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Electronic Supplementary Information for:

Modulation of Perovskite-Related Framework Induced by Alkaline Earth Metal in Phosphate Fluorides A_2MPO_4F (A= K, Rb; M = Ba, Ca)

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Table S1. Crystal data and structure refinement for K_2CaPO_4F.

Empirical formula	K_2CaPO_4F
Formula weight	232.25
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group, *Z*	*Pnma*, 4
Unit cell dimensions	*a* = 12.661(3) Å
	b = 5.8589(16) Å
	c = 7.325(2) Å
Volume	543.4(2) $Å^3$
Calculated density	2.839 g/cm^3
Absorption coefficient	2.931 mm^{-1}
F(000)	456
Limiting indices	$-16 \leq h \leq 16$, $-7 \leq k \leq 17$, $-9 \leq l \leq 5$
Reflections collected / unique	2849 / 695 [*R*(int) = 0.0434]
Completeness	99.4 %
Data / restraints / parameters	695 / 0 / 53
Goodness-of-fit on F_o^2	1.247
Final *R* indices [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1= 0.0727, wR_2 = 0.1725
R indices (all data) [a]	R_1 = 0.0751, wR_2 = 0.1735
Largest diff. peak and hole	1.095 and -0.941 $e \cdot Å^{-3}$

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

Table S2. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS for Rb_2CaPO_4F. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	BVS
Rb(1)	763(1)	2500	7015(1)	15(1)	1.16
Rb(2)	3120(1)	2500	4895(1)	15(1)	1.25
Ca(1)	738(1)	2500	2002(1)	8(1)	2.12
P(1)	3414(1)	2500	9836(2)	7(1)	5.00
O(1)	3649(2)	403(3)	8712(3)	15(1)	2.11
O(2)	4112(2)	2500	11513(5)	16(1)	2.11
O(3)	2268(2)	2500	10371(4)	15(1)	2.1
F(1)	0	0	0	13(1)	0.90

Table S3. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS for K_2CaPO_4F. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	BVS
K(1)	6876(2)	7500	9961(4)	24(1)	0.97
K(2)	5740(2)	2500	-2910(4)	21(1)	0.96
Ca(1)	5710(2)	2500	2022(3)	10(1)	2.31
P(1)	6614(2)	7500	4882(3)	7(1)	5.10
O(1)	5985(7)	7500	6647(13)	26(2)	2.09
O(2)	6323(5)	5360(10)	3799(9)	26(2)	2.08
O(3)	7804(6)	7500	5254(14)	26(2)	2.00
F(1)	5000	0	0	16(1)	1.12

Table S4. Selected bond distances (Å) and bond angles (deg) for Rb_2CaPO_4F.

Rb(1)-F(1)#1	2.8498(15)	F(1)#1-Rb(1)-F(1)#2	63.16(5)
Rb(1)-F(1)#2	2.8498(15)	F(1)#1-Rb(1)-O(2)#3	129.34(7)
Rb(1)-O(3)#3	3.013(2)	F(1)#2-Rb(1)-O(2)#3	66.17(7)
Rb(1)-O(3)#4	3.013(2)	F(1)#1-Rb(1)-O(2)#4	66.17(7)
Rb(1)-O(2)#5	3.048(3)	F(1)#2-Rb(1)-O(2)#4	129.34(7)
Rb(1)-O(2)#6	3.048(3)	O(2)#3-Rb(1)-O(2)#4	164.49(13)
Rb(1)-O(2)#3	3.100(3)	F(1)#1-Rb(1)-O(1)#5	92.57(6)
Rb(1)-O(2)#7	3.100(3)	F(1)#2-Rb(1)-O(1)#5	67.33(5)
Rb(1)-O(4)	3.162(4)	O(2)#3-Rb(1)-O(1)#5	67.60(8)
Rb(1)-O(3)#5	3.378(4)	O(2)#4-Rb(1)-O(1)#5	115.65(7)
Rb(2)-O(3)#8	2.821(4)	F(1)#1-Rb(1)-O(1)#6	67.33(5)
Rb(2)-F(1)#9	2.8475(16)	F(1)#2-Rb(1)-O(1)#6	92.57(6)
Rb(2)-F(1)#10	2.8475(16)	O(2)#3-Rb(1)-O(1)#6	115.65(7)
Rb(2)-O(2)#3	2.997(3)	O(2)#4-Rb(1)-O(1)#6	67.60(8)
Rb(2)-O(2)#7	2.997(3)	O(1)#5-Rb(1)-O(1)#6	48.51(9)
Rb(2)-O(4)#3	3.047(2)	F(1)#1-Rb(1)-O(1)#3	173.86(4)
Rb(2)-O(4)#4	3.047(2)	F(1)#2-Rb(1)-O(1)#3	114.12(6)
Rb(2)-O(2)#11	3.177(3)	O(2)#3-Rb(1)-O(1)#3	48.30(8)
Rb(2)-O(2)	3.177(3)	O(2)#4-Rb(1)-O(1)#3	116.28(8)
Rb(2)-O(4)#8	3.539(4)	O(1)#5-Rb(1)-O(1)#3	81.29(7)
Ca(1)-O(1)#7	2.290(2)	O(1)#6-Rb(1)-O(1)#3	107.94(5)
Ca(1)-O(1)#3	2.290(2)	F(1)#1-Rb(1)-O(1)#7	114.12(6)
Ca(1)-F(1)	2.3131(12)	F(1)#2-Rb(1)-O(1)#7	173.86(4)
Ca(1)-F(1)#14	2.3131(12)	O(2)#3-Rb(1)-O(1)#7	116.28(8)
Ca(1)-O(3)#8	2.315(3)	O(2)#4-Rb(1)-O(1)#7	48.30(8)
Ca(1)-O(2)#5	2.370(3)	O(1)#5-Rb(1)-O(1)#7	107.94(5)
P(1)-O(3)	1.531(3)	O(1)#6-Rb(1)-O(1)#7	81.29(7)
P(1)-O(1)#11	1.535(2)	O(1)#3-Rb(1)-O(1)#7	81.29(7)
P(1)-O(1)	1.535(2)	O(1)#3-Rb(1)-O(1)#7	67.98(9)

