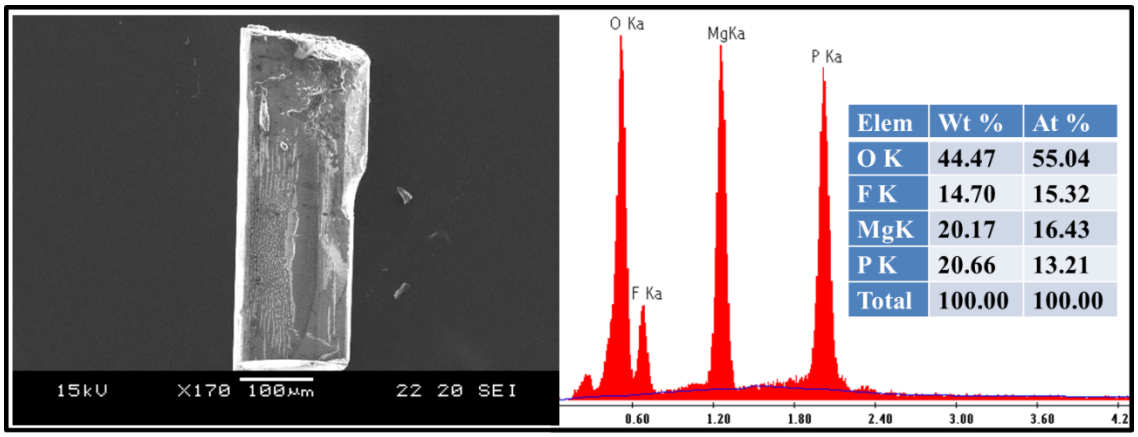
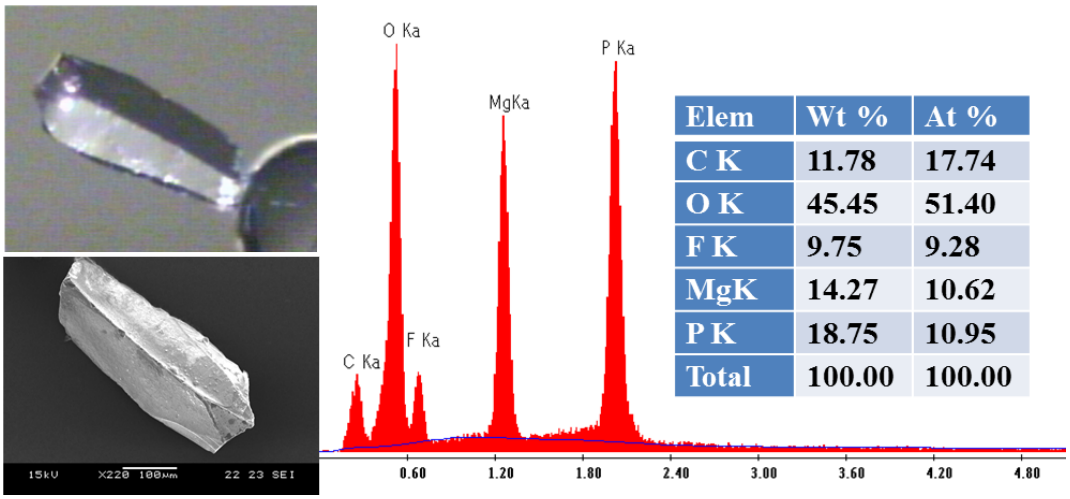
Supplementary information



Elem	Wt %	At %
O K	44.47	55.04
F K	14.70	15.32
MgK	20.17	16.43
P K	20.66	13.21
Total	100.00	100.00

Figure S1. SEM images and EDX analyses of the $Li_2Mg[PO_4]F$ single crystal used for the data collection.



Elem	Wt %	At %
C K	11.78	17.74
O K	45.45	51.40
F K	9.75	9.28
MgK	14.27	10.62
P K	18.75	10.95
Total	100.00	100.00

Figure S2. SEM and CCD images, and EDX analyses of the $Li_9Mg_3[PO_4]_4F_3$ single crystal used for the data collection.

