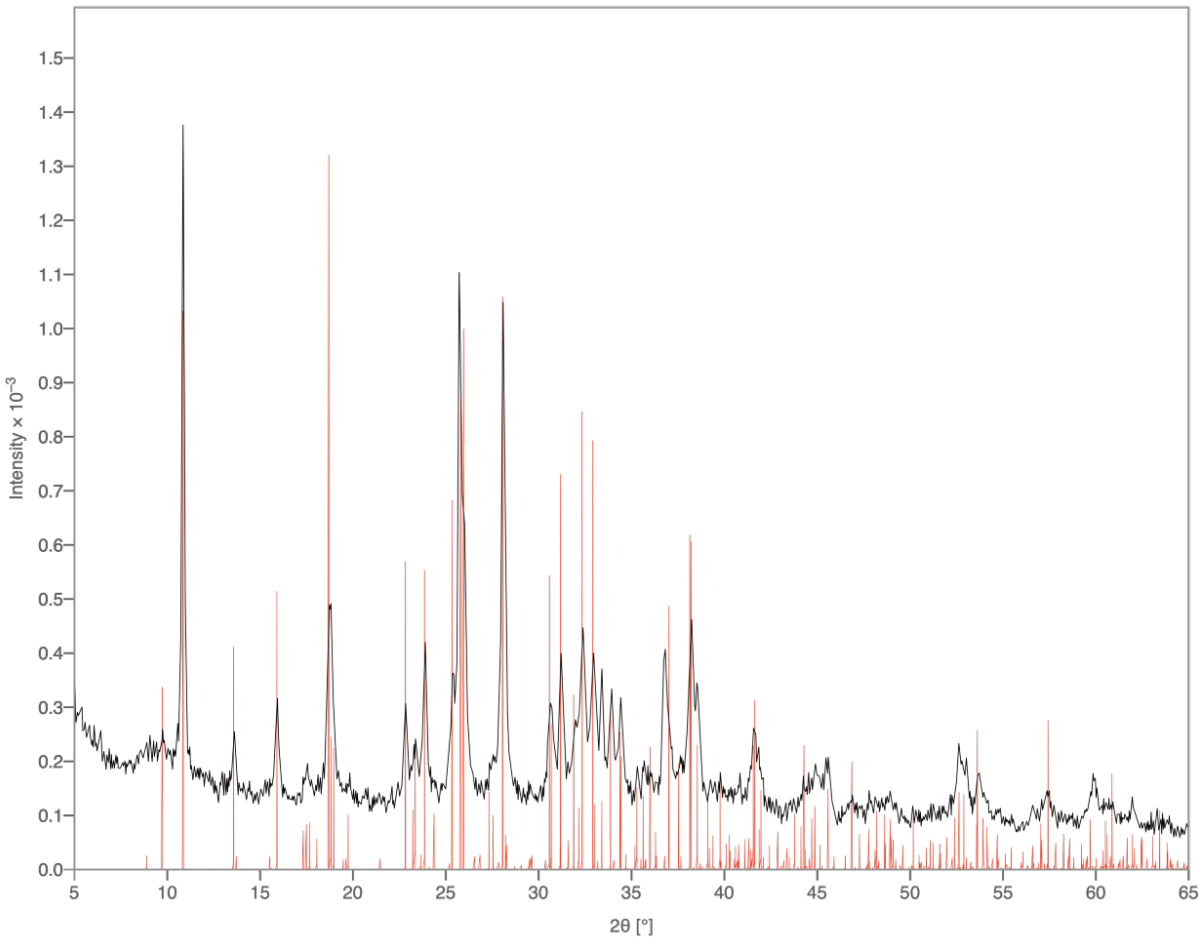

Fig S2. Experimental (black) and calculated (red) PXRD patterns of $Rb_4Sm_2(P_2S_6)(PS_4)_2$.

