## **Electronic Supplementary Information**

## Novel Open-Framework Europium Silicates Prepared under High-Temperature and High-Pressure Conditions

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Figure S1 EDS spectra of 1 and 2.

Table S1 EDS analysis	s data of 1	and <b>2</b>
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	K	Na	Eu	Si
1	0	5.01	1.0	3.99
2	1.99	0	1.0	4.0



Figure S2 Thermal ellipsoid plot (50% probability) of the asymmetric unit of 1.



Figure S3 Thermal ellipsoid plot (50% probability) of the asymmetric unit of 2.

bond	bond length (Å)	bond angle	value (deg)
Eu(1)-O(4)#1	2.295(4)	O(4)#1-Eu(1)-O(4)#2	180.00(14)
Eu(1)-O(4)#2	2.295(4)	O(4)#1-Eu(1)-O(4)#3	98.5(2)
Eu(1)-O(4)#3	2.295(4)	O(4)#2-Eu(1)-O(4)#3	81.5(2)
Eu(1)-O(4)#4	2.295(4)	O(4)#1-Eu(1)-O(4)#4	81.5(2)
Eu(1)-O(1)#5	2.307(5)	O(4)#2-Eu(1)-O(4)#4	98.5(2)
Eu(1)-O(1)	2.307(5)	O(4)#3-Eu(1)-O(4)#4	180.00(14)
Si(1)-O(1)	1.585(6)	O(4)#1-Eu(1)-O(1)#5	97.83(15)
Si(1)-O(2)	1.586(5)	O(4)#2-Eu(1)-O(1)#5	82.17(16)
Si(1)-O(3)#15	1.608(4)	O(4)#3-Eu(1)-O(1)#5	82.17(16)
Si(1)-O(3)	1.608(4)	O(4)#4-Eu(1)-O(1)#5	97.83(15)
Si(2)-O(6)	1.562(4)	O(4)#1-Eu(1)-O(1)	82.17(16)
Si(2)-O(4)	1.597(4)	O(4)#2-Eu(1)-O(1)	97.83(15)
Si(2)-O(5)	1.615(2)	O(4)#3-Eu(1)-O(1)	97.83(15)
Si(2)-O(3)	1.637(4)	O(4)#4-Eu(1)-O(1)	82.17(16)
Eu(2)/Na(2)-O(6)#6	2.336(4)	O(1)#5-Eu(1)-O(1)	180.000(1)
Eu(2)/Na(2)-O(6)#2	2.336(4)	O(1)-Si(1)-O(2)	117.0(3)
Eu(2)/Na(2)-O(2)#7	2.416(6)	O(1)-Si(1)-O(3)#15	110.7(2)
Eu(2)/Na(2)-O(1)#8	2.477(6)	O(2)-Si(1)-O(3)#15	106.7(2)
Eu(2) /Na(2)-O(4)	2.545(4)	O(1)-Si(1)-O(3)	110.7(2)
Eu(2)/Na(2)-O(4)#9	2.545(4)	O(2)-Si(1)-O(3)	106.7(2)
Eu(3)/Na(3)-O(2)#7	2.316(5)	O(3)#15-Si(1)-O(3)	104.2(4)
Eu(3)/Na(3)-O(2)#10	2.316(5)	O(6)-Si(2)-O(4)	117.2(2)
Eu(3)/Na(3)-O(4)#9	2.693(4)	O(6)-Si(2)-O(5)	111.0(2)
Eu(3)/Na(3)-O(4)#11	2.693(4)	O(4)-Si(2)-O(5)	105.3(3)
Eu(3)/Na(3)-O(4)#12	2.693(4)	O(6)-Si(2)-O(3)	110.6(3)
Eu(3)/Na(3)-O(4)	2.693(4)	O(4)-Si(2)-O(3)	105.8(3)
Eu(3)/Na(3)-O(5)	2.727(9)	O(5)-Si(2)-O(3)	106.3(3)

