Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Four new quaternary chalcogenides $A_2Ba_7Sn_4Q_{16}$ (A=Li, Na; Q=S, Se): syntheses, crystal structures, nonlinear optical performances

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Table S1. Bond lengths (Å) and angles (deg.) for $Na_2Ba_7Sn_4S_{16}$.

Sn(1)-S(2)	2.379(9)	S(1)#6-Ba(1)-S(1)#7	74.37(17)
Sn(1)-S(1)#1	2.386(5)	S(1)#2-Ba(1)-S(1)#7	129.91(13)
Sn(1)-S(1)	2.386(5)	S(1)-Ba(1)-S(1)#7	141.58(18)
Sn(1)-S(1)#2	2.386(5)	S(1)#6-Ba(1)-S(2)#8	156.27(15)
Sn(1)-Ba(1)#3	3.9412(17)	S(1)#2-Ba(1)-S(2)#8	74.39(14)
Sn(1)-Ba(1)#4	3.9412(17)	S(1)-Ba(1)-S(2)#8	73.71(14)
Sn(1)-Ba(2)#1	4.0616(12)	S(1)#7-Ba(1)-S(2)#8	84.51(17)
Sn(1)-Ba(2)#5	4.0616(11)	S(1)#6-Ba(1)-S(2)#9	74.39(14)
Ba(1)-S(1)#6	3.152(5)	S(1)#2-Ba(1)-S(2)#9	156.27(15)
Ba(1)-S(1)#2	3.152(5)	S(1)-Ba(1)-S(2)#9	84.51(17)
Ba(1)-S(1)	3.203(4)	S(1)#7-Ba(1)-S(2)#9	73.71(14)
Ba(1)-S(1)#7	3.203(4)	S(2)#8-Ba(1)-S(2)#9	110.29(14)
Ba(1)-S(2)#8	3.224(4)	S(1)#6-Ba(1)-S(1)#10	67.02(6)
Ba(1)-S(2)#9	3.224(4)	S(1)#2-Ba(1)-S(1)#10	67.02(6)
Ba(1)-S(1)#10	3.594(5)	S(1)-Ba(1)-S(1)#10	70.92(14)
Ba(1)-S(1)#11	3.594(5)	S(1)#7-Ba(1)-S(1)#10	141.38(16)
S(1)-Na(1)	2.688(5)	S(2)#8-Ba(1)-S(1)#10	132.98(17)
S(1)-Ba(1)#3	3.152(5)	S(2)#9-Ba(1)-S(1)#10	96.16(8)
S(1)-Ba(1)#13	3.594(5)	S(1)#6-Ba(1)-S(1)#11	67.02(6)
S(2)-Ba(1)#14	3.224(4)	S(1)#2-Ba(1)-S(1)#11	67.02(6)
S(2)-Ba(1)#15	3.224(4)	S(1)-Ba(1)-S(1)#11	141.38(16)
S(2)-Ba(1)#16	3.224(4)	S(1)#7-Ba(1)-S(1)#11	70.92(14)
Na(1)-S(1)#17	2.688(5)	S(2)#8-Ba(1)-S(1)#11	96.16(8)
Na(1)-S(1)#18	2.688(5)	S(2)#9-Ba(1)-S(1)#11	132.98(17)
Na(1)-S(1)#10	2.688(5)	S(1)#10-Ba(1)-S(1)#11	92.68(16)
S(2)-Sn(1)-S(1)#1	111.62(11)	S(1)-Na(1)-S(1)#17	94.77(5)
S(2)-Sn(1)-S(1)	111.62(11)	S(1)-Na(1)-S(1)#18	146.49(19)
S(1)#1-Sn(1)-S(1)	107.24(12)	S(1)#17-Na(1)-S(1)#18	94.77(5)
S(2)-Sn(1)-S(1)#2	111.62(11)	S(1)-Na(1)-S(1)#10	94.77(5)
S(1)#1-Sn(1)-S(1)#2	107.24(12)	S(1)#17-Na(1)-S(1)#10	146.49(19)
S(1)-Sn(1)-S(1)#2	107.24(12)	S(1)#18-Na(1)-S(1)#10	94.77(5)
S(1)#6-Ba(1)-S(1)#2	111.13(17)	S(1)-Na(1)-S(2)	63.34(15)
S(1)#6-Ba(1)-S(1)	129.91(13)	S(1)#17-Na(1)-S(2)	140.36(9)
S(1)#2-Ba(1)-S(1)	74.37(17)	S(1)#18-Na(1)-S(2)	89.55(14)
S(1)#10-Na(1)-S(2)	71.73(10)		