3. $Rb_4Nd_2(P_2S_6)(PS_4)_2$ PXRD pattern

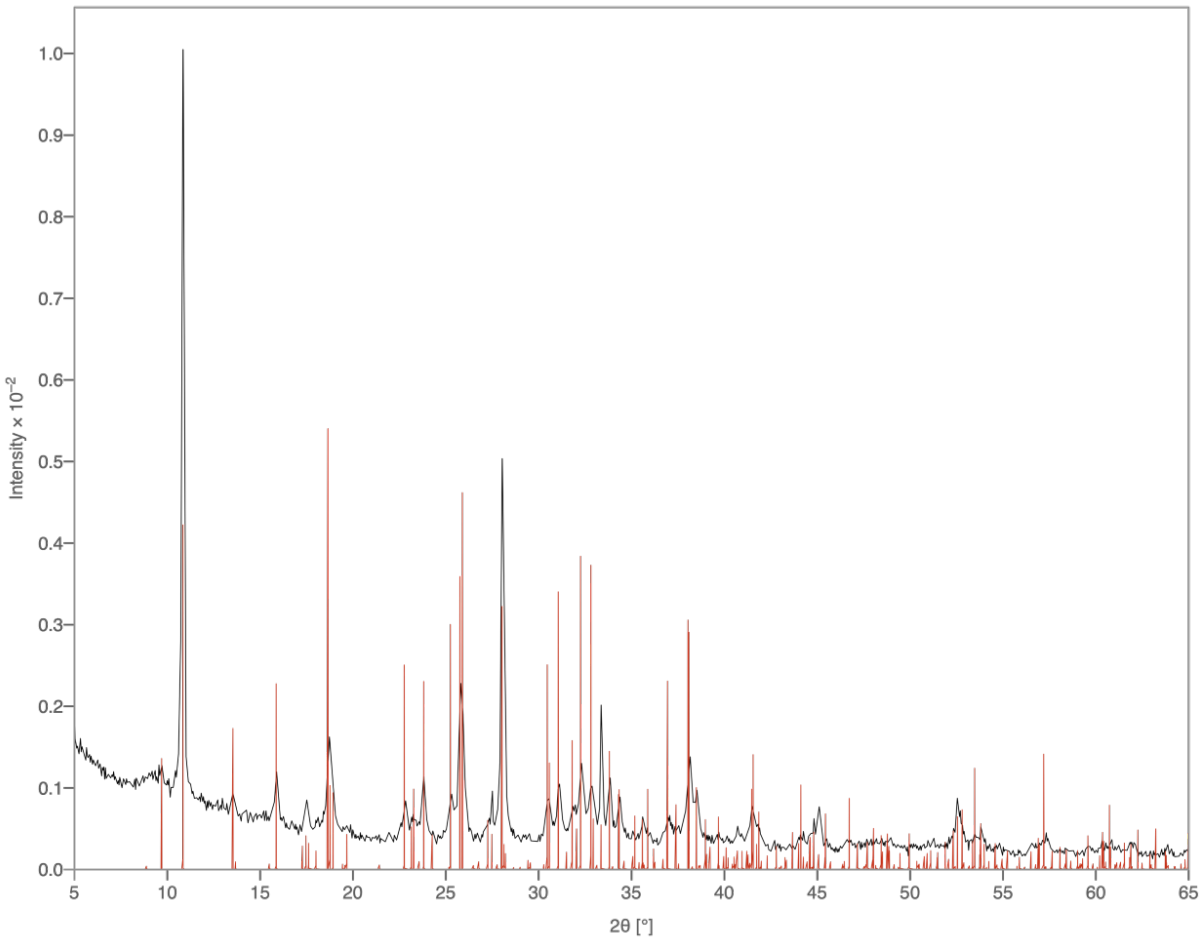

Fig S3. Experimental (black) and calculated (red) PXRD patterns of $Rb_4Nd_2(P_2S_6)(PS_4)_2$.