P(1)-O(2)	1.538(3)	F(1)#1-Rb(1)-O(3)	66.23(6)

Symmetry transformations used to generate equivalent atoms:

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

#5 x-1/2, y, -z+3/2 #6 x-1/2, -y+1/2, -z+3/2 #7 -x+1/2, y+1/2, z-1/2 #8 x, y, z-1

#9 x+1/2, -y+1/2, -z+1/2 #10 -x+1/2, -y, z+1/2 #11 x, -y+1/2, z

#12 x+1/2, y, -z+3/2 #13 -x+1/2, -y+1, z+1/2 #14 -x, y+1/2, -z #15 -x, -y, -z+1

#16 -x, -y+1, -z+1 #17 x-1/2, y, -z+1/2 #18 -x, -y, -z

Table S5. Selected bond distances (Å) and bond angles (deg) for K_2CaPO_4F.

K(1)-O(1)	2.677(10)	O(2)-Ca(1)-O(2)#1	95.7(3)
K(1)-F(1)#9	2.791(2)	O(2)-Ca(1)-F(1)	172.35(18)
K(1)-F(1)#10	2.791(2)	O(2)#1-Ca(1)-F(1)	91.91(17)
K(1)-O(2)#11	2.955(7)	O(2)-Ca(1)-F(1)#2	91.91(17)
K(1)-O(2)#12	2.955(7)	O(2)#1-Ca(1)-F(1)#2	172.35(18)
K(1)-O(3)#13	2.9651(17)	F(1)-Ca(1)-F(1)#2	80.44(7)
K(1)-O(3)#12	2.9651(16)	O(2)-Ca(1)-O(3)#3	92.5(2)
K(1)-O(2)#14	3.157(7)	O(2)#1-Ca(1)-O(3)#3	92.5(2)
K(1)-O(2)#15	3.157(7)	F(1)-Ca(1)-O(3)#3	87.5(2)
K(2)-F(1)#2	2.751(2)	F(1)#2-Ca(1)-O(3)#3	87.5(2)
K(2)-F(1)	2.751(2)	O(2)-Ca(1)-O(1)#4	94.3(2)
K(2)-O(3)#3	2.961(10)	O(2)#1-Ca(1)-O(1)#4	94.3(2)
K(2)-O(1)#7	2.9636(15)	F(1)-Ca(1)-O(1)#4	84.8(2)
K(2)-O(1)#8	2.9636(15)	F(1)#2-Ca(1)-O(1)#4	84.8(2)
K(2)-O(2)#17	2.969(7)	O(3)#3-Ca(1)-O(1)#4	169.9(4)
K(2)-O(2)#6	2.969(7)	O(1)-K(1)-F(1)#9	69.54(16)
K(2)-O(2)#18	3.027(7)	O(1)-K(1)-F(1)#10	69.54(16)
K(2)-O(2)#7	3.027(7)	F(1)#9-K(1)-F(1)#10	63.32(6)
Ca(1)-O(2)	2.260(6)	O(1)-K(1)-O(2)#11	93.7(2)
Ca(1)-O(2)#1	2.260(6)	F(1)#9-K(1)-O(2)#11	163.21(17)
Ca(1)-F(1)	2.2683(16)	F(1)#10-K(1)-O(2)#11	111.23(12)
Ca(1)-F(1)#2	2.2683(16)	O(1)-K(1)-O(2)#12	93.7(2)
Ca(1)-O(3)#3	2.284(8)	F(1)#9-K(1)-O(2)#12	111.23(12)
Ca(1)-O(1)#4	2.357(9)	F(1)#10-K(1)-O(2)#12	163.21(17)