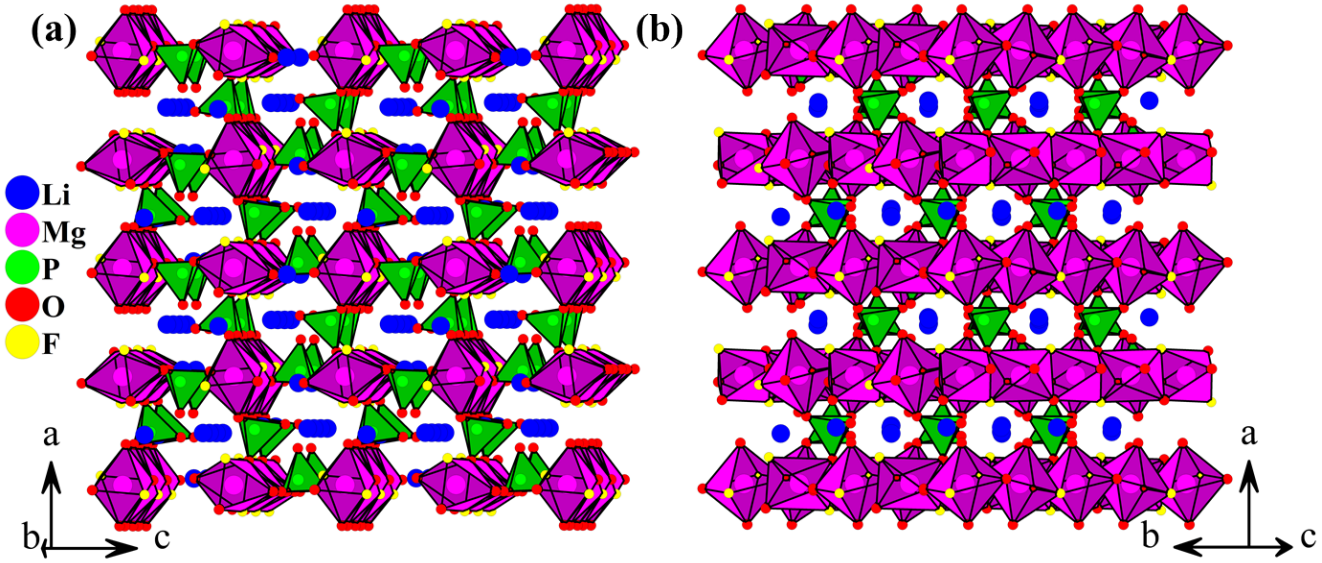


Figure S3. Views of the tunnels running along the [010] (a), and [011] directions (b).

$Li_2Ni[PO_4]F$:$Li_4Ni_2[PO_4]_2F_2$	Li1	Li2	Li3	Ni1	Ni2	P1	P2	O1	O2	O3	O4	O5	O6	F1	F2
Pnma (no. 62)	8*d*	4*c*	4*c*	4*a*	4*b*	4*c*	4*c*	8*d*	4*c*	4*c*	4*c*	4*c*	8*d*	4*c*	4*c*
a = 10.4730 Å	0.240	0.271	0.027	0	0	0.0236	0.2432	0.1891	0.2184	0.1694	0.3890	0.4739	0.0320	0.1272	0.4503
b = 6.2887 Å	0.012	1/4	1/4	0	0	1/4	1/4	0.0494	1/4	1/4	1/4	1/4	0.5517	1/4	1/4
c = 10.8460 Å	0.335	0.582	0.27	0	1/2	0.7441	0.0781	0.0150	0.2167	0.7440	0.0522	0.6215	0.3195	0.4729	0.3838
$\square_2Mg_{1-x}Fe_xAl_3[BO_3][SiO_4]O_2$	Vacant	Mg1	Al3	Al1	Al2	B	Si	O6	O1	Vacant	O4	O3	O7	O5	O2
Pnma (no. 62)		4*c*	4*c*	4*a*	4*b*	4*c*	4*c*	8*d*	4*c*		4*c*	4*c*	8*d*	4*c*	4*c*
a = 10.990 Å		0.2812	0.0522	0	0	0.0003	0.2367	0.1703	0.2119		0.3789	0.4964	–0.0019	0.0992	0.4782
b = 5.750 Å		1/4	1/4	0	0	1/4	1/4	0.0239	1/4		1/4	1/4	0.5462	1/4	1/4
c = 10.34 Å		0.4067	0.2738	0	1/2	0.7492	0.0661	0.0077	0.2240		0.0263	0.6217	0.3196	0.4540	0.3813

Figure S4. Comparison of the atomic positions in $Li_2Ni[PO_4]F$ and $Mg_{1-x}Fe_xAl_3[BO_3][SiO_4]O_2$ structures.

Figure S5. Group-subgroup scheme in the Bärnighausen formalism [31, 32] for the structure of $Li_2Ni[PO_4]F$ and comparison with $Li_5M(PO_4)_2F_2$ (M = V and Cr) structures. The indices of the *translationengleiche* (t) transition, as well as the unit cell and origin shift transformations are given.