4. Crystallographic Details

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_4La_2(P_2S_6)(PS_4)_2$

Atom	*x*	*y*	*z*	U_{eq} [$Å^2$]
La1	3107.3(2)	5192.6(2)	6504.8(2)	17.18(4)
Rb1	6441.6(3)	9897.5(4)	8021.1(2)	36.59(8)
Rb2	7602.1(3)	9954.4(4)	5146.9(2)	30.06(7)
P1	3982.1(7)	4840.7(9)	8352.4(3)	15.83(12)
P2	5782.6(7)	4959.3(9)	5464.7(3)	16.55(12)
S1	4155.5(8)	7290.2(9)	8928.5(3)	23.87(14)
S2	4440.4(7)	2530.1(9)	8982.3(3)	21.99(13)
S3	5377.8(7)	4959.3(10)	7660.9(3)	23.54(14)
S4	1976.4(7)	4385.6(10)	7832.7(3)	22.94(13)
S5	5420.7(7)	7403.9(9)	5994.8(4)	22.70(14)
S6	7666.5(7)	4855.6(9)	5126.7(3)	22.15(13)
S7	5276.5(7)	2587(9)	5992.3(3)	22.48(14)

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_4Ce_2(P_2S_6)(PS_4)_2$

Atom	*x*	*y*	*z*	U_{eq} [$Å^2$]
Ce1	3108.5(2)	5208(3)	6505.6(2)	15.92(6)
Rb1	6434.1(5)	9909.6(8)	8017.7(3)	35.86(11)
Rb2	7600.5(5)	9957.2(6)	5156(2)	29.31(10)
S1	4111.2(12)	7295.8(15)	8926.4(5)	22.2(2)
S2	4422.1(11)	2527.7(14)	8982.8(5)	20.5(2)
S3	5365.6(11)	4970.1(17)	7656.9(5)	22.4(2)
S4	1965.6(11)	4345.1(16)	7818.5(5)	21.1(2)
S5	5400(12)	7410.5(15)	5998.7(6)	22.3(2)
S6	7669.6(11)	4853.3(16)	5135.4(5)	21.7(2)
S7	5251.4(12)	2593.4(14)	5999.3(5)	21.6(2)
P1	3959.5(10)	4841.8(14)	8348.8(5)	14.6(18)
P2	5777.2(11)	4959.1(14)	5469.7(5)	15.9(18)

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_4Pr_2(P_2S_6)(PS_4)_2$

Atom	*x*	*y*	*z*	U_{eq} [$Å^2$]
Pr1	3109(2)	5221.4(2)	6506.6(2)	15.78(3)
Rb1	6428.7(3)	9915.0(4)	8014.9(2)	35.21(6)
Rb2	7600.9(3)	9958.3(3)	5163.5(2)	29.48(6)
S1	4080.6(6)	7295.8(7)	8925.5(3)	22.14(10)
S2	4402.7(6)	2527.9(7)	8985.1(3)	20.4(10)
S3	5358(6)	4974.6(8)	7654.9(3)	22.21(11)
S4	1959.6(5)	4315.3(8)	7808.6(3)	19.76(10)
S5	5382.7(6)	7414.3(7)	6000.4(3)	21.83(10)
S6	7671.1(6)	4853.8(8)	5141.4(3)	22.01(10)
S7	5233.8(6)	2598(7)	6003.9(3)	21.37(10)
P1	3944.6(5)	4836.2(7)	8346.2(3)	14.58(9)
P2	5770.3(6)	4960.9(7)	5472.1(3)	15.83(10)

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_4Nd_2(P_2S_6)(PS_4)_2$

Atom	*x*	*y*	*z*	U_{eq} [$Å^2$]
Nd1	1511.3(2)	9720.6(3)	2314.2(2)	14.97(6)
Rb1	163.8(2)	4878.1(5)	1124.3(3)	27.71(9)
Rb2	1980.2(2)	10027.9(6)	276.2(2)	32.97(10)
P1	3343.6(4)	10091.5(11)	3636.3(5)	12.86(15)
P2	473.5(4)	9846.7(11)	3121.4(5)	14.13(15)
S1	2796.7(4)	10641.2(13)	2375.3(5)	20.09(16)
S2	2655.9(4)	9971.2(12)	4006.5(5)	19.99(17)
S3	3983.2(4)	12407.9(11)	4176.6(5)	19.32(16)
S4	3923.4(4)	7634.5(12)	3992(5)	20.95(16)
S5	1004.7(4)	12239.9(12)	3140.1(5)	19.68(16)
S6	146.5(5)	9844.8(12)	3912.6(5)	20.69(17)
S7	1000.7(4)	7418.7(11)	3156.8(5)	19.77(16)