Symmetry transformations used to generate equivalent atoms:

#1 z-1/2,-x+1/2,-y+1 #2 -y+1/2,-z+1,x+1/2

#3 z-1/2,x+1/2,y-1/2 #4 y-1,-z+1,-x+1/2

#5 -y+1/2,z+0,-x+1 #6 y-1/2,z+1/2,x+1/2

#7 -x+0,-y+3/2,z+0 #8 -y+1/4,-x+3/4,z-1/4

#9 y-1/4,x+3/4,z-1/4 #10 z-1/4,-y+5/4,-x+3/4

#11 -z+1/4,y+1/4,-x+3/4 #12 y-3/4,-x+3/4,-z+5/4

#13 -z+3/4,y-1/4,-x+1/4 #14 z-1/4,y-1/4,x+3/4

#15 -x+1/4,-z+3/4,y-1/4 #16 y-3/4,x+1/4,z+1/4

#17 -z+3/4,-y+5/4,x+1/4 #18 -x+1/2,y+0,-z+1

Table S2. Bond lengths (Å)and angles (deg) for $Li_2Ba_7Sn_4S_{16}$.

Sn(1)-S(2)	2.353(5)	S(2)#7-Ba(1)-S(1)#2	157.21(9)
Sn(1)-S(1)#1	2.393(3)	S(1)#8-Ba(1)-S(1)#2	109.56(11)
Sn(1)-S(1)	2.393(3)	S(2)#6-Ba(1)-S(1)	73.30(9)
Sn(1)-S(1)#2	2.393(3)	S(2)#7-Ba(1)-S(1)	87.40(10)
Ba(1)-S(2)#6	3.120(2)	S(1)#8-Ba(1)-S(1)	129.50(9)
Ba(1)-S(2)#7	3.120(2)	S(1)#2-Ba(1)-S(1)	72.95(11)
Ba(1)-S(1)#8	3.229(3)	S(2)#6-Ba(1)-S(1)#9	87.40(10)
Ba(1)-S(1)#2	3.229(3)	S(2)#7-Ba(1)-S(1)#9	73.30(9)
Ba(1)-S(1)	3.277(3)	S(1)#8-Ba(1)-S(1)#9	72.95(11)
Ba(1)-S(1)#9	3.277(3)	S(1)#2-Ba(1)-S(1)#9	129.50(9)
Ba(1)-S(1)#10	3.451(3)	S(1)-Ba(1)-S(1)#9	145.42(11)
Ba(1)-S(1)#11	3.451(3)	S(2)#6-Ba(1)-S(1)#10	130.99(11)
S(1)-Li(1)	2.480(3)	S(2)#7-Ba(1)-S(1)#10	93.77(6)
S(1)-Ba(1)#5	3.229(3)	S(1)#8-Ba(1)-S(1)#10	68.18(4)
S(1)-Ba(1)#13	3.451(3)	S(1)#2-Ba(1)-S(1)#10	68.18(4)
S(2)-Ba(1)#14	3.120(2)	S(1)-Ba(1)-S(1)#10	66.75(9)
S(2)-Ba(1)#15	3.120(2)	S(1)#9-Ba(1)-S(1)#10	141.07(10)
S(2)-Ba(1)#16	3.120(2)	S(2)#6-Ba(1)-S(1)#11	93.77(6)
Li(1)-S(1)#17	2.480(3)	S(2)#7-Ba(1)-S(1)#11	130.99(11)
Li(1)-S(1)#10	2.480(3)	S(1)#8-Ba(1)-S(1)#11	68.18(4)
Li(1)-S(1)#18	2.480(3)	S(1)#2-Ba(1)-S(1)#11	68.18(4)
S(2)-Sn(1)-S(1)#1	111.05(8)	S(1)-Ba(1)-S(1)#11	141.07(10)
S(2)-Sn(1)-S(1)	111.05(8)	S(1)#9-Ba(1)-S(1)#11	66.75(9)
S(1)#1-Sn(1)-S(1)	107.84(8)	S(1)#10-Ba(1)-S(1)#11	99.73(11)
S(2)-Sn(1)-S(1)#2	111.05(8)	S(1)#17-Li(1)-S(1)	140.30(14)
S(1)#1-Sn(1)-S(1)#2	107.84(8)	S(1)#17-Li(1)-S(1)#10	96.62(5)
S(1)-Sn(1)-S(1)#2	107.84(8)	S(1)-Li(1)-S(1)#10	96.62(5)
S(2)#6-Ba(1)-S(2)#7	111.91(9)	S(1)#17-Li(1)-S(1)#18	96.62(5)
S(2)#6-Ba(1)-S(1)#8	157.21(9)	S(1)-Li(1)-S(1)#18	96.62(5)
S(2)#7-Ba(1)-S(1)#8	73.97(9)	S(1)#10-Li(1)-S(1)#18	140.30(14)
S(2)#6-Ba(1)-S(1)#2	73.97(9)		