Symmetry transformations used to generate equivalent atoms:

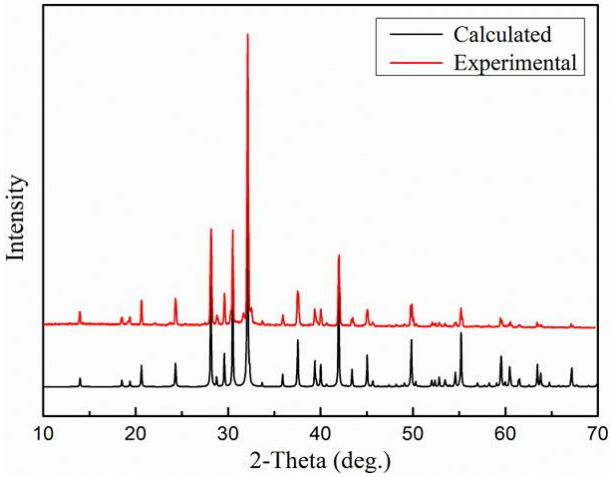
#1 x+1/2, -y+3/2, -z+1/2 #2 -x+1/2, -y+1, z+1/2 #3 -x+1/2, -y, z-1/2

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

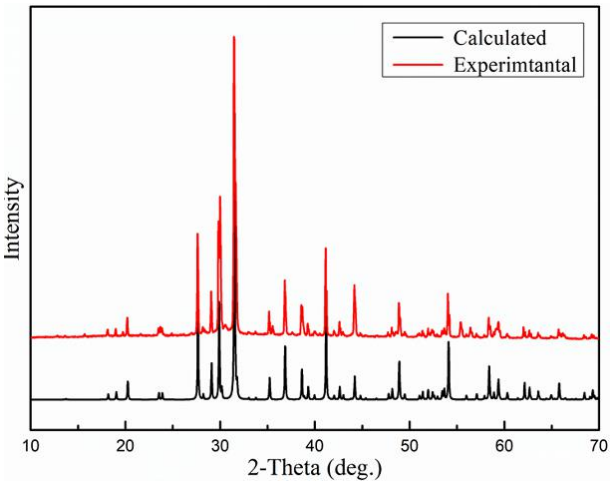
#7 -x+1/2, y+1/2, z-1/2 #8 -x+1/2, -y+2, z+1/2 #9 x, -y+1/2, z #10 x, y+1, z
#11 -x+1/2, y+1/2, z+1/2 #12 -x, y-1/2, -z #13 -x, -y+1, -z+1 #14 x-1/2, y, -z+1/2
#15 x-1/2, y+1, -z+1/2 #16 -x+1/2, -y+2, z-1/2 #17 x, y-1, z
#18 -x+1/2, -y, z+1/2 #19 -x, -y+2, -z

Table S6. Comparison of BVS and GII values in $Rb_2CaPO_4F$and K_2BaPO_4F.

Compounds	BVS				GII	
	Rb^+	K^+	Ca^{2+}	Ba^{2+}	Rb^+ & Ca^+	K^+ & Ba^{2+}
Rb_2CaPO_4F	1.16 & 1.25	0.76 & 0.86	2.12	5.12	0.046	0.392
K_2BaPO_4F	1.59	1.29	0.76	1.82	0.277	0.079



(a)



(b)

Figure S1. XRD patterns of: (a) K_2CaPO_4F; (b) Rb_2CaPO_4F.