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_4Sm_2(P_2S_6)(PS_4)_2$

Atom	*x*	*y*	*z*	U_{eq} [$Å^2$]
Sm1	1518.2(2)	5315.1(2)	7320.9(2)	15.59(4)
Rb1	5174.6(2)	5139.9(5)	8880.1(2)	30.02(8)
Rb2	1981.3(2)	4982.5(5)	5278.9(2)	34.65(9)
S1	3919.9(4)	7380.2(11)	8961.3(5)	20.88(16)
S2	3983.4(4)	2596.4(11)	9163.1(5)	19.85(15)
S3	2654.2(4)	5047.8(12)	8999.2(5)	21.85(16)
S4	2782.5(4)	4350.4(11)	7362.9(5)	19.11(15)
S5	1003.6(4)	7609.6(11)	8141.4(5)	21.32(16)
S6	1009.4(4)	2785.5(11)	8122.8(5)	20.83(16)
S7	163.8(4)	5174.8(12)	8923(5)	22.79(16)
P1	3339.8(4)	4912(10)	8621.9(5)	14.31(14)
P2	477.6(4)	5177.6(11)	8117(5)	15.72(14)

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_4Gd_2(P_2S_6)(PS_4)_2$

Atom	***x***	***y***	***z***	**U_{eq} [$Å^2$]**
Gd1	1527.3(2)	5324.9(2)	7327.9(2)	16.14(3)
Rb1	5184.7(2)	5144.6(3)	8885.1(2)	30.44(6)
Rb2	1980.7(2)	4996.1(4)	5278.3(2)	35.17(6)
S1	3919.4(3)	7397.5(8)	8944.5(3)	21.18(11)
S2	3984.4(3)	2600(8)	9146(3)	20.06(10)
S3	2654.8(3)	5059.8(9)	8996.2(3)	22.15(11)
S4	2773.4(3)	4348.4(8)	7352.7(3)	19.25(10)
S5	1003.1(3)	7619.9(8)	8123.4(4)	21.44(11)
S6	1012.2(3)	2790.9(8)	8106.1(4)	21.4(11)
S7	181(3)	5173.1(9)	8933.1(4)	24.92(12)
P1	3340(3)	4924.1(7)	8611.6(3)	14.7(10)
P2	481.9(3)	5181.4(8)	8112.7(3)	16.51(10)

