Supporting information

Denticity and mobility of the carbonate groups in $AMCO_3F$ fluorocarbonates: a study on $KMnCO_3F$ and high temperature $KCaCO_3F$ polymorph.

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Table S1**.** Crystallographic data and refinement parameters for the $KMnCO_3F$ structure by means of electron diffraction tomography.

Formula	$KMnCO_3F$
Space group	$P\bar{6}c2$
a, Å	5.11895(3)*
c, Å	8.42020(6)*
V, Å^3	191.080(4)
Z	2
ρ, g/cm^3	3.008
Radiation	Electron, λ = 0.0251 Å
Scanned angular range, deg.	73
Number of reflections	1037
Number of independent reflections	172
Number of independent reflections (I > 3σ(I))	58
Parameters refined	4
R_F	0.184

* - unit cell parameter from powder X-ray diffraction data.

Table S2. Fractional atomic coordinates, atomic displacement parameters for the $KMnCO_3F$ structure. The refined parameters from electron diffraction tomography and joint SXPD/NPD refinements are in the top and bottom rows, respectively.

Atom	Position	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}, Å^2
K1	2*a*	0	0	0	0.003(2) 0.0157(1)
Mn1	2*f*	2/3	1/3	1/4	0.003(2) 0.01348(2)
C1	2*d*	1/3	2/3	1/4	0.003(2) 0.0125(3)
O1	6*k*	0.292(4) 0.2818(2)	0.408(5) 0.3933(2)	1/4	0.003(2) 0.0226(2)
F1	2*e*	2/3	1/3	0	0.003(2) 0.0286(2)

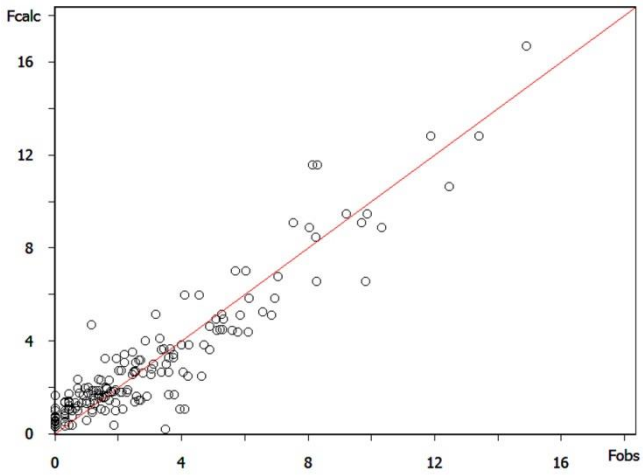

Figure S1. F_{obs}-F_{calc} plot for $KMnCO_3F$ after refinement from EDT data.

Table S3**.** Crystallographic data and refinement parameters for the $KMnCO_3F$ structure by means of joint Rietveld refinement from SXPD/NPD data.

Formula	$KMnCO_3F$
Space group	$P\bar{6}c2$
a, Ås	5.119800(8)
c, Å	8.42117(1)
V, $Å^3$	191.1654(6)
Z	2
ρ, g/cm^3	3.006
Parameters refined	8
SXPD data set:	
Radiation	Synchrotron X-ray, λ = 0.4137 Å
2θ range, step, deg.	2.6 – 43.7, 0.001
Number of reflections	346
R_F, R_P, R_{wP}	0.044, 0.069, 0.089
NPD data set:	
Radiation	neutron CW, λ = 1.494 Å
2θ range, step, deg.	9.4 – 164.5, 0.05
Number of reflections	167
R_F, R_P, R_{wP}	0.047, 0.050, 0.063

Table S4**.** Main interatomic distances for the $KMnCO_3F$ structure by means of joint Rietveld refinement from SXPD/NPD data.

