$K_{2.64}Cs_{0.36}SiF_7$: A New Fluorosilicate with a Trans-perovskite Structure

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Table S1. Crystal data and structure refinement for $K_{2.64}Cs_{0.36}SiF_7$.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $K_{2.64}Cs_{0.36}SiF_7$.

Table S3. Bond lengths [Å] and angles [deg] for $K_{2.64}Cs_{0.36}SiF_7$.

Table S4. The compounds in M_3SiF_7 system in ICSD

Fig.S1 The structural information of the $[SiF_6]^{2-}$ octahedra.

Fig.S2 The FM_6 octahedra of M_3SiF_7 ($M = K^+, Rb^+, Cs^+, NH_4^+$)

Fig.S3 Band structure and calculated band gap of K_3SiF_7, Cs_3SiF_7 and $K_{2.64}Cs_{0.36}SiF_7$.

Fig.S4 Calculated birefringence of K_3SiF_7 and Cs_3SiF_7.

Table S1. Crystal data and structure refinement for $K_{2.64}Cs_{0.36}SiF_7$.

Empirical formula	$K_{2.64}Cs_{0.36}SiF_7$
Formula weight	312.16
Wavelength	0.71073 Å
Crystal system, space group	Tetragonal, P4/*mbm*
Unit cell dimensions	a = 7.768(4) Å
	b = 7.768(4) Å
	c = 5.560(6) Å
Z	2
Volume	335.5(5) Å^3
Calculated density	3.090 Mg/m^3
Absorption coefficient	3.979 mm^{-1}
F(000)	294
Theta range for data collection	3.66 to 27.51 °
Limiting indices	$-6 \leq h \leq 9$, $-10 \leq k \leq 8$, $-7 \leq l \leq 7$
Reflections collected / unique	1808 / 236 [R(int) = 0.0819]
Completeness to theta = 27.51°	99.2 %
Max. and min. transmission	0.7456 and 0.6307
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	236 / 0 / 23
Goodness-of-fit on F^2	1.086
Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1 = 0.0448, wR_2 = 0.1016
R indices (all data) [a]	R_1 = 0.0571, wR_2 = 0.1068
Extinction coefficient	0.019(7)
Largest diff. peak and hole	0.638 and -0.768 e•A^{-3}

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $K_{2.64}Cs_{0.36}SiF_7$. U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
K(1)/Cs(1)	10000	0	5000	26(1)
K(2)	12999(2)	2001(2)	0	23(1)
Si(1)	5000	0	5000	16(1)
F(1)	3503(6)	1497(6)	5000	58(2)
F(2)	10000	0	0	36(2)
F(3)	6060(3)	1060(3)	2837(7)	43(1)

Table S3. Bond lengths [Å] and angles [deg] for $K_{2.64}Cs_{0.36}SiF_7$.