5. SEM Images

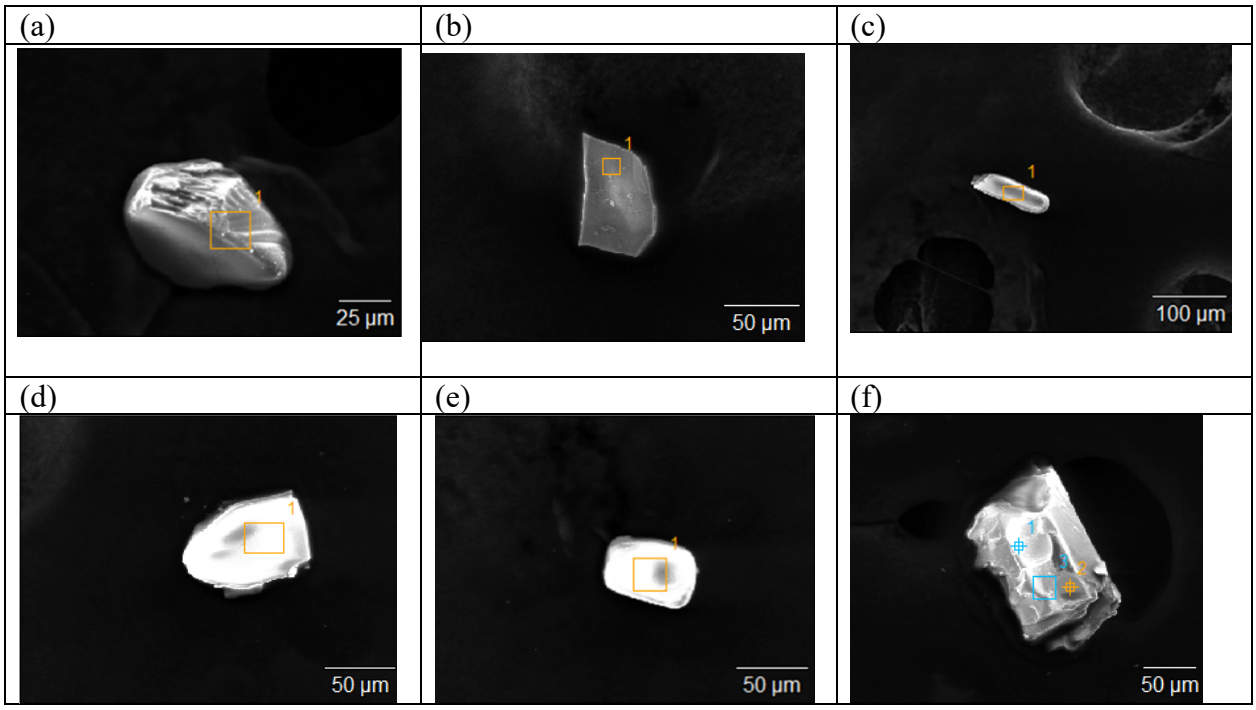

Fig S4. SEM images of single crystals of (a) $Rb_4La_2(P_2S_6)(PS_4)_2$, (b) $Rb_4Ce_2(P_2S_6)(PS_4)_2$, (c) $Rb_4Sm_2(P_2S_6)(PS_4)_2$, (d) $Rb_4Pr_2(P_2S_6)(PS_4)_2$, (e) $Rb_4Gd_2(P_2S_6)(PS_4)_2$, (f) $Rb_4Nd_2(P_2S_6)(PS_4)_2$

6. Elemental Compositions

Table S7. Elemental Compositions of the thiophosphates determined by EDS.

$Rb_4La_2(P_2S_6)(PS_4)_2$		$Rb_4Ce_2(P_2S_6)(PS_4)_2$		$Rb_4Sm_2(P_2S_6)(PS_4)_2$	
Element	Atom, %	Element	Atom, %	Element	Atom, %
P	18.55	P	17.92	P	18.23
S	58.40	S	60.07	S	59.01
Rb	15.22	Rb	15.03	Rb	14.35
La	7.83	Ce	6.99	Sm	8.41
$Rb_4Pr_2(P_2S_6)(PS_4)_2$		$Rb_4Gd_2(P_2S_6)(PS_4)_2$		$Rb_4Nd_2(P_2S_6)(PS_4)_2$	
Element	Atom, %	Element	Atom, %	Element	Atom, %
P	18.23	P	17.82	P	17.39
S	58.31	S	60.30	S	58.54
Rb	15.09	Rb	14.27	Rb	17.14
Pr	8.37	Gd	7.60	Nd	6.93

