# Structural relationships among $LiNaMg[PO_4]F$ and $Na_2M[PO_4]F$ ($M$ = Mn-Ni, and Mg), and the magnetic structure of $LiNaNi[PO_4]F$

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5

*Supplementary information*

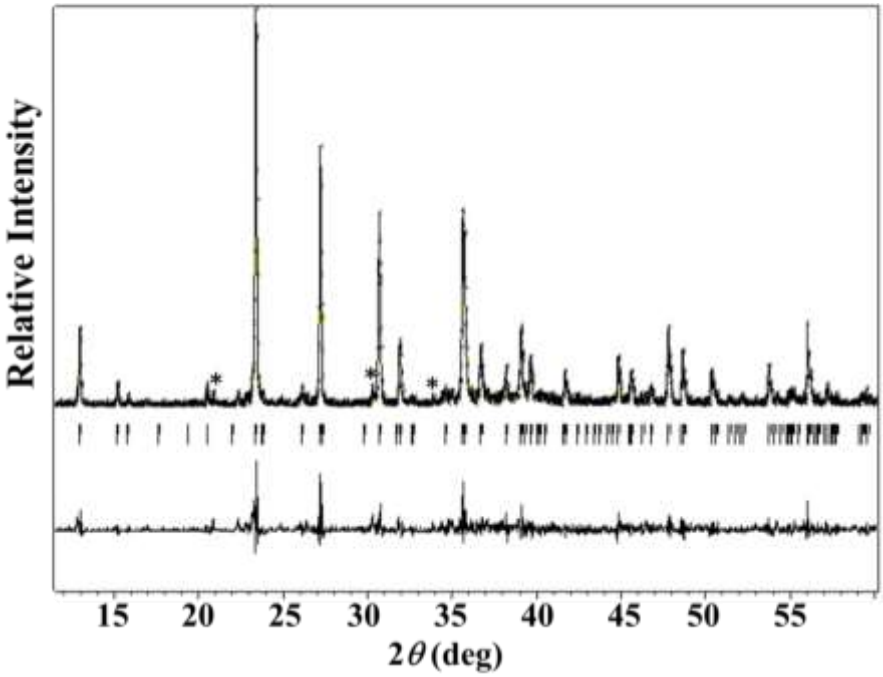


**Fig. S1.** Final observed, calculated and difference plots for XRPD (Cu-$K_{\alpha1-\alpha2}$ radiation) refinement of $LiNaMg[PO_4]F$. The asterisk corresponds to non-identified impurities.

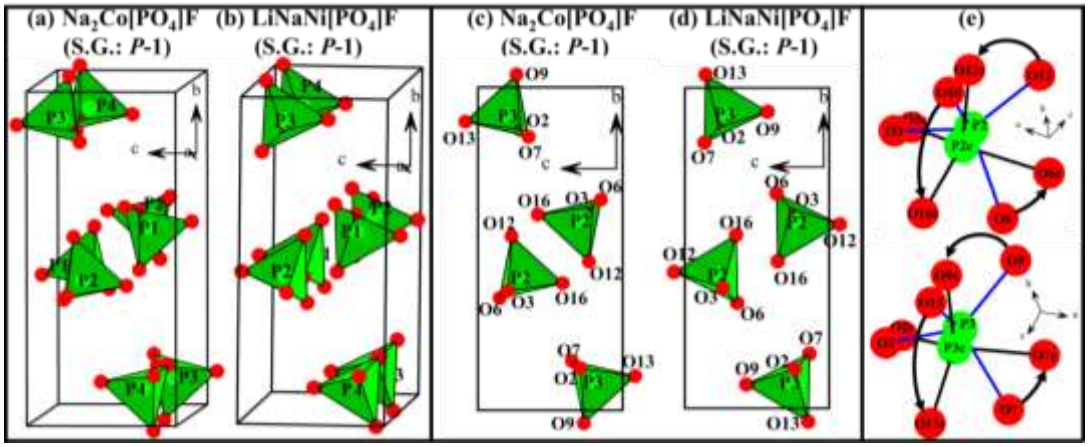


**Fig. S2.** Orientation of the $PO_4$ tetrahedra in $Na_2Co[PO_4]F$ (a, c) and $LiNaNi[PO_4]F$ (b, d), and superposition of $P2O_4$ and $P2cO_4$, and $P3O_4$ and $P3cO_4$ tetrahedra (e). P2c and P3c correspond to the P atomic positions in the cobalt phase and the arrows indicate the direction of the tetrahedra tilts (e).