K(1)/Cs(1)-F(3)#1	3.390(3)	K(2)-F(3)#12	2.945(3)
K(1)/Cs(1)-F(3)#2	3.390(3)	K(2)-F(3)#10	2.945(3)
K(1)/Cs(1)-F(3)#3	3.390(3)	K(2)-F(3)#13	2.945(3)
K(1)/Cs(1)-F(3)#4	3.390(3)	K(2)-F(3)#14	2.945(3)
K(1)/Cs(1)-F(3)	3.390(3)	K(2)-F(3)#5	2.651(4)
K(1)/Cs(1)-F(3)#5	3.390(3)	K(2)-F(3)#15	2.651(4)
K(1)/Cs(1)-F(3)#6	3.390(3)	K(2)-F(2)#16	2.8008(16)
K(1)/Cs(1)-F(3)#7	3.390(3)	K(2)-F(2)	2.8008(16)
K(1)/Cs(1)-F(2)#6	2.780(3)	K(2)-F(1)#11	2.835(3)
K(1)/Cs(1)-F(2)	2.780(3)	K(2)-F(1)#10	2.835(3)
K(1)/Cs(1)-F(1)#7	2.959(3)	Si(1)-F(3)#9	1.674(4)
K(1)/Cs(1)-F(1)#8	2.959(3)	Si(1)-F(3)#20	1.674(4)
K(1)/Cs(1)-F(1)#9	2.959(3)	Si(1)-F(3)#21	1.674(4)
K(1)/Cs(1)-F(1)#10	2.959(3)	Si(1)-F(3)	1.674(4)
F(2)#6-K(1)/Cs(1)-F(3)#4	69.23(6)	Si(1)-F(1)#9	1.645(6)
F(2)-K(1)/Cs(1)-F(3)#2	110.77(6)	Si(1)-F(1)	1.645(6)
F(2)-K(1)/Cs(1)-F(3)#5	69.23(6)	F(3)#3-K(1)/Cs(1)-F(3)#5	97.23(4)
F(2)-K(1)/Cs(1)-F(3)#4	110.77(6)	F(3)#1-K(1)/Cs(1)-F(3)#2	41.55(13)
F(2)-K(1)/Cs(1)-F(3)#1	69.23(6)	F(3)#1-K(1)/Cs(1)-F(3)#5	138.45(13)
F(2)#6-K(1)/Cs(1)-F(3)	110.77(6)	F(3)#1-K(1)/Cs(1)-F(3)#4	180.00(13)
F(2)#6-K(1)/Cs(1)-F(3)#2	69.23(6)	F(3)-K(1)/Cs(1)-F(3)#2	97.23(4)
F(2)-K(1)/Cs(1)-F(3)	69.23(6)	F(3)-K(1)/Cs(1)-F(3)#5	82.77(4)
F(2)#6-K(1)/Cs(1)-F(3)#1	110.77(6)	F(3)#2-K(1)/Cs(1)-F(3)#5	180.00(4)
F(2)#6-K(1)/Cs(1)-F(3)#3	69.23(6)	F(3)#4-K(1)/Cs(1)-F(3)	97.23(4)
F(2)#6-K(1)/Cs(1)-F(3)#5	110.77(6)	F(3)#4-K(1)/Cs(1)-F(3)#2	138.45(13)
F(2)-K(1)/Cs(1)-F(3)#3	110.77(6)	F(3)#1-K(1)/Cs(1)-F(3)#3	97.23(4)
F(2)#6-K(1)/Cs(1)-F(2)	180	F(3)#3-K(1)/Cs(1)-F(3)#2	82.77(4)
F(3)#5-K(2)-F(3)#14	156.71(7)	F(3)#4-K(1)/Cs(1)-F(3)#3	82.77(4)