7. EDS Spectra

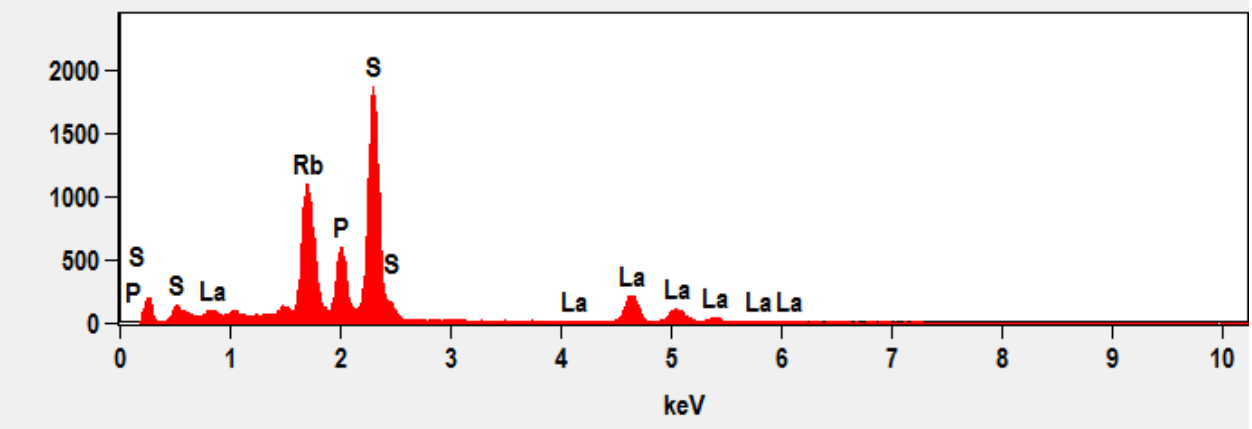

Figure S5. EDS spectrum of $Rb_4La_2(P_2S_6)(PS_4)_2$.

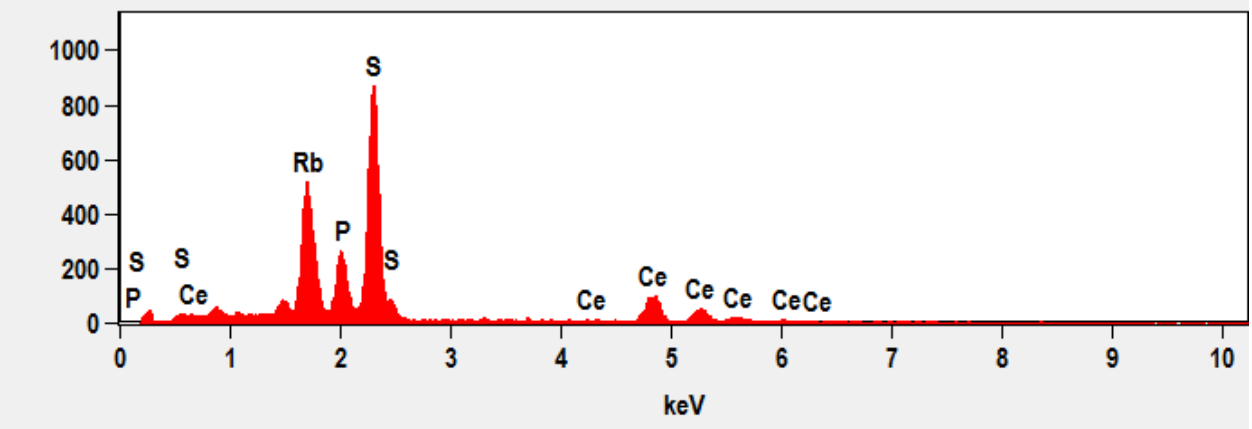

Figure S6. EDS spectrum of $Rb_4Ce_2(P_2S_6)(PS_4)_2$.