TableS2 Bond lengths [Å] and angles [deg] for 1

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y+1/2,z+1/2 #2 x-1/2,-y+3/2,-z+1/ #3 x-1/2,-y+3/2,z+1/2 #4 -x+3/2,y+1/2,-z+1/2 #5 -x+1,-y+2,-z+1 #6 x-1/2,-y+3/2,z-1/2 #7 -x+3/2,y+1/2,z-1/2 #8 -x+3/2,y-1/2,z-1/2 #9 x,y,-z #10 x+1/2,-y+3/2,-z+1/2 #11 -x+2,-y+2,z #12 -x+2,-y+2,-z #15 x,y,-z+1

bond	bond	angle	Value	angle	value
	length		(deg)		(deg)
	(Å)				
Eu(1)-F(1)	2.240(2)	Si(4)-O(1)	1.590(5)	O(5)-Si(1)-O(6)	108.7(3)
Eu(1)-O(4)#1	2.240(5)	Si(4)-O(11)	1.620(2)	O(2)-Si(1)-O(7)	113.6(3)
Eu(1)-F(2)	2.266(1)	Si(4)-O(10)	1.631(5)	O(5)-Si(1)-O(7)	105.0(3)
Eu(1)-O(1)#2	2.267(4)	Si(4)-O(6)	1.637(5)	O(6)-Si(1)-O(7)	102.7(2)
Eu(1)-O(2)	2.293(5)	F(1)-Eu(1)-O(4)#1	100.6(2)	O(3)-Si(2)-O(9)	113.2(3)
Eu(1)-O(3)	2.298(4)	F(1)-Eu(1)-F(2)	174.2(2)	O(3)-Si(2)-O(8)	112.6(3)
Si(1)-O(2)	1.580(5)	O(4)#1-Eu(1)-F(2)	85.1(2)	O(9)-Si(2)-O(8)	107.0(3)
Si(1)-O(5)	1.630(3)	F(1)-Eu(1)-O(1)#2	92.1(2)	O(3)-Si(2)-O(7)	112.3(2)
Si(1)-O(6)	1.634(5)	O(4)#1-Eu(1)-O(1)#2	90.42(1)	O(9)-Si(2)-O(7)	106.5(3)
Si(1)-O(7)	1.647(5)	F(2)-Eu(1)-O(1)#2	88.64(19)	O(8)-Si(2)-O(7)	104.6(2)
Si(2)-O(3)	1.581(5)	F(1)-Eu(1)-O(2)	83.31(19)	O(4)-Si(3)-O(8)	113.0(3)
Si(2)-O(9)	1.630(3)	O(4)#1-Eu(1)-O(2)	175.67(1)	O(4)-Si(3)-O(12)	114.1(3)
Si(2)-O(8)	1.634(5)	F(2)-Eu(1)-O(2)	91.0(2)	O(8)-Si(3)-O(12)	104.6(3)
Si(2)-O(7)	1.637(5)	O(1)#2-Eu(1)-O(2)	91.21(16)	O(4)-Si(3)-O(10)#4	111.9(3)
Si(3)-O(4)	1.564(5)	F(1)-Eu(1)-O(3)	90.5(2)	O(8)-Si(3)-O(10)#4	109.2(2)
Si(3)-O(8)	1.626(5)	O(4)#1-Eu(1)-O(3)	89.49(17)	O(12)-Si(3)-O(10)#4	103.5(3)
Si(3)-O(12)	1.644(3)	F(2)-Eu(1)-O(3)	88.8(2)	O(1)-Si(4)-O(11)	112.3(3)
Si(3)-O(10)#4	1.646(5)	O(1)#2-Eu(1)-O(3)	177.44(1)	O(1)-Si(4)-O(10)	111.0(3)
		O(2)-Eu(1)-O(3)	88.70(16)	O(11)-Si(4)-O(10)	107.3(3)
		O(2)-Si(1)-O(5)	113.2(3)	O(1)-Si(4)-O(6)	110.5(3)
		O(2)-Si(1)-O(6)	112.9(3)	O(11)-Si(4)-O(6)	108.4(3)
				O(10)-Si(4)-O(6)	107.2(2)