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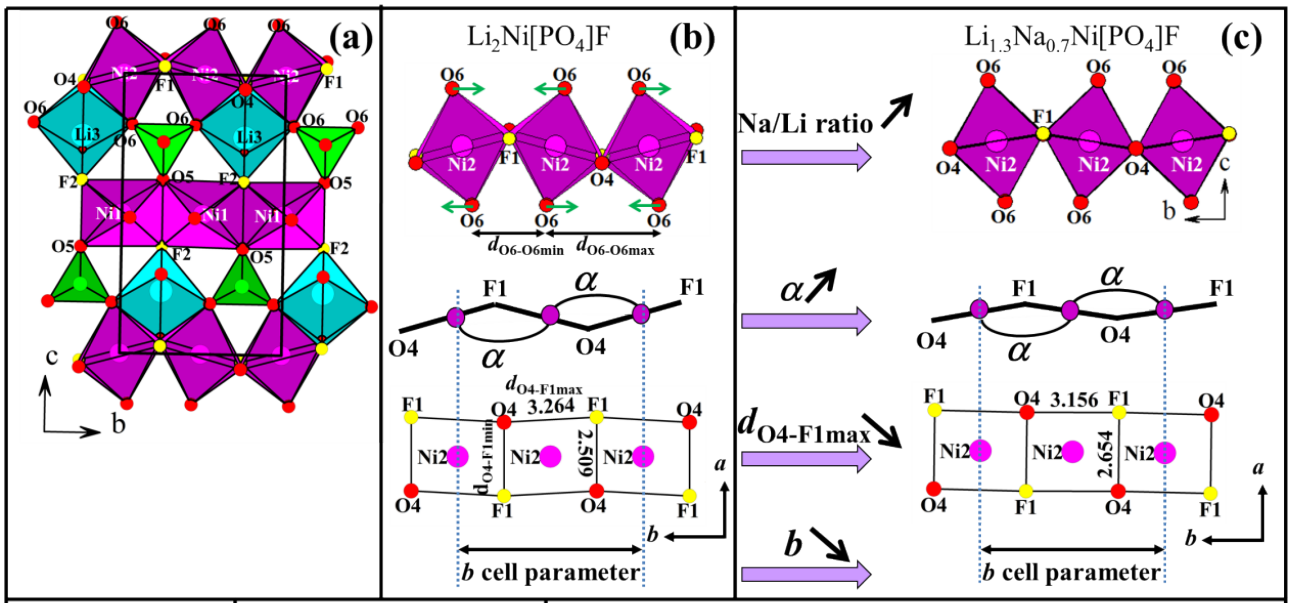
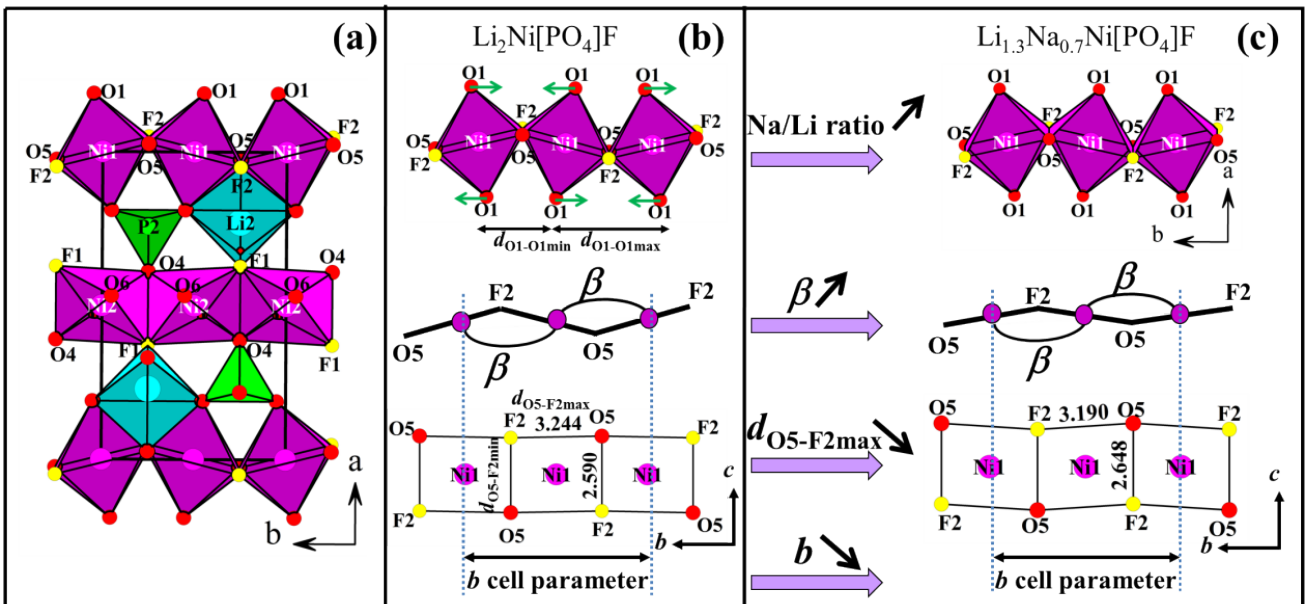
3.3.3. Effect of the Li/Na ratio on the compounds with the $Li_2Ni[PO_4]F$-type structure