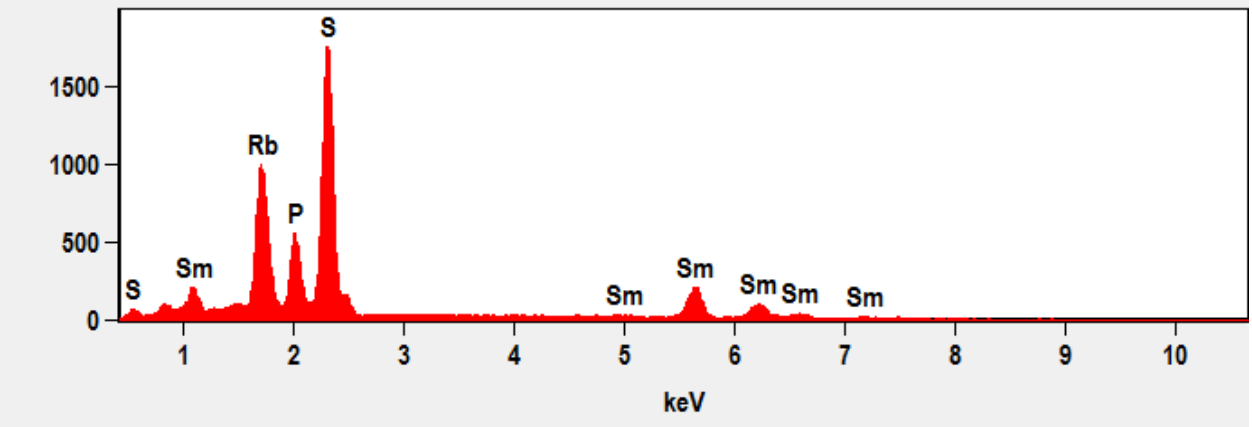

Figure S7. EDS spectrum of $Rb_4Sm_2(P_2S_6)(PS_4)_2$.

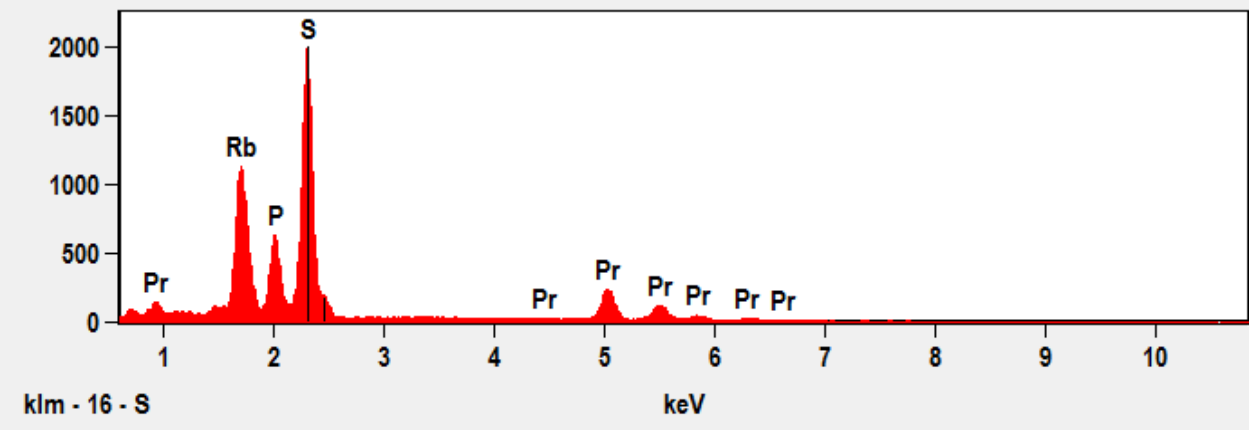

Figure S8. EDS spectrum of $Rb_4Pr_2(P_2S_6)(PS_4)_2$.