F(3)#10-K(2)-F(3)#13	46.56(14)	F(3)#4-K(1)/Cs(1)-F(3)#5	41.55(13)
F(3)#13-K(2)-F(3)#12	83.47(13)	F(3)-K(1)/Cs(1)-F(3)#3	180
F(3)#15-K(2)-F(3)#14	106.33(14)	F(3)#1-K(1)/Cs(1)-F(3)	82.77(4)
F(3)#14-K(2)-F(3)#12	46.56(14)	F(2)-K(1)/Cs(1)-F(1)#9	90
F(3)#5-K(2)-F(3)#10	106.33(14)	F(2)#6-K(1)/Cs(1)-F(1)#7	90
F(3)#14-K(2)-F(3)#13	64.77(15)	F(2)#6-K(1)/Cs(1)-F(1)#9	90
F(3)#15-K(2)-F(3)#10	156.71(7)	F(2)#6-K(1)/Cs(1)-F(1)#8	90
F(3)#5-K(2)-F(3)#12	156.71(7)	F(2)-K(1)/Cs(1)-F(1)#7	90
F(3)#14-K(2)-F(3)#10	83.47(13)	F(2)-K(1)/Cs(1)-F(1)#8	90
F(3)#10-K(2)-F(3)#12	64.77(15)	F(2)#6-K(1)/Cs(1)-F(1)#10	90
F(3)#5-K(2)-F(3)#13	106.33(14)	F(2)-K(1)/Cs(1)-F(1)#10	90
F(3)#5-K(2)-F(3)#15	73.02(19)	F(1)#10-K(1)/Cs(1)-F(3)	137.29(11)
F(3)#15-K(2)-F(3)#13	156.71(7)	F(1)#7-K(1)/Cs(1)-F(3)#5	42.71(11)
F(3)#15-K(2)-F(3)#12	106.33(14)	F(1)#7-K(1)/Cs(1)-F(3)#3	125.32(11)
F(3)#5-K(2)-F(2)	80.94(4)	F(1)#7-K(1)/Cs(1)-F(3)	54.68(11)
F(3)#5-K(2)-F(2)#16	80.94(4)	F(1)#9-K(1)/Cs(1)-F(3)	42.71(11)
F(3)#15-K(2)-F(2)	80.94(4)	F(1)#8-K(1)/Cs(1)-F(3)	125.32(11)
F(3)#15-K(2)-F(2)#16	80.94(4)	F(1)#9-K(1)/Cs(1)-F(3)#5	125.32(11)
F(3)#5-K(2)-F(1)#11	137.77(17)	F(1)#8-K(1)/Cs(1)-F(3)#4	137.29(11)
F(3)#15-K(2)-F(1)#11	64.74(15)	F(1)#10-K(1)/Cs(1)-F(3)#1	125.32(11)
F(3)#5-K(2)-F(1)#10	64.74(15)	F(1)#9-K(1)/Cs(1)-F(3)#2	54.68(11)
F(3)#15-K(2)-F(1)#10	137.77(17)	F(1)#9-K(1)/Cs(1)-F(3)#1	54.68(11)
F(2)#16-K(2)-F(3)#13	122.26(8)	F(1)#10-K(1)/Cs(1)-F(3)#2	125.32(11)
F(2)-K(2)-F(3)#14	76.03(7)	F(1)#8-K(1)/Cs(1)-F(3)#3	54.68(11)
F(2)-K(2)-F(3)#13	76.03(7)	F(1)#7-K(1)/Cs(1)-F(3)#2	137.29(11)
F(2)#16-K(2)-F(3)#10	76.03(7)	F(1)#10-K(1)/Cs(1)-F(3)#5	54.68(11)
F(2)-K(2)-F(3)#10	122.26(8)	F(1)#9-K(1)/Cs(1)-F(3)#4	125.32(11)
F(2)#16-K(2)-F(3)#14	122.26(8)	F(1)#8-K(1)/Cs(1)-F(3)#5	137.29(11)
F(2)-K(2)-F(3)#12	122.26(8)	F(1)#10-K(1)/Cs(1)-F(3)#4	54.68(11)