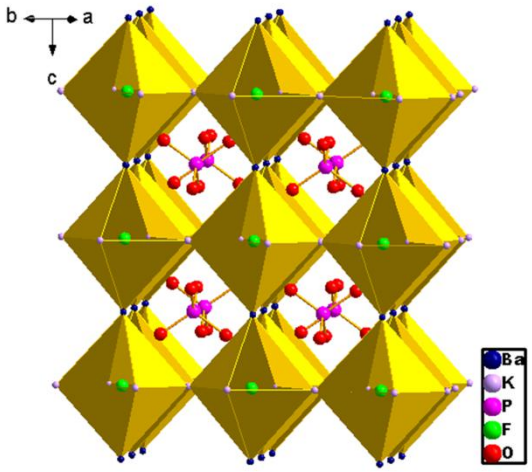
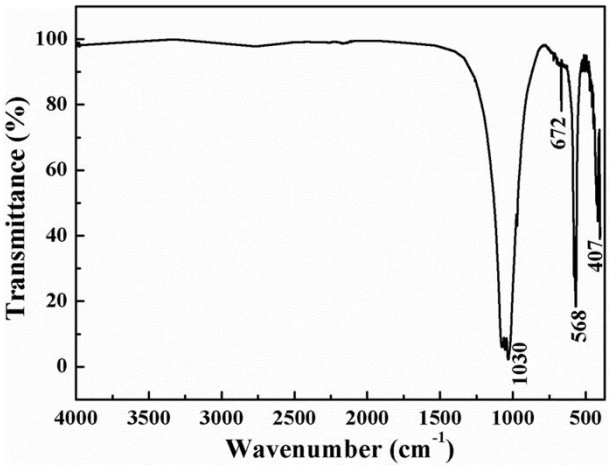
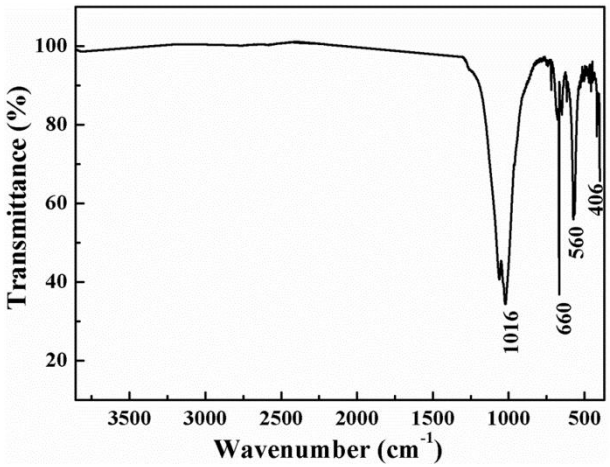


Figure S2. The 3D framework of K_2BaPO_4F.

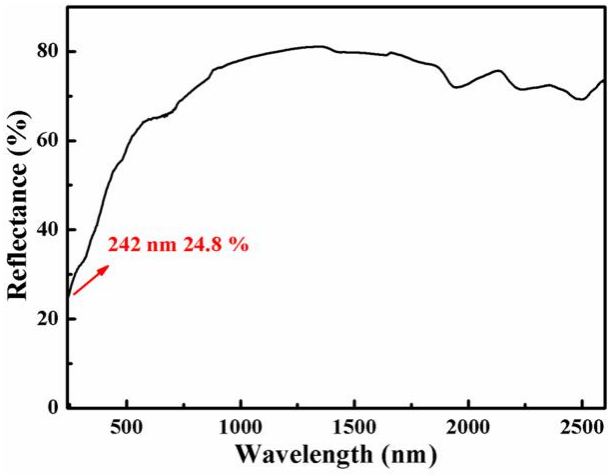


(a)

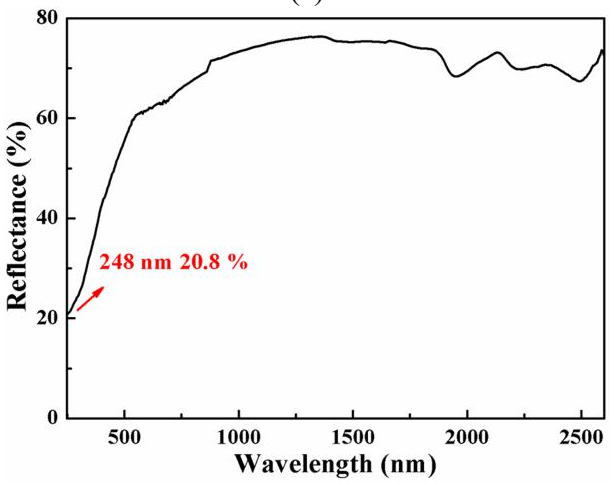


(b)

Figure S3. IR spectra of : (a) K_2CaPO_4F; (b) Rb_2CaPO_4F.