Symmetry transformations used to generate equivalent atoms:

#1 z-1/2,-x+1/2,-y+1 #2 -y+1/2,-z+1,x+1/2

#3 -y+1/2,z+0,-x+1 #4 y-1,-z+1,-x+1/2

#5 z-1/2,x+1/2,y-1/2 #6 -y+1/4,-x+3/4,z-1/4

#7 y-1/4,x+3/4,z-1/4 #8 y-1/2,z+1/2,x+1/2

#9 -x+0,-y+3/2,z+0 #10 z-1/4,-y+5/4,-x+3/4

#11 -z+1/4,y+1/4,-x+3/4 #12 y-3/4,-x+3/4,-z+5/4

#13 -z+3/4,y-1/4,-x+1/4 #14 z-1/4,y-1/4,x+3/4

#15 y-3/4,x+1/4,z+1/4 #16 -x+1/4,-z+3/4,y-1/4
#17 -x+1/2,y+0,-z+1 #18 -z+3/4,-y+5/4,x+1/4

Table S3. Bond lengths (Å) and angles (deg) for $Na_2Ba_7Sn_4Se_{16}$.

Sn(1)-Se(1)	2.498(3)
Sn(1)-Se(2)	2.5239(16)

Sn(1)-Se(2)#1	2.5239(16)
Sn(1)-Se(2)#2	2.5239(16)
Ba(1)-Se(2)#3	3.2662(18)

Ba(1)-Se(2)#4	3.2662(18)
Ba(1)-Se(2)#5	3.3178(16)

Ba(1)-Se(2)#6	3.3178(16)
Ba(1)-Se(1)	3.3651(16)

Ba(1)-Se(1)#7	3.3651(16)
Ba(1)-Se(2)#8	3.7222(19)

Ba(1)-Se(2)#9	3.7222(19)
Se(2)-Na(1)	2.8061(16)

Se(2)-Ba(1)#10	3.2662(18)
Se(2)-Ba(1)#11	3.3178(16)

Se(2)-Ba(1)#12	3.7222(19)
Se(1)-Ba(1)#2	3.3651(16)
Se(1)-Ba(1)#13	3.3651(16)

Na(1)-Se(2)#14	2.8061(16)
Na(1)-Se(2)#15	2.8061(16)

	Na(1)-Se(2)#16	2.8061(16)
	Se(1)-Sn(1)-Se(2)	111.35(5)

	Se(1)-Sn(1)-Se(2)#1	111.35(5)
	Se(2)-Sn(1)-Se(2)#1	107.52(5)

	Se(1)-Sn(1)-Se(2)#2	111.35(5)
	Se(2)-Sn(1)-Se(2)#2	107.52(5)

	Se(2)#1-Sn(1)-Se(2)#2	107.52(5)
	Se(2)#3-Ba(1)-Se(2)#4	110.36(7)

	Se(2)#3-Ba(1)-Se(2)#5	128.92(4)
	Se(2)#4-Ba(1)-Se(2)#5	76.39(5)