F(2)#16-K(2)-F(3)#12	76.03(7)	F(1)#7-K(1)/Cs(1)-F(3)#1	137.29(11)
F(2)-K(2)-F(2)#16	157.41(8)	F(1)#7-K(1)/Cs(1)-F(3)#4	42.71(11)
F(2)#16-K(2)-F(1)#10	92.19(2)	F(1)#10-K(1)/Cs(1)-F(3)#3	42.71(11)
F(2)#16-K(2)-F(1)#11	92.19(2)	F(1)#8-K(1)/Cs(1)-F(3)#1	42.71(11)
F(2)-K(2)-F(1)#11	92.19(2)	F(1)#8-K(1)/Cs(1)-F(3)#2	42.71(11)
F(2)-K(2)-F(1)#10	92.19(2)	F(1)#9-K(1)/Cs(1)-F(3)#3	137.29(11)
F(3)#9-Si(1)-F(3)	180	F(1)#7-K(1)/Cs(1)-F(1)#8	180
F(3)#21-Si(1)-F(3)	88.1(3)	F(1)#9-K(1)/Cs(1)-F(1)#8	90
F(3)#20-Si(1)-F(3)	91.9(3)	F(1)#9-K(1)/Cs(1)-F(1)#7	90
F(3)#20-Si(1)-F(3)#9	88.1(3)	F(1)#10-K(1)/Cs(1)-F(1)#7	90
F(3)#20-Si(1)-F(3)#21	180	F(1)#10-K(1)/Cs(1)-F(1)#8	90
F(3)#21-Si(1)-F(3)#9	91.9(3)	F(1)#9-K(1)/Cs(1)-F(1)#10	180
F(1)-Si(1)-F(3)#9	90	F(1)#10-K(2)-F(3)#10	47.86(13)
F(1)-Si(1)-F(3)#20	90	F(1)#10-K(2)-F(3)#14	112.31(15)
F(1)-Si(1)-F(3)#21	90	F(1)#11-K(2)-F(3)#12	47.86(13)
F(1)#9-Si(1)-F(3)#21	90	F(1)#11-K(2)-F(3)#10	112.31(15)
F(1)#9-Si(1)-F(3)	90	F(1)#11-K(2)-F(3)#14	47.86(13)
F(1)-Si(1)-F(3)	90	F(1)#10-K(2)-F(3)#12	112.31(15)
F(1)#9-Si(1)-F(3)#9	90	F(1)#11-K(2)-F(3)#13	112.31(15)
F(1)#9-Si(1)-F(1)	180	F(1)#10-K(2)-F(3)#13	47.86(13)
F(1)#9-Si(1)-F(3)#20	90	F(1)#10-K(2)-F(1)#11	157.5(3)

Table S4. The compounds in M_3SiF_7 system in ICSD

Compounds	Space group	a	b	c
K_3SiF_7	*P*4/*mbm*	7.725	7.725	5.555
Rb_3SiF_7	*P*4/*mbm*	7.959	7.959	5.823
Cs_3SiF_7	*P*4/*mbm*	8.306	8.306	6.17
NH_4SiF_7	*P*4/*mbm*	8.075	8.075	5.86
Rb_2CsSiF_7	*P*4/*mbm*	8.099	8.099	5.899
KCs_2SiF_7	*P*4/*mbm*	8.115	8.115	5.972
KRb_2SiF_7	*P*4/*mbm*	7.883	7.883	5.724
$RbCs_2SiF_7$	*P*4/*mbm*	8.198	8.198	6.019

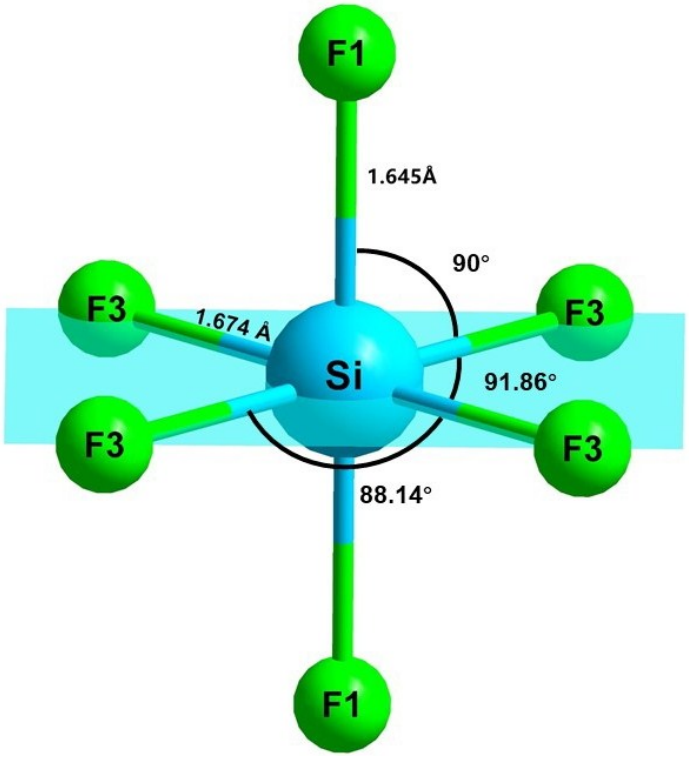


Fig.S1 The structural information of the $[SiF_6]^{2-}$ octahedra.