(a)



(b)

Figure S4. UV-Vis-NIR diffuse reflectance spectra of: (a) K_2CaPO_4F; (b) Rb_2CaPO_4F.

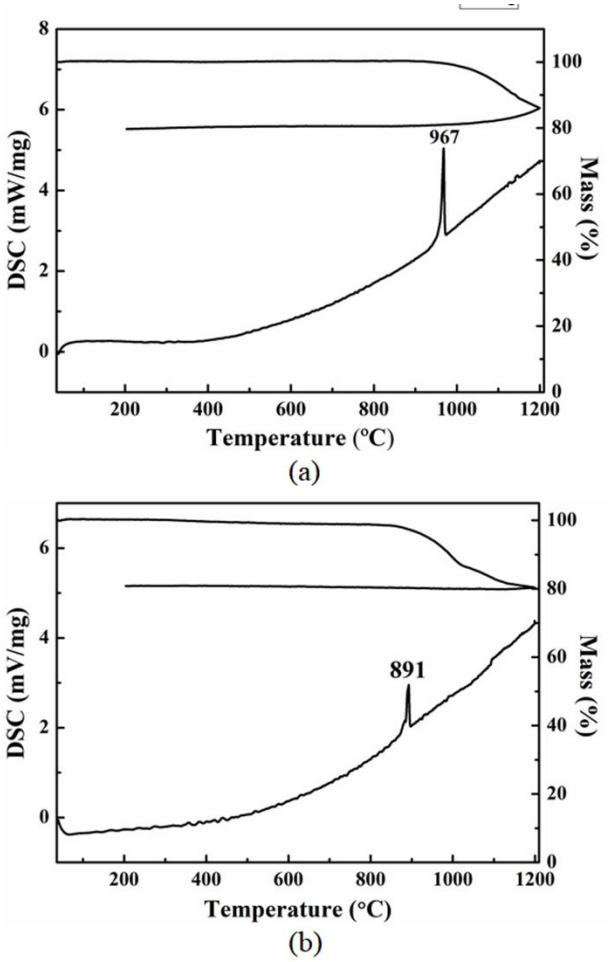


Figure S5. TG-DSC curves of: (a) K_2CaPO_4F; (b) Rb_2CaPO_4F.

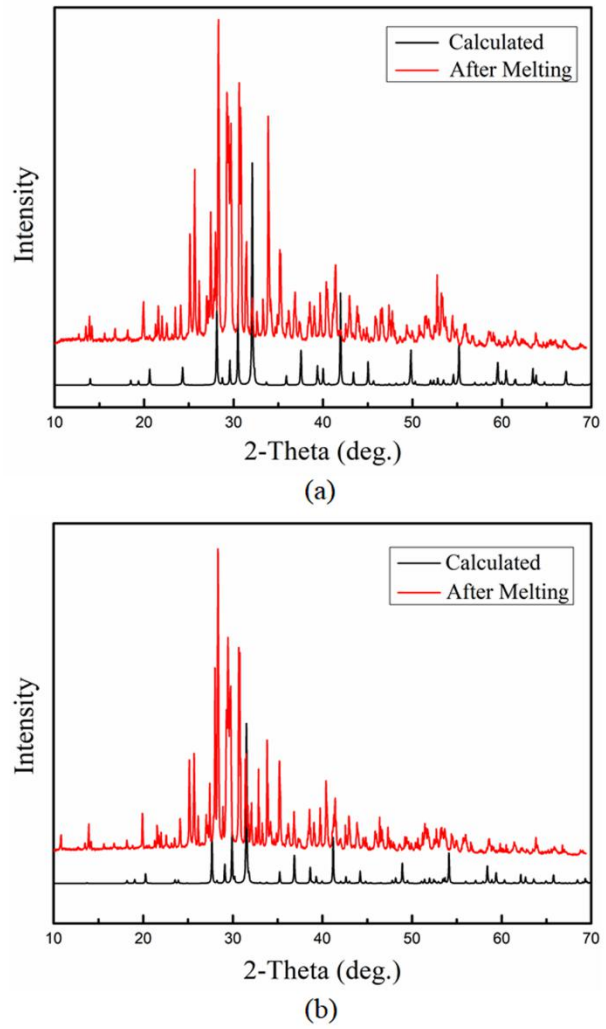


Figure S6. Calculated and after melting powder XRD patterns of: (a) K_2CaPO_4F; (b) Rb_2CaPO_4F.