When the lithium is replaced by sodium in $Li_2Ni[PO_4]F$, one would expect an increase of the cell parameters due to the large difference between the ionic radii of Li^+ and Na^+. However, we observed that only the *a* and *c* cell parameters increased, whereas *b* decreased. This phenomenon has been also observed in the cobalt and iron $Li_{2-x}Na_xM[PO_4]F$-systems (see the table in Fig. S6†). In order to explain the origin of this common behavior, projection views of the $Ni2O_3F$ infinite chains in $Li_2Ni[PO_4]F$ and $Li_{1.3}Na_{0.7}Ni[PO_4]F$ are depicted on Fig. S6b, c†, respectively. One can see clearly a significant tilt of the octahedra forming the $Ni2O_3F$ infinite chains, when the lithium is partially replaced by sodium. The directions of the tilts are represented by green arrows on Fig. S6b†. As a consequence of these tilts, we observe an increase of the $\alpha_{O4\text{-}F1\text{-}O4}$ angle from 148.84 to 160.37 °, a decrease of the $d_{O6\text{-}O6max}$ distance from 3.795 to 3.693 Å, and an increase of the $d_{O6\text{-}O6min}$ distance from 2.494 to 2.526Å. This flattening of the $\alpha_{O4\text{-}F1\text{-}O4}$ angle should induce an increase of the $d_{Ni\text{-}Ni}$ distance and the cell parameter *b*, since $b = 2 \times d_{Ni\text{-}Ni}$. This is in contradiction with experimental results which shows a decrease of cell parameter *b*. A more careful examination of the interatomic distances shows a decrease of the $d_{O4\text{-}F1max}$ from 3.264 to 3.156 Å and an increase of $d_{O4\text{-}F1min}$ from 2.509 to 2.654 Å. It is therefore concluded that when lithium is replace by sodium atoms, the $Ni2O_3F$ infinite chains are first compressed along the *b*-axis ($d_{O4\text{-}F1max}$, $d_{Ni\text{-}Ni,}$ and *b* decrease) inducing some strains, which could be reduced by a relaxation along [100] ($d_{O4\text{-}F1min}$ and *a* increase) and a tilt of the $Ni2O_4F_2$ octahedra along [010] ($\alpha_{O4\text{-}F1\text{-}O4}$ and $d_{O6\text{-}O6min}$ increase, whereas $d_{O6\text{-}O6max}$ decreases). It is worth to mention that the $\alpha_{O4\text{-}F1\text{-}O4}$ angle is flexible and may reach 180 ° when the sodium content is increased. However, since O6-O6 corresponds to the edge of the PO_4 tetrahedra, the increase of $d_{O6\text{-}O6min}$ distance is limited. This restrains the increase of the $\alpha_{O4\text{-}F1\text{-}O4}$ angle and induces a structural transition to a layered $LiNaNi[PO_4]F$ structure when a critical $d_{O6\text{-}O6min}$ distance is reached.[11] Similar to $Ni2O_3F$, the $Ni1O_3F$ infinite chains are compressed along [010] ($d_{O5\text{-}F2max}$, $d_{Ni\text{-}Ni,}$ and *b* decrease) however, the $\beta_{O5\text{-}F2\text{-}O5}$ angle is less flattened than $\alpha_{O4\text{-}F1\text{-}O4}$ (see table in Fig. S7†). The flattening of the $\alpha_{O4\text{-}F1\text{-}O4}$ angle affects strongly the coordination sphere of the Li3 atom (Fig. S6a†), whereas the flattening of the $\beta_{O5\text{-}F2\text{-}O5}$ angle affects little the coordination sphere of the Li2 atom (Fig. S7a†). In the cobalt, iron and magnesium $Li_{2-x}Na_xM[PO_4]F$-systems, the same behaviors as in the nickel-system are observed, when Na replaces Li (see the table in Fig. S6, 7†).



	Cell parameters			Structural details around *M*2				
Compounds	*a* (Å)	*b* (Å)	*c* (Å)	$d_{O4\text{-}F1min}$(Å)	$d_{O4\text{-}F1max}$(Å)	$d_{O6\text{-}O6min}$(Å)	$d_{O6\text{-}O6max}$(Å)	$\alpha_{O4\text{-}F1\text{-}O4}$ (^{0})
$Li_2Ni[PO_4]F$	10.4730	6.2887	10.8460	2.509	3.264	2.494	3.795	148.84
$Li_{1.3}Na_{0.7}Ni[PO_4]F$	10.7874	6.2196	11.1780	2.654	3.156	2.526	3.693	160.37
$Li_2Co[PO_4]F$	10.4520	6.3911	10.8740	2.341	3.335	2.493	3.899	144.53
$LiNaCo[PO_4]F$	10.9334	6.2933	11.3556	2.762	3.185	2.539	3.754	162.22
$Li_{1.65}Na_{0.35}Fe[PO_4]F$	10.5108	6.4996	11.0504	2.625	3.408	2.509	3.991	144.98
$LiNaFe[PO_4]F$	10.9851	6.3686	11.4343	2.832	3.236	2.570	3.798	159.40