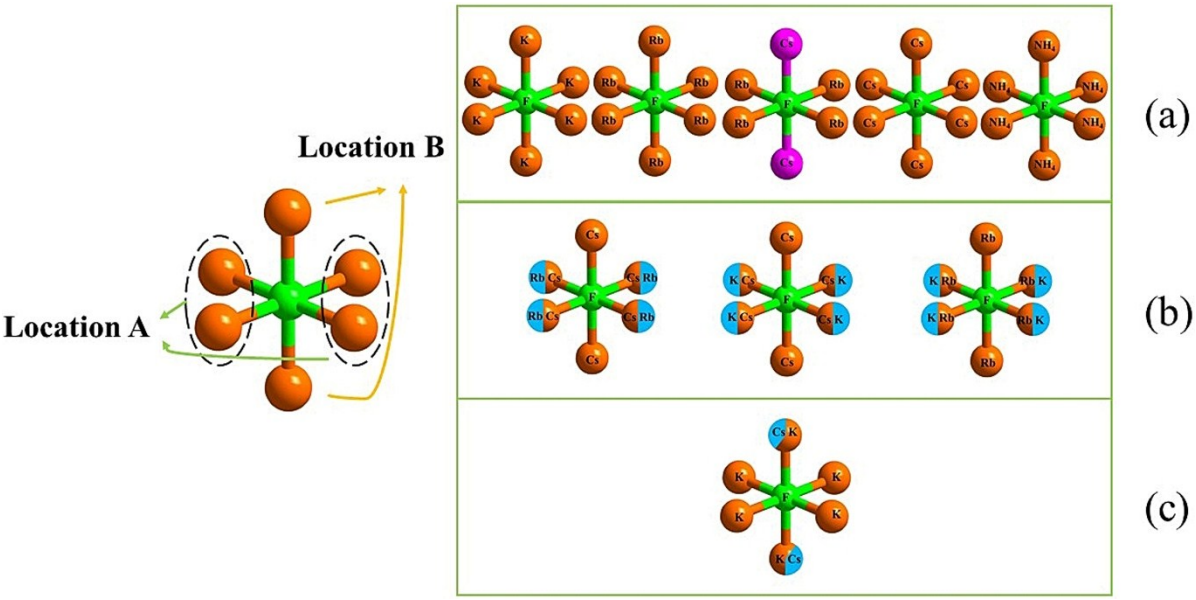
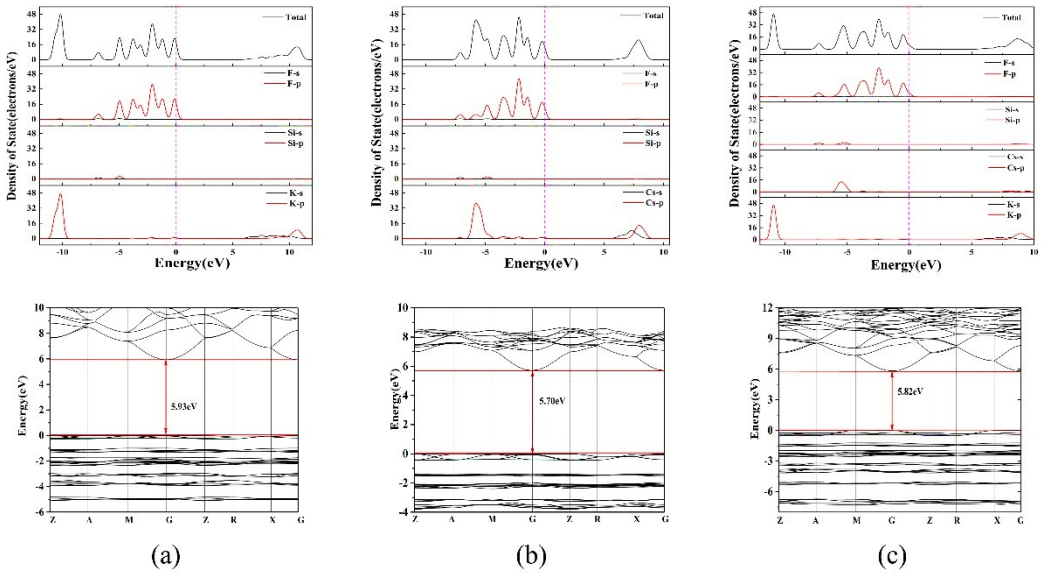
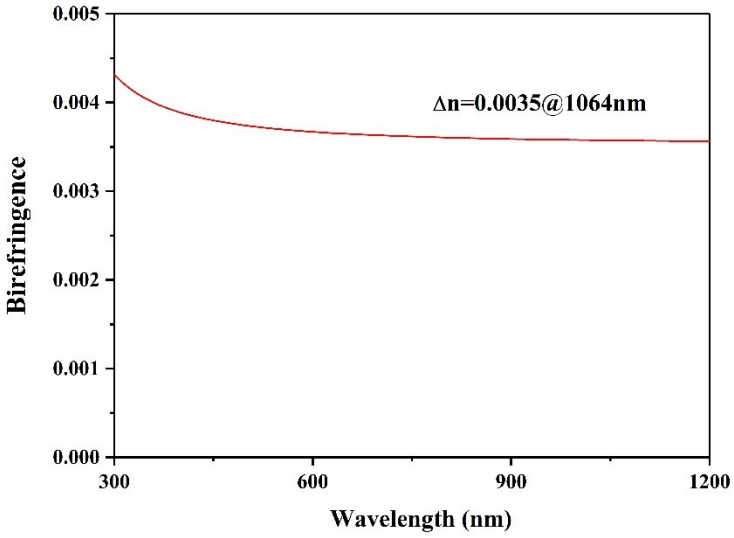