		Se(2)#3-Ba(1)-Se(2)#6	76.39(5)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,z-1/2,-x+3/2 #2 -z+3/2,-x+1,y+1/2
#3 z-3/4,-y+3/4,-x+5/4 #4 -z+7/4,y-1/4,-x+5/4
#5 -y+5/4,-x+3/4,z-1/4 #6 y-1/4,x-1/4,z-1/4
#7 -x+1,-y+1/2,z+0 #8 y,z-1,x #9 -y+1,-z+3/2,x+0
#10 -z+5/4,y+1/4,-x+7/4 #11 y+1/4,x+1/4,z+1/4
#12 z,x,y+1 #13 y+1/2,z-1/2,x+1/2
#14 -z+7/4,-y+5/4,x+1/4 #15 z-1/4,-y+5/4,-x+7/4
#16 -x+3/2,y+0,-z+2 #17 y+3/4,-x+5/4,-z+7/4

Table S4. Bond lengths (Å) and angles (deg) for $Li_2Ba_7Sn_4Se_{16}$.

Sn(1)-Se(2)	2.4818(16)	Se(2)#3-Ba(1)-Se(1)#1	74.16(2)
Sn(1)-Se(1)#1	2.5215(8)	Se(2)#4-Ba(1)-Se(1)#1	157.94(2)
Sn(1)-Se(1)#2	2.5215(8)	Se(1)#5-Ba(1)-Se(1)#1	109.75(3)
Sn(1)-Se(1)	2.5215(8)	Se(2)#3-Ba(1)-Se(1)#6	85.47(3)
Ba(1)-Se(2)#3	3.2714(7)	Se(2)#4-Ba(1)-Se(1)#6	73.57(2)
Ba(1)-Se(2)#4	3.2714(7)	Se(1)#5-Ba(1)-Se(1)#6	75.19(3)
Ba(1)-Se(1)#5	3.3325(9)	Se(1)#1-Ba(1)-Se(1)#6	128.46(2)
Ba(1)-Se(1)#1	3.3325(9)	Se(2)#3-Ba(1)-Se(1)	73.57(2)
Ba(1)-Se(1)#6	3.3768(8)	Se(2)#4-Ba(1)-Se(1)	85.47(3)
Ba(1)-Se(1)	3.3768(8)	Se(1)#5-Ba(1)-Se(1)	128.46(2)
Ba(1)-Se(1)#7	3.5664(10)	Se(1)#1-Ba(1)-Se(1)	75.19(3)
Ba(1)-Se(1)#8	3.5664(10)	Se(1)#6-Ba(1)-Se(1)	142.87(4)
Se(1)-Li(1)	2.5841(8)	Se(2)#3-Ba(1)-Se(1)#7	130.66(3)
Se(1)-Ba(1)#10	3.3325(9)	Se(2)#4-Ba(1)-Se(1)#7	94.662(14)
Se(1)-Ba(1)#11	3.5664(10)	Se(1)#5-Ba(1)-Se(1)#7	68.220(13)
Se(2)-Ba(1)#12	3.2714(7)	Se(1)#1-Ba(1)-Se(1)#7	68.220(13)
Se(2)-Ba(1)#13	3.2714(7)	Se(1)#6-Ba(1)-Se(1)#7	143.38(3)
Se(2)-Ba(1)#14	3.2714(7)	Se(1)-Ba(1)-Se(1)#7	66.92(2)
Li(1)-Se(1)#7	2.5841(8)	Se(2)#3-Ba(1)-Se(1)#8	94.662(14)
Li(1)-Se(1)#15	2.5841(8)	Se(2)#4-Ba(1)-Se(1)#8	130.66(3)
Li(1)-Se(1)#16	2.5841(8)	Se(1)#5-Ba(1)-Se(1)#8	68.220(13)
Se(2)-Sn(1)-Se(1)#1	110.41(2)	Se(1)#1-Ba(1)-Se(1)#8	68.220(13)
Se(2)-Sn(1)-Se(1)#2	110.41(2)	Se(1)#6-Ba(1)-Se(1)#8	66.92(2)
Se(1)#1-Sn(1)-Se(1)#2	108.52(2)	Se(1)-Ba(1)-Se(1)#8	143.38(3)
Se(2)-Sn(1)-Se(1)	110.41(2)	Se(1)-Li(1)-Se(1)#7	95.700(10)
Se(1)#1-Sn(1)-Se(1)	108.52(2)	Se(1)-Li(1)-Se(1)#15	143.26(3)