Figure S6. Projection view along [100] of the structure of $Li_2Ni[PO_4]F$ (a), and views of the infinite chains $Ni2O_3F$, in $Li_2Ni[PO_4]F$ (b) and $Li_{1.3}Na_{0.7}Ni[PO_4]F$ (c). Crystallographic details about the compounds with $Li_2Ni[PO_4]F$-type structure are reported in the table.



	Cell parameters			Structural details around *M*1				
Compounds	***a*** **(Å)**	***b*** **(Å)**	***c*** **(Å)**	$d_{O5\text{-}F2min}$**(Å)**	$d_{O5\text{-}F2max}$**(Å)**	$d_{O1\text{-}O1min}$**(Å)**	$d_{O1\text{-}O1max}$**(Å)**	$\beta_{O5\text{-}F2\text{-}O5}$ **(°)**
$Li_2Ni[PO_4]F$	10.4730	6.2887	10.8460	2.590	3.244	2.523	3.766	151.56
$Li_{1.3}Na_{0.7}Ni[PO_4]F$	10.7874	6.2196	11.1780	2.648	3.190	2.533	3.687	154.33
$Li_2Co[PO_4]F$	10.4520	6.3911	10.8740	2.645	3.325	2.493	3.899	147.87
$LiNaCo[PO_4]F$	10.9334	6.2933	11.3556	2.730	3.241	2.530	3.763	152.36
$Li_{1.65}Na_{0.35}Fe[PO_4]F$	10.5108	6.4996	11.0504	2.701	3.388	2.381	4.118	147.21
$LiNaFe[PO_4]F$	10.9851	6.3686	11.4343	2.744	3.298	2.513	3.856	149.88

Figure S7. Projection view along [001] of the structure of $Li_2Ni[PO_4]F$ (a), and views of the infinite chains $Ni1O_3F$, in $Li_2Ni[PO_4]F$ (b) and $Li_{1.3}Na_{0.7}Ni[PO_4]F$(c). Crystallographic details about the compounds with $Li_2Ni[PO_4]F$-type structure are reported in the table.

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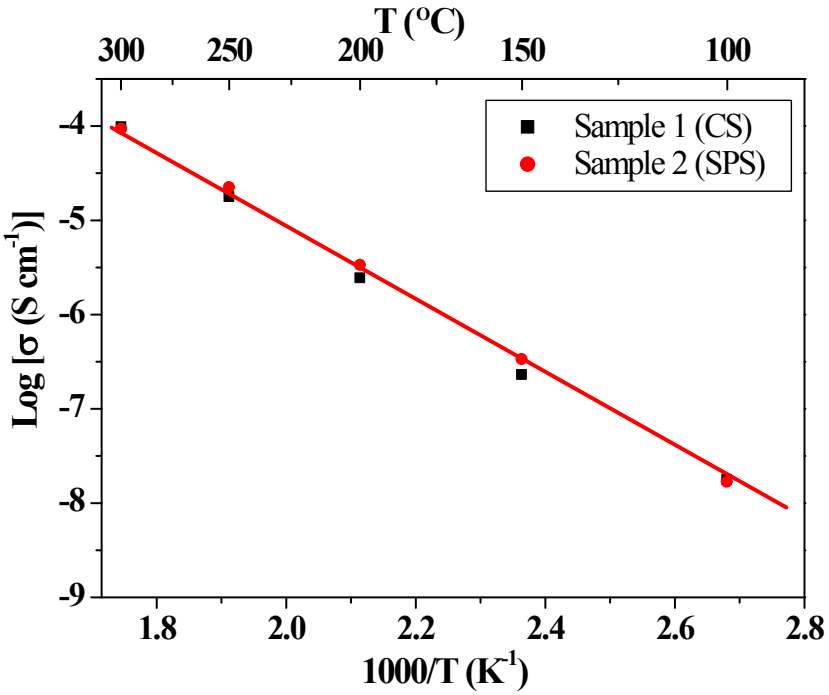

Figure S8. Arrhenius plot of the ionic conductivity σ of $Li_9Mg_3[PO_4]_4F_3\square_1$, in air. Closed squarea and open circles show samples of conbentinal and SPS sintering, respectively.