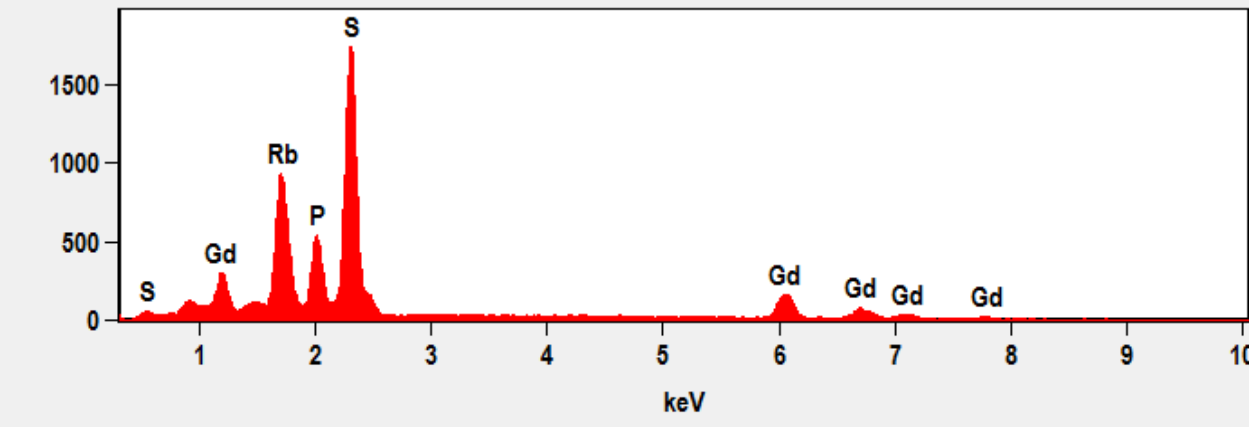

Figure S9. EDS spectrum of $Rb_4Gd_2(P_2S_6)(PS_4)_2$.

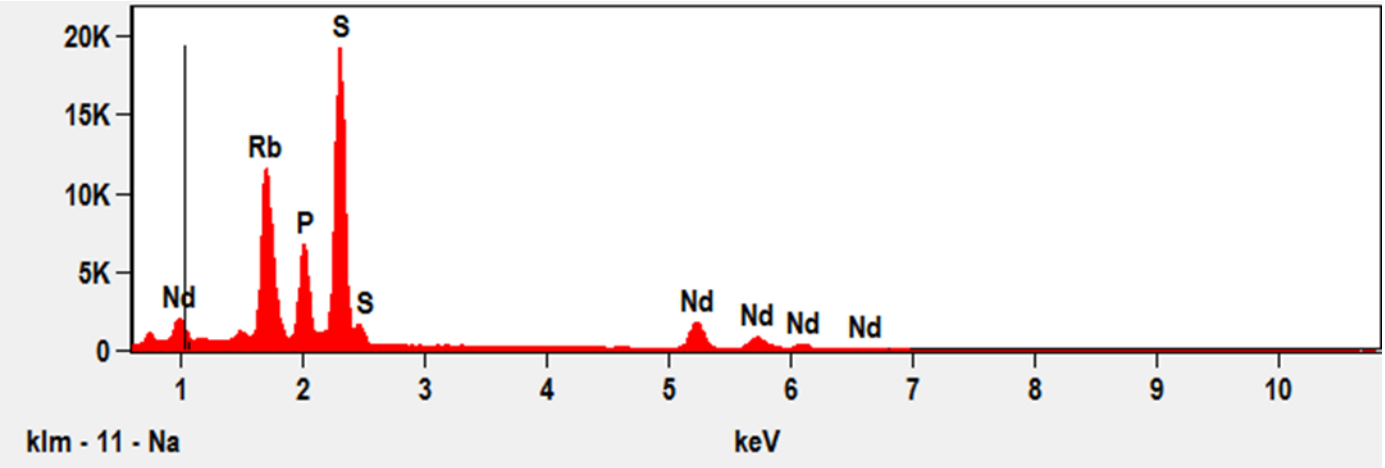

Figure S10. EDS spectrum of $Rb_4Nd_2(P_2S_6)(PS_4)_2$.

8. Effective Magnetic Moments and Weiss Constants

Table S8. Effective Magnetic Moments and Weiss Constants for Compounds of $Rb_4Nd_2(P_2S_6)(PS_4)_2$, $Rb_4Ce_2(P_2S_6)(PS_4)_2$, and $Rb_4Sm_2(P_2S_6)(PS_4)_2$

	$Rb_2Nd_2(P_2S_6)(PS_4)_2$	$Rb_2Ce_2(P_2S_6)(PS_4)_2$	$Rb_2Sm_2(P_2S_6)(PS_4)_2$
μ_{eff}, μ_B	3.77	2.66	0.65
θ, K	-28.3	-23.9	-1.1
Calculated μ_{eff}, μ_B	3.62	2.54	0.85