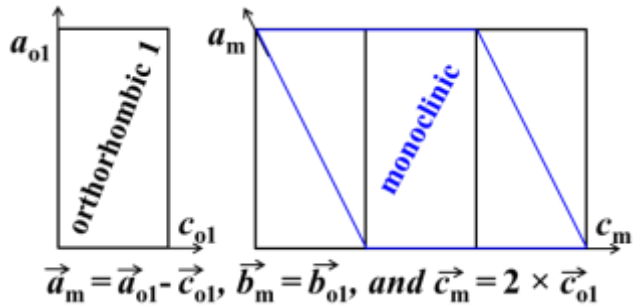


**Fig. S3.** Geometrical relations between the orthorhombic subcell1 of $LiNaNi[PO_4]F$ and the monoclinic supercell of $Na_2Ni[PO_4]F$.

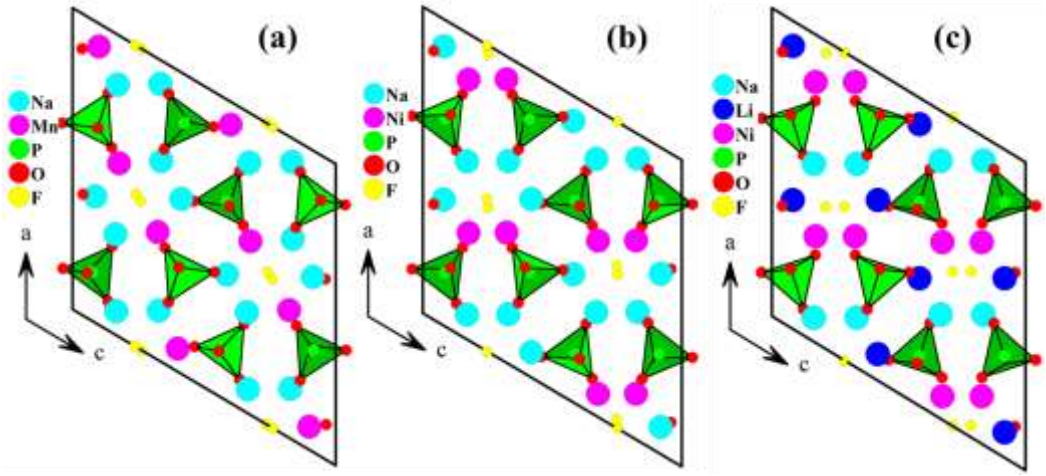


**Fig. S4.** Comparison of the crystal structures of $P\bar{1}$-$Na_2Mn[PO_4]F$ (a), $P\bar{1}$-$Na_2Ni[PO_4]F$ (b), and $P\bar{1}$-$LiNaNi[PO_4]F$ (c). The main difference consists in the arrangement of the transition metal and alkali metal atoms and the orientation of the $PO_4$ tetrahedra.