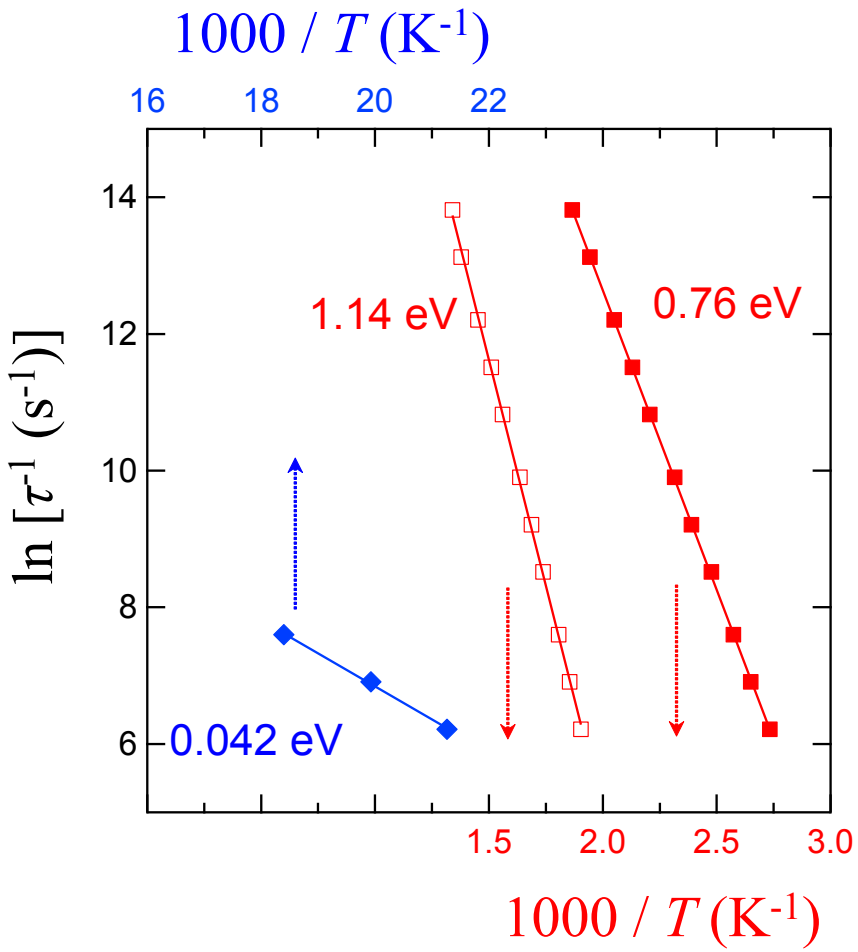

Figure S9. Arrhenius plots of the reluxation time τ^{-1} of $Li_9Mg_3[PO_4]_4F_3\square_1$. Red closed and open squares show montions of lithium ion and anion, *e.g.* oxide and/or fluoride ion, respectively. Blue closed diamond is conserened with a mode of defective origin.[36]