Distance, Å		Distance, Å	
K1-O1	2.7683(4) ×6	Mn1-O1	2.1404(9) ×3
K1-F1	2.95592(1) ×3	Mn1-O1	3.008(1) ×3
		Mn1-F1	2.1053(1) ×1
C1-O1	1.2881(9) ×3		

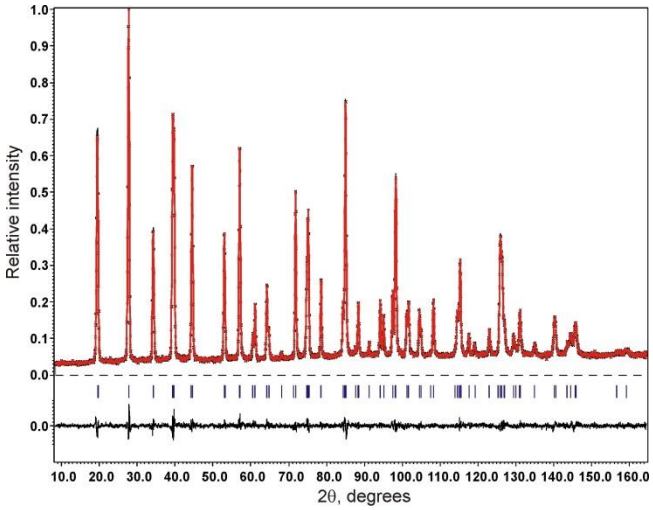

Figure S2. The experimental, calculated and difference NPD diffraction profiles after the Rietveld refinement of the LT-$KCaCO_3F$ structure.

Table S5**.** Crystallographic data and refinement parameters for the LT-$KCaCO_3F$ structure.

Formula	$KCaCO_3F$
Space group	$P\bar{6}m2$
a, Å	5.10098(8)
c, Å	4.45608(9)
V, Å^3	100.413(3)
Z	1
ρ, g/cm^3	2.616
Parameters refined	17
Temperature, ^{o}C	25
Radiation	neutron CW, λ = 1.494 Å
2θ range, step, deg.	8.4 – 164.5, 0.05
Number of reflections	121
R_F, R_P, R_{wP}	0.009, 0.042, 0.054

Table S6. Fractional atomic coordinates, atomic displacement parameters for the LT-$KCaCO_3F$ structure.

Atom	Position	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å^2
K1	1*a*	0	0	0	0.0151(7)
Ca1	1*d*	1/3	2/3	1/2	0.0088(5)
C1	1*f*	2/3	1/3	1/2	0.0086(5)
O1	3*k*	0.8118(1)	-*x*	1/2	0.0155(3)
F1	1*c*	1/3	2/3	0	0.0214(6)

* - $U_{eq}=1/3[a^{*2}a^2U_{11} + b^{*2}b^2U_{22} + c^{*2}c^2U_{33} + 2aba^*b^*(\cos\gamma)U_{12} + 2aca^*c^*(\cos\beta)U_{13} + 2bcb^*c^*(\cos\alpha)U_{23}]$

Table S7. Anisotropic atomic displacement parameters (Å^2) for the disordered model of the LT-$KCaCO_3F$ structure.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K1	0.0176(7)	0.0176(7)	0.010(1)	0.0088(4)	0	0
Ca1	0.0090(6)	0.0090(6)	0.0083(9)	0.0045(3)	0	0
C1	0.0073(6)	0.0073(6)	0.0113(8)	0.0036(3)	0	0
O1	0.0118(3)	0.0118(3)	0.0253(5)	0.0077(4)	0	0
F1	0.0270(7)	0.0270(7)	0.0101(9)	0.0135(4)	0	0

Table S8**.** Main interatomic distances for the LT-$KCaCO_3F$ structure.

Distance, Å		Distance, Å	
K1-O1	2.7801(4) ×6	Ca1-O1	2.5576(4) ×6
K1-F1	2.9451(1) ×3	Ca1-F1	2.22804(9) ×2
		C1-O1	1.2822(6) ×3

Table S9**.** Crystallographic data and refinement parameters for the HT-$KCaCO_3F$ structure.