Se(1)#2-Sn(1)-Se(1)	108.52(2)	Se(1)#7-Li(1)-Se(1)#15	95.700(10)
Se(2)#3-Ba(1)-Se(2)#4	110.75(3)	Se(1)-Li(1)-Se(1)#16	95.700(10)
Se(2)#3-Ba(1)-Se(1)#5	157.94(2)	Se(1)#7-Li(1)-Se(1)#16	143.26(3)
Se(2)#4-Ba(1)-Se(1)#5	74.16(2)	Se(1)#15-Li(1)-Se(1)#16	95.700(10)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1/2,-z+1,x+1/2 #2 z-1/2,-x+1/2,-y+1

#3 -y+1/4,-x+3/4,z-1/4 #4 y-1/4,x+3/4,z-1/4

#5 y-1/2,z+1/2,x+1/2 #6 -x+0,-y+3/2,z+0

#7 z-1/4,-y+5/4,-x+3/4 #8 -z+1/4,y+1/4,-x+3/4

#9 y-3/4,-x+3/4,-z+5/4 #10 z-1/2,x+1/2,y-1/2

#11 -z+3/4,y-1/4,-x+1/4 #12 z-1/4,y-1/4,x+3/4

#13 y-3/4,x+1/4,z+1/4 #14 -x+1/4,-z+3/4,y-1/4

#15 -x+1/2,y+0,-z+1 #16 -z+3/4,-y+5/4,x+1/4

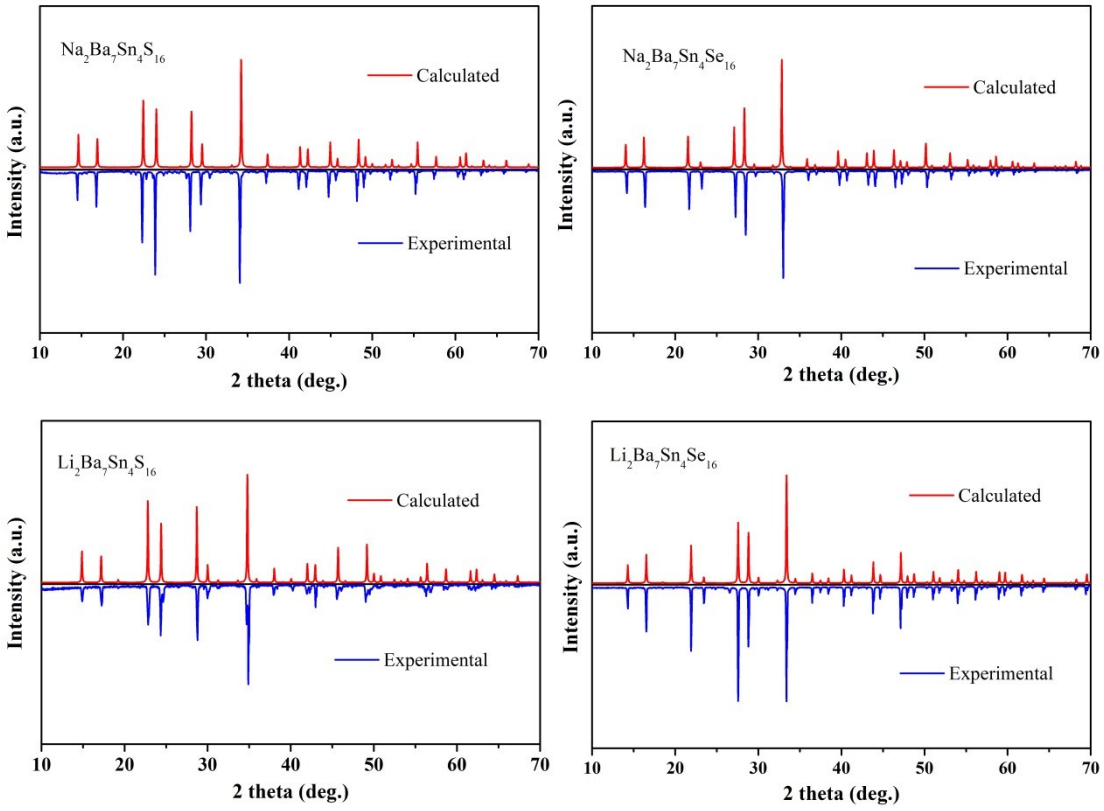

Fig. S1. Powder X-ray diffraction patterns of $A_2Ba_7Sn_4Q_{16}$ (A=Li, Na; Q=S, Se)