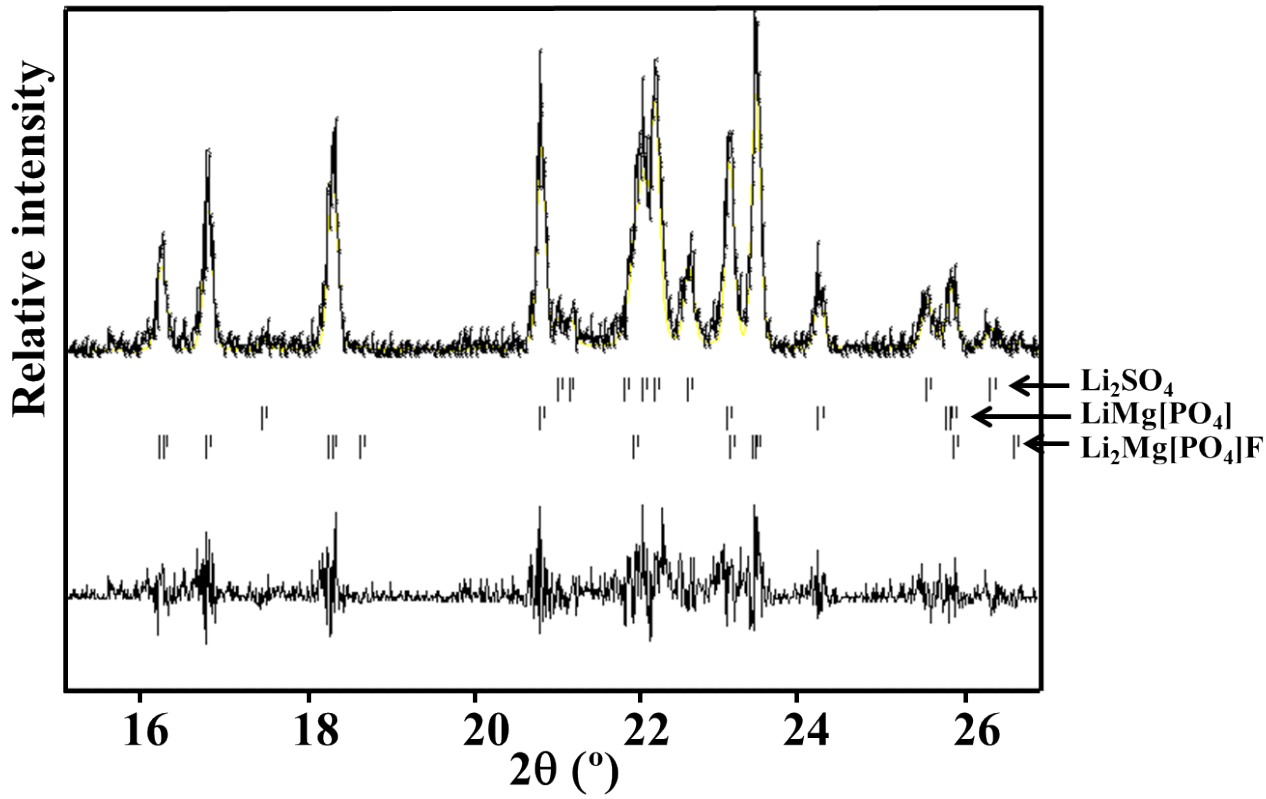

Figure S10. Observed, calculated and difference plots for the XRPD (Cu-$K\alpha$) radiation) profile refinement of the composite $Li_6Mg_4[PO_4]_3[SO_4]F_3$ material. The three phases Li_2SO_4, $LiMg[PO_4]$ and $Li_2Mg[PO_4]F$ clearly coexist.

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Table S1. Anisotropic ADPs (Å^2) for $Li_2Mg[PO_4]F$ and $Li_9Mg_3[PO_4]_4F_3$. The anisotropic ADP factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11}+...+2hka^*b^*U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$Li_2Mg[PO_4]F$						
Li1	0.0382(15)	0.0345(18)	0.0253(14)	0.0087(10)	0.0047(9)	0.0079(10)
Li2	0.0143(13)	0.0137(14)	0.0141(13)	0	0.0017(9)	0
Li3/Mg3	0.0266(13)	0.0043(9)	0.0145(9)	0	-0.0023(8)	0
Mg1	0.0093(3)	0.0100(3)	0.0085(3)	-0.00051(19)	-0.00085(15)	0.00112(15)
Mg22/Li22	0.0088(3)	0.0081(3)	0.0043(3)	0.00049(19)	0.00032(15)	-0.00042(15)
P1	0.0110(2)	0.0091(2)	0.0055(2)	0	0.00110(11)	0
P2	0.0067(2)	0.0087(2)	0.0080(2)	0	0.00035(11)	0
O1	0.0096(4)	0.0102(3)	0.0166(4)	-0.0013(3)	-0.0020(2)	-0.0014(3)
O2	0.0168(6)	0.0180(5)	0.0090(5)	0	0.0023(4)	0
O3	0.0113(6)	0.0262(6)	0.0131(5)	0	0.0022(4)	0
O4	0.0081(5)	0.0106(4)	0.0171(5)	0	0.0028(4)	0
O5	0.0134(5)	0.0105(5)	0.0066(4)	0	-0.0001(3)	0
O6	0.0224(4)	0.0097(4)	0.0082(3)	0.0019(3)	0.0007(3)	0.0011(3)
F1	0.0104(5)	0.0138(4)	0.0182(4)	0	-0.0025(3)	0
F2	0.0173(5)	0.0146(4)	0.0107(4)	0	0.0001(3)	0
$Li_9Mg_3[PO_4]_4F_3$						
Li1	0.013(3)	0.021(3)	0.021(3)	0.0043(17)	0.002(2)	0.007(2)
Li2	0.035(3)	0.021(2)	0.017(3)	0.008(3)	0.003(3)	-0.0047(19)
Li3	0.0028(17)	0.003(2)	0.0064(17)	-0.0010(13)	0.0020(18)	0.002(2)
Mg1	0.0090(3)	0.0082(4)	0.0102(4)	0.0044(3)	-0.0001(5)	0.0000(4)
P1	0.0085(3)	0.0067(3)	0.0086(3)	0.00422(19)	0.0001(3)	0.0003(4)
P2	0.0073(3)	0.0073(3)	0.0085(6)	0.00366(15)	0	0
O1	0.0110(10)	0.0104(9)	0.0120(8)	0.0069(6)	0.0006(8)	0.0015(8)
O2	0.0093(8)	0.0130(9)	0.0165(9)	0.0055(9)	0.0009(7)	-0.0008(12)
O3	0.0161(10)	0.0106(9)	0.0116(9)	0.0082(8)	-0.0010(7)	-0.0014(7)
O4	0.0172(10)	0.0098(9)	0.0111(11)	0.0068(8)	-0.0035(8)	-0.0032(7)
O5	0.0138(8)	0.0109(8)	0.0103(8)	0.0063(7)	0.0020(7)	0.0009(9)
O6	0.0141(9)	0.0141(9)	0.0117(14)	0.0070(5)	0	0
F1	0.0115(8)	0.0111(6)	0.0132(6)	0.0036(6)	0.0029(7)	0.0007(5)

Table S2. Comparison of the crystallographic data of $Li_9Mg_3[PO_4]_4F_3\square_1$ and $Na_8Mn_4[PO_4]_4F_4$ after lowering the symmetries from $P6_3$ and $P2_1/c$ to $P2_1$, respectively. The main differences are highlighted in red.