Formula	$KCaCO_3F$
Space group	$P\bar{6}2m$
a, Å	9.1477(2)
c, Å	4.4169(2)
V, Å^3	320.09(1)
Z	3
ρ, g/cm^3	2.462
Parameters refined	35 (ordered model)/ 32 (disordered model)
Temperature, ^{o}C	500
Radiation	neutron CW, λ = 1.494 Å
2θ range, step, deg.	8.4 – 164.5, 0.05
Number of reflections	285
R_F, R_P, R_{wP}	0.036, 0.035, 0.045

Table S10. Fractional atomic coordinates, atomic displacement parameters for the ordered model of the HT-$KCaCO_3F$ structure.

Atom	Position	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}, Å^2
K1	3*g*	0.711(1)	0	1/2	0.069(4)
Ca1	3*f*	0.3781(4)	0	0	0.024(2)
C1	2*c*	1/3	2/3	0	0.026(1)
C2	1*a*	0	0	0	0.032(2)
O1	6*j*	0.3127(4)	0.5174(4)	0	0.041(1)
O2	3*f*	0.1319(6)	0	0	0.115(4)
F1	3*g*	0.3772(6)	0	1/2	0.073(3)

Table S11. Fractional atomic coordinates, atomic displacement parameters for the disordered model of the HT-$KCaCO_3F$ structure.

Atom	Position	Occupancy	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}*/U_{iso}, Å^2
K1	3*g*	1	0.705(1)	0	½	0.085(5)
Ca1	3*f*	1	0.3772(4)	0	0	0.026(2)
C1	2*c*	1	1/3	2/3	0	0.023(1)
C2	1*a*	1	0	0	0	0.034(2)
O1	12*l*	0.5	0.3121(4)	0.5168(4)	0.0467(8)	0.0215(7)
O2	12*l*	0.5	0.1482(9)	0.032(1)	0.075(1)	0.040(3)
F1	3*g*	1	0.3774(6)	0	½	0.071(3)

* - $U_{eq}=1/3[a^{*2}a^2U_{11} + b^{*2}b^2U_{22} + c^{*2}c^2U_{33} + 2aba^*b^*(\cos\gamma)U_{12} + 2aca^*c^*(\cos\beta)U_{13} + 2bcb^*c^*(\cos\alpha)U_{23}]$

Table S12. Anisotropic atomic displacement parameters (Å^2) for the disordered model of the HT-$KCaCO_3F$ structure.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K1	0.113(7)	0.075(6)	0.053(5)	0.038(3)	0	0
Ca1	0.026(2)	0.037(2)	0.019(3)	0.019(1)	0	0
F1	0.094(3)	0.100(4)	0.020(3)	0.050(2)	0	0
C1	0.012(1)	0.012(1)	0.043(3)	0.0062(5)	0	0
C2	0.019(2)	0.019(2)	0.064(6)	0.0095(9)	0	0

Table S13**.** Main interatomic distances for the disordered HT-$KCaCO_3F$ structure.*

Distance, Å		Distance, Å	
K1-O1	2.798(5) ×4	Ca1-O1	2.485(3) ×4
K1-O1	3.107(6) ×4	Ca1-O1	2.512(6) ×4
K1-O2	2.81(1) ×4	Ca1-O2	2.28(1) ×4
K1-O2	3.20(1) ×4	Ca1-F1	2.2085(3) ×2
K1-O2	3.29(1) ×4		
K1-F1	3.00(1) ×1	C1-O1	1.301(4) ×3
K1-F1	3.14(1) ×2	C1-O2	1.28(1) ×3

* - not all K-O and Ca-O distances are realized simultaneously because of disorder in the oxygen sublattice.