 $TableS3 \; \text{Bond lengths} \; [\text{\AA}] \; \text{and angles} \; [\text{deg}] \; \text{for} \; 2$ 

Symmetry transformations used to generate equivalent atoms:

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

	Х	у	Z	U(eq)
Eu(1)	0.5000	1.00000	0.5000	0.012(1)
Eu(2)	0.7518(2)	0.7657(2)	0.0000	0.018(1)
Na(2)	0.7518(2)	0.7657(2)	0.0000	0.018(1)
Eu(3)	1.0000	1.0000	0.0000	0.015(1)
Na(3)	1.0000	1.0000	0.0000	0.015(1)
Na(1)	0.5000	1.0000	0.0000	0.051(2)
Na(4)	0.7605(3)	0.5249(3)	0.2482(3)	0.029(1)
Si(1)	0.7871(2)	0.7600(2)	0.5000	0.007(1)
Si(2)	0.9911(1)	0.7870(2)	0.2764(2)	0.008(1)
O(1)	0.7112(5)	0.9408(8)	0.5000	0.027(1)
O(2)	0.7084(5)	0.5816(7)	0.5000	0.023(1)
O(3)	0.8790(5)	0.7503(7)	0.3791(5)	0.043(2)
O(4)	0.9405(4)	0.7150(5)	0.1428(4)	0.025(1)
O(5)	1.00000	1.00000	0.2600(8)	0.057(3)
O(6)	1.11172(4)	0.7089(7)	0.3258(4)	0.035(1)

Table S4 Atomic coordinates and equivalent isotropic displacement parameters  $({\rm \AA}^2)$  for 1

	X	у	Z	U(eq)
Eu(1)	0.2106(1)	-0.0050(1)	0.2886(1)	0.007(1)
K(1)	0.0573(2)	0.250000	0.4457(2)	0.019(1)
K(2)	0.5885(2)	0.250000	0.0804(2)	0.018(1)
K(3)	0.5089(2)	0.250000	0.4712(2)	0.023(1)
K(4)	0.9668(2)	0.250000	0.0344(2)	0.026(1)
Si(1)	0.2800(2)	0.0718(2)	0.0305(2)	0.008(1)
Si(2)	0.4903(2)	-0.0701(2)	0.2429(2)	0.007(1)
Si(3)	0.7477(2)	0.0720(2)	0.3798(2)	0.009(1)
Si(4)	0.1110(2)	0.0644(2)	-0.2355(2)	0.007(1)
O(1)	-0.0074(4)	-0.0381(6)	-0.2500(4)	0.0103(1)
O(2)	0.1798(4)	0.0541(6)	0.0891(4)	0.013(1)
O(3)	0.4182(4)	-0.0370(6)	0.3297(4)	0.014(1)
O(4)	0.7507(5)	0.0462(6)	0.5123(4)	0.016(1)
O(5)	0.3323(6)	0.250000	0.0375(7)	0.016(2)
O(6)	0.2299(4)	0.0122(6)	-0.1122(4)	0.014(1)
O(7)	0.4045(4)	-0.0369(6)	0.0979(4)	0.011(1)
O(8)	0.6110(4)	0.0436(5)	0.2728(4)	0.011(1)
O(9)	0.5395(6)	-0.250000	0.2510(6)	0.013(1)
O(10)	0.1508(4)	0.0394(6)	-0.3526(4)	0.013(1)
O(11)	0.0871(6)	0.250000	-0.2264(7)	0.014(1)
O(12)	0.7859(6)	0.250000	0.3546(6)	0.011(1)
F(1)	0.1723(6)	-0.250000	0.2157(6)	0.020(1)
F(2)	0.2487(6)	0.250000	0.3434(6)	0.021(1)

Table S5 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for  ${\bf 2}$