$Li_9Mg_3[PO_4]_4F_3\square_1$ [Space group : $P2_1$ (No. 4)] a = 12.6159(6) Å, b = 5.0082(4) Å, c = 12.6159(6) Å, β = 120 °, V = 690.32(7) Å^3, Z = 2				**$Na_8Mn_4[PO_4]_4F_4$** [Space group : $P2_1$ (No. 4)] a = 13.6830 Å, b = 5.3170 Å, c = 13.7683 Å β = 120.04 °, V = 867.13 Å^3, Z = 2			
Atom	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***
Li1a	0.91596	0.34609	0.08346	Na1_2	0.92016	0.26170	0.08350
Li1b	0.83250	0.84609	0.91596	Na4_2	0.83455	0.73700	0.92191
Li1c	0.91654	0.34609	0.83250	Mn2_2	0.92356	0.22901	0.85041
Li2a	0.82524	0.79962	0.42936	Na4_1	0.83455	0.76300	0.42191
Li2b	0.60412	0.79962	0.17476	Na2_2	0.58023	0.75620	0.16325
Li2c	0.57064	0.79962	0.39588	Mn1_1	0.57610	0.77224	0.42666
Li3a	0.91379	0.27109	0.57909	Na1_1	0.92016	0.23830	0.58350
Li3b	0.66530	0.27109	0.08621	Na3_2	0.66608	0.25860	0.08680
Li3c	0.42091	0.27109	0.33470	Na2_1	0.41977	0.24380	0.33675
Mg1a	0.93254	0.26874	0.35849	Mn2_1	0.92356	0.27099	0.35041
Mg1b	0.42594	0.26874	0.06745	Mn1_2	0.42390	0.22776	0.07334
Mg1c	0.64152	0.26874	0.57406	Na3_1	0.66608	0.24140	0.58680
P1b	0.84677	0.75424	0.16576	P2_2	0.83782	0.78350	0.17335
O2b	0.90816	0.75313	0.08608	O5_2	0.90370	0.70190	0.11520
O5b	0.83408	0.45809	0.19409	O4_1	0.85110	0.07170	0.19420
O4b	0.92631	0.90619	0.28440	O1_1	0.88340	0.64650	0.28620
O3b	0.71920	0.88192	0.09711	O6_2	0.71190	0.72140	0.09830
P2	0.33333	0.79544	0.66667	P1_1	0.33795	0.78560	0.66529
O1c	0.59815	0.18600	0.20247	O2_2	0.59730	0.21450	0.21010
O1b	0.79753	0.18600	0.39568	O8_1	0.78750	0.22010	0.38520
O1a	0.60432	0.18600	0.40185	O3_1	0.61400	0.14660	0.39900
O6	0.66667	0.60217	0.33333	O7_1	0.65150	0.57390	0.34630
P1a	0.83424	0.75424	0.68101	P2_1	0.83782	0.71650	0.67335
O3a	0.90289	0.88192	0.62208	O5_1	0.90370	0.79810	0.61520
O5a	0.80591	0.45809	0.63999	O4_2	0.85110	0.42830	0.69420
O2a	0.91392	0.75313	0.82209	O1_2	0.88340	0.85350	0.78620
O4a	0.71560	0.90619	0.64191	O6_1	0.88340	0.85350	0.78620
P1c	0.68101	0.25424	0.84677	P1_2	0.66205	0.21440	0.83471
O3c	0.62208	0.38192	0.71920	O2_1	0.59730	0.28550	0.71010
O4c	0.64191	0.40619	0.92631	O3_2	0.61400	0.35340	0.89900
O2c	0.82209	0.25313	0.90816	O8_2	0.78750	0.27990	0.88520
O5c	0.63999	-0.04191	0.83408	O7_2	0.65150	-0.07390	0.84630
F1a	0.03892	0.07408	0.52264	F1_1	0.00030	0.00040	0.48680
F1b	0.51628	0.57408	0.03892	F2_2	0.49270	0.50160	0.00860
F1c	0.47736	0.07408	0.51628	F2_1	0.49270	-0.00160	0.50860
Vacant	-	-	-	F1_2	0.00030	0.49960	0.98680