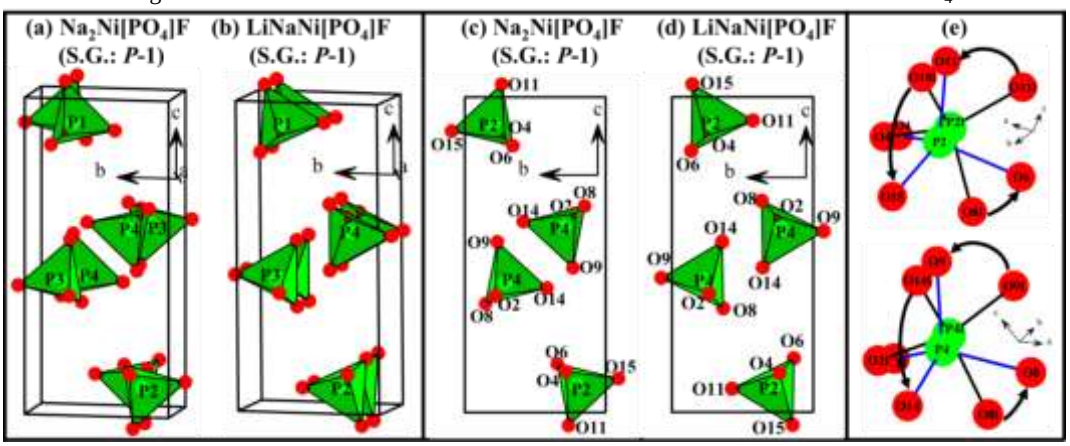


**Fig. S5.** Orientation of the $PO_4$ tetrahedra in $Na_2Ni[PO_4]F$ (a, c) and $LiNaNi[PO_4]F$ (b, d), and superposition of $P2O_4$ and $P2lO_4$, and $P4O_4$ and $P4lO_4$ tetrahedra (e). P2l and P3l correspond to the P atomic positions in the $LiNaNi[PO_4]F$ phase and the arrows indicate the direction of the tetrahedra tilts (e).