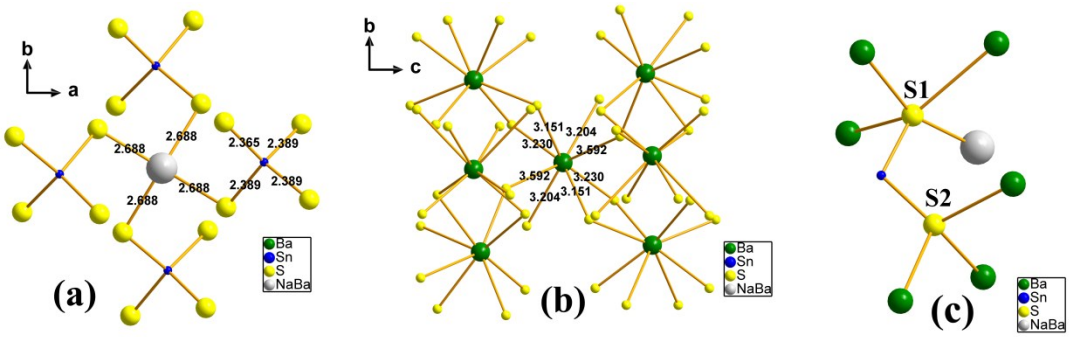

Fig. S2. (a)View environment of the Na/BaS_4 and SnS_4 tetrahedra with the bound distances. (b) The environment of Ba atoms, and Ba-S bound distances. (c) Two different coordination environments of S atoms.

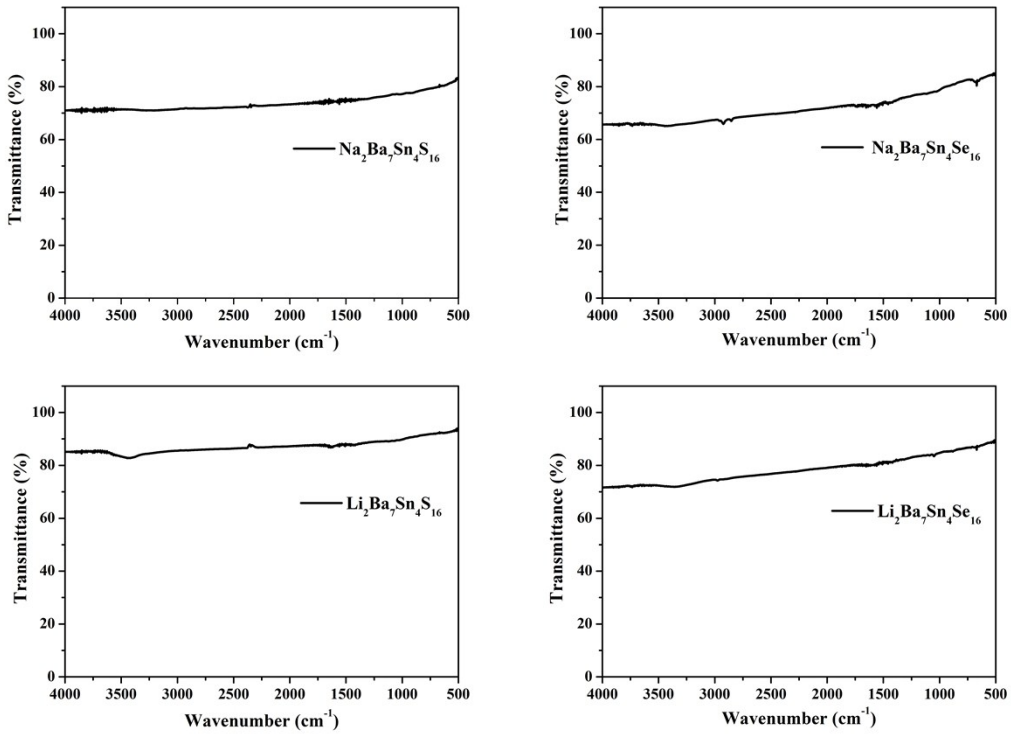

Fig. S3. IR spectra of title compounds.