Fig.S2 The FM_6 octahedra of M_3SiF_7 ($M = K^+$, Rb^+, Cs^+, NH_4^+), (a) The FM_6 octahedra of K_3SiF_7, Rb_3SiF_7, Rb_2CsSiF_7, Cs_3SiF_7, and $(NH_4)_3SiF_7$; (b) The FM_6 octahedra of Cs_2RbSiF_7, Cs_2KSiF_7, and Rb_2KSiF_7; (c) The FM_6 octahedra of $K_{2.64}Cs_{0.36}SiF_7$.

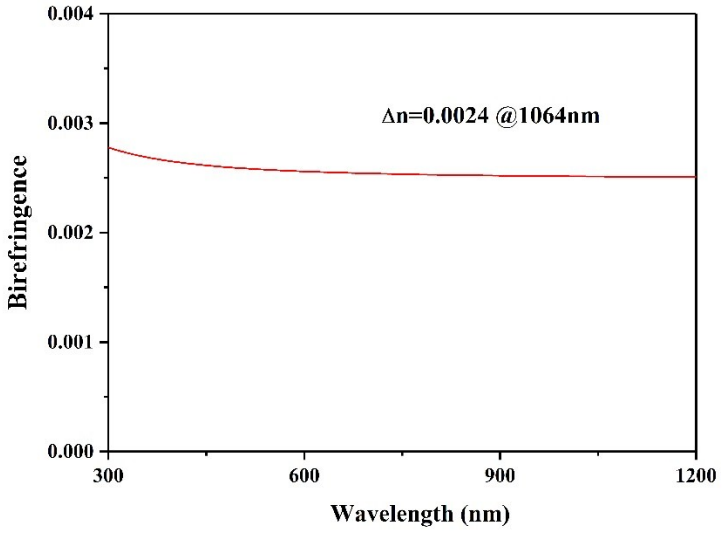


(a) (b) (c)

Fig.S3 Band structure and calculated band gap of (a) K_3SiF_7; (2) Cs_3SiF_7; (3) $K_{2.64}Cs_{0.36}SiF_7$.



(a)



(b)

Fig.S4 Calculated birefringence of (a) K_3SiF_7; (b) Cs_3SiF_7.