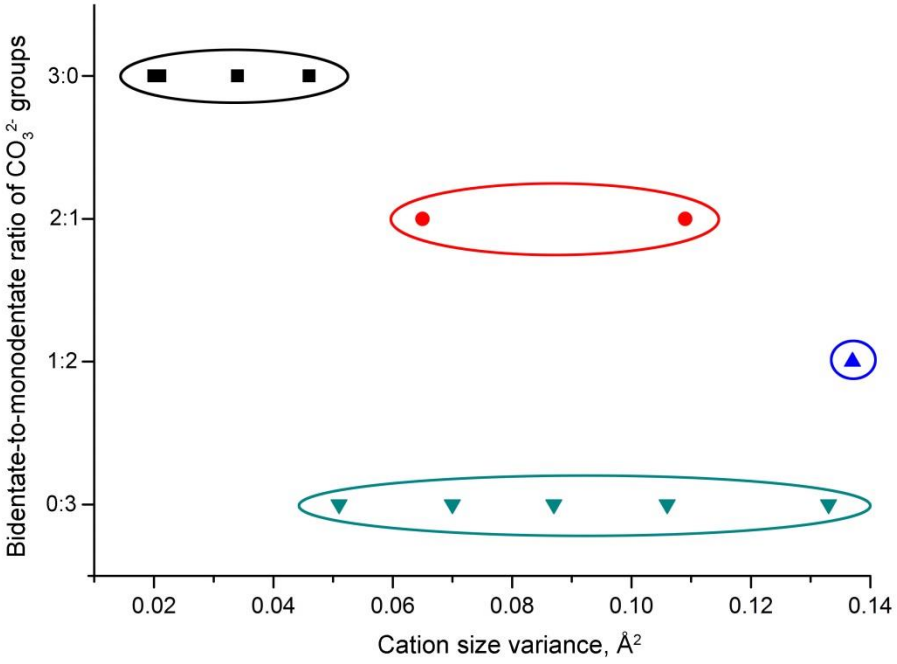

Figure S3. Dependence of the bidentate-to-monodentate ratio of the carbonate groups on the cation size variance in the $AMCO_3F$ structures. Increasing size variance decreases the fraction of the bidentate groups, but the materials with the monodentate groups only do not follow the trend.

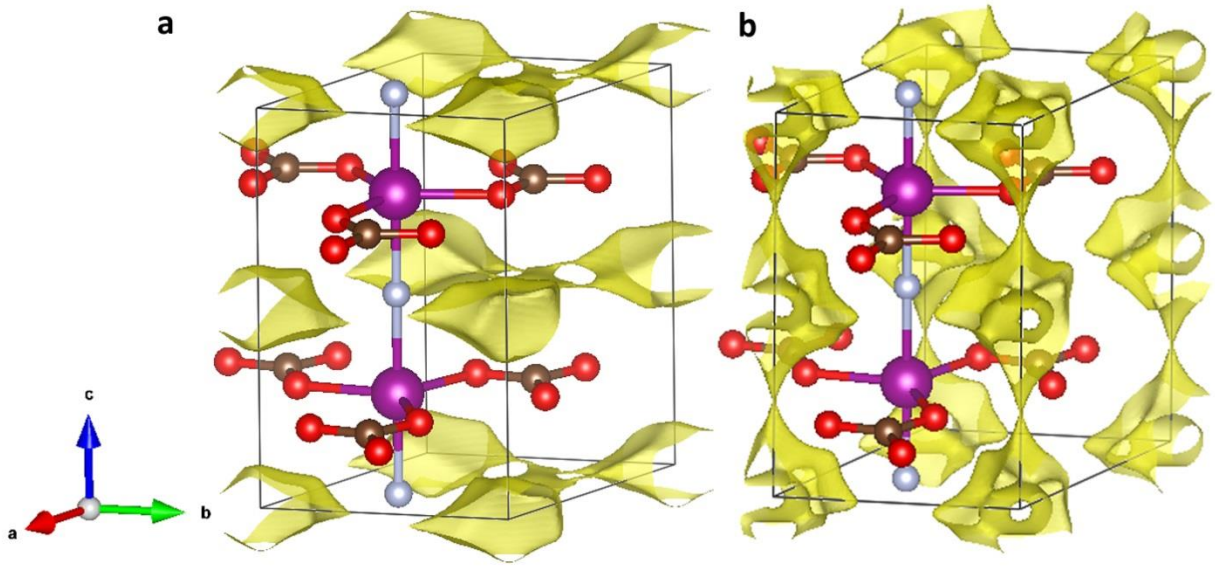

Figure S4. Lowest barrier alkali cation diffusion pathways in $KMnCO_3F$ (a) and hypothetical $LiMnCO_3F$ (b).