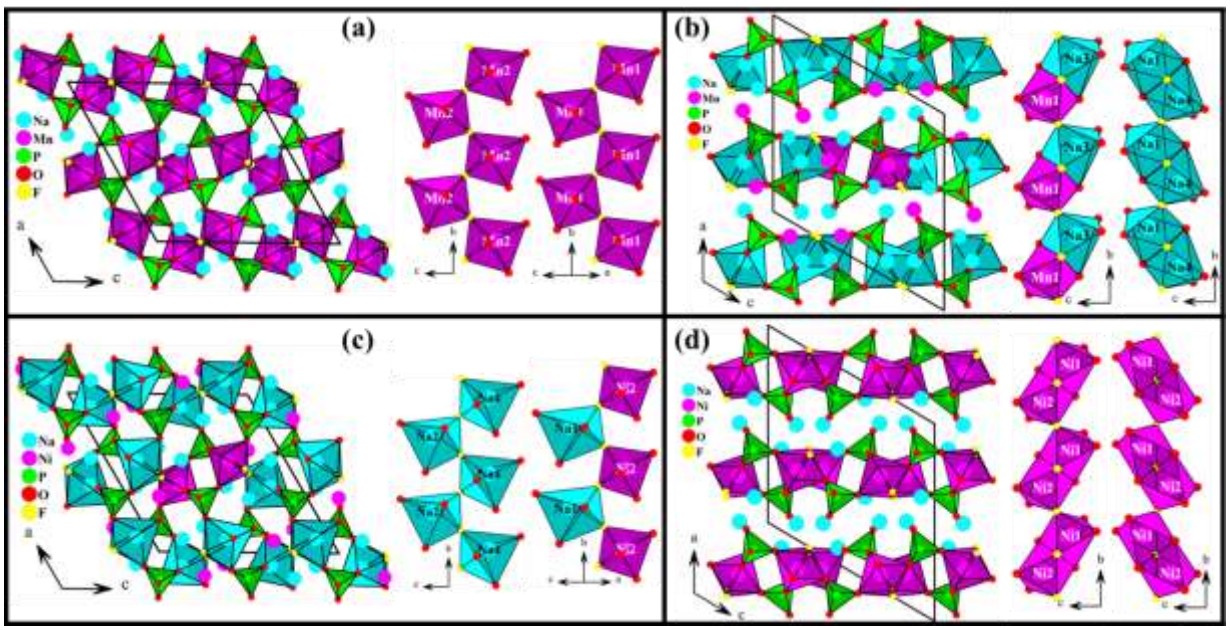


**Fig. S6**. The crystal structures of $P2_1/c$-$Na_2Mn[PO_4]F$ (a, b) and $P2_1/a$-$Na_2Ni[PO_4]F$ (c, d).

### 3.3. Structural relationship of $A_2M[PO_4]F$ (*A* = Li and Na; *M* = Mn-Ni, and Mg) to other known oxides.

#### *3.3.1. LiNaM[PO$_4$]F (M = Mg, Ni) - Ca$_2$Na[SiO$_4$]F - Ca$_2$Ca[SiO$_4$]O structural relationship*

The crystal structure of LiNaNi[$PO_4$]F ($P2_1/c$, $a$ = 6.772(4), $b$ = 11.154(6), $c$ = 5.021(3) Å, $\beta$ = 90 °) is strongly related to $Ca_2Na[SiO_4]F$ (*Pnma*, $a$ = 5.335, $b$ = 7.144, $c$ = 12.438 Å)[25] and $Ca_2Ca[SiO_4]O$ ($P6_3/mmc$, $a = b$ = 7.099, $c$ = 5.687 Å)[26] structures, although a clear difference in the symmetry of these compounds. The difference in symmetry is mainly due to the difference of the chemical compositions (For more details see section 3.4. of ref. 12).

#### *3.3.2. LiNaM[PO$_4$]F (M = Mg and Ni) – Na$_2$M[PO$_4$]F (M = Fe, Co, and Mg) structural relationship*

Several transformations are required in order to determine the phase transition mechanism from the LiNaNi[$PO_4$]F-type ($P2_1/c$, $a_0$ = 6.772, $b_0$ = 11.154, $c_0$ = 5.021 Å, $\beta$ = 90 °) to the $Na_2Co[PO_4]F$-type structure (*Pbcn*, $a$ = 5.2475, $b$ = 13.7950, $c$ = 11.6890 Å).[27-29] For LiNaNi[$PO_4$]F, we have first performed an isomorphic enlargement of the original unit cell ($P2_1/c$, $a_1 = 2 \times a_0$ = 13.545, $b_1 = b_0$ =11.154, $c_1 = c_0$ =5.021 Å, $\beta$ = 90 °) then reduced the symmetry to $P\bar{1}$ (*translationengleiche* of index 2). For $Na_2Co[PO_4]F$, we transformed the cell parameters to $a_2 = b$ = 13.7950, $b_2 = c$ = 11.6890, and $c_2 = a$ = 5.2475 Å (*S.G.: Pbna*) then reduced the symmetry to $P\bar{1}$. The final atomic positions, after origin shift, are listed in Table S4. The deviation of the atomic coordinates, $\Delta x$, $\Delta y$, and $\Delta z$, indicates no significant change of atomic positions of the cations. However, the anionic framework is strongly distorted. Indeed, the highest deviation is observed for O6, O12, and O16, forming the $P2O_4$ tetrahedron and O7, O9, and O13, forming the $P3O_4$ tetrahedron (Fig. S2 and Table S4). It worth noting that these deviations occur mainly in the (100) plane, since for these atoms the $\Delta y$ and $\Delta z$ values are very high and the $\Delta x$ values are negligible. Therefore, we can conclude that the structural transition from the LiNaNi[$PO_4$]F-type to the $Na_2Co[PO_4]F$-type structure is mainly due to tilting of the $PO_4$ tetrahedra (Fig. S2e and video1).

#### *3.3.3. LiNaM[PO$_4$]F (M = Mg and Ni) – Na$_2$Ni[PO$_4$]F structural relationship*

The $Na_2Ni[PO_4]F$ cell may be described as a supercell of the LiNaNi[$PO_4$]F subcell (Fig. S3). It should therefore be possible, starting from the LiNaNi[$PO_4$]F structure ($P2_1/c$, $a_0$ = 6.772, $b_0$ = 11.154, $c_0$ = 5.021 Å, $\beta$ = 90 °), to build a superstructure similar to $Na_2Ni[PO_4]F$ ($P2_1/c$, $a$ = 13.4581, $b$ = 5.1991, $c$ = 13.6978 Å, $\beta$ = 120.58 °). This can be done using the following transformations:

-Isomorphic enlargement of the unit cell of LiNaNi[$PO_4$]F using the matrix (200, 010, 001) ($P2_1/c$, $a_1 = 2 \times a_0$ = 13.554, $b_1 = b_0$ =11.154, $c_1 = c_0$ =5.021 Å, $\beta$ = 90 °) followed by symmetry reduction from $P2_1/c$ to $P1$;

-Cell transformation using the matrix (100, 00$\bar{1}$, 010) ($P1$, $a_2 = a_1$ = 13.554, $b_2 = c_1$ = 5.021, $c_2 = b_1$ = 11.154 Å) followed by a second cell transformation using the matrix (100, 010, $\bar{1}$/201) ($P1$, $a_3$ = 13.5448, $b_3$ = 5.021, $c_3$ = 13.0488 Å, $\beta_3$ = 121.26 °);

-Origin shift (1/2$b$+1/2$c$) followed by transformation of the space group from $P1$ to $P\bar{1}$ (Fig. S4c).

-Symmetry reduction from $P2_1/c$-$Na_2Ni[PO_4]F$ to $P\bar{1}$ followed by transformation of the unit cell using the matrix (001, 0$\bar{1}$0, 100) ($a_4 = c$ = 13.6978, $b_4 = b$ = 5.1991, $c_4 = a$ = 13.4581Å, $\beta$ = 120.58 °) (Fig. S4b).

The final atomic positions of the transformed structures of $Na_2Ni[PO_4]F$ and LiNaNi[$PO_4$]F are listed in Table S5. The highest deviations ($\Delta y$ and $\Delta z$) are observed for O6, O11, and O15, forming the $P2O_4$ tetrahedra and O8, O9, and O14, forming the $P4O_4$ tetrahedra (Fig. S5 and Table S5). Therefore, we can conclude that the structural transition from the LiNaNi[$PO_4$]F-type to the $Na_2Ni[PO_4]F$-type structure is due to tilting of the $PO_4$ tetrahedra (Fig. S5e and video2). This is very similar to the mechanism of structural transition from the LiNaNi[$PO_4$]F-type to the $Na_2Co[PO_4]F$-type structure. However, it should be noted that for these two transitions, it is different tetrahedra that have been tilted (Video1 and 2).

#### *3.3.4. LiNaM[PO$_4$]F (M = Mg and Ni) – Na$_2$Mn[PO$_4$]F structural relationship*

The crystal structure of $Na_2Mn[PO_4]F$ is usually described as a 3D-Mn[$PO_4$]F framework with channels filled with sodium atoms (Fig. S6a),[30] whereas LiNaNi[$PO_4$]F is described as a layered structure (Fig. 3). These conventional descriptions indicate a huge difference between the structures, despite the strong similarity between them. When the LiNaNi[$PO_4$]F subcell ($P2_1/c$, $a_0$ = 6.772, $b_0$ = 11.154, $c_0$ = 5.021 Å, $\beta$ = 90 °) is transformed to LiNaNi[$PO_4$]F supercell ($P\bar{1}$, $a_3$ = 13.5448, $b_3$ = 5.021, $c_3$ = 13.0488 Å, $\beta_3$ = 121.26 °), as described in section 3.3.3., and the symmetry is lowered from $P2_1/c$ to $P\bar{1}$ ($a$ = 13.6830, $b$ = 5.3170, $c$ = 13.7683Å, $\beta$ = 120.04 °, and $V$ = 867.10Å$^3$ ) for $Na_2Mn[PO_4]F$, the structural relationship between both compounds becomes evident. The transformed structures of $Na_2Mn[PO_4]F$ and LiNaNi[$PO_4$]F are listed in Table S6 and the crystal structures are depicted on Fig. S4a and c. One can see clearly that, in $Na_2Mn[PO_4]F$, the Mn1, Mn2, Mn3, Na6, Na7, and Na8 atoms fill the atomic positions corresponding to Na4, Li1, Li4, Ni1, Ni3, and Ni4, respectively, and the $P2O_4$ and $P4O_4$ tetrahedra are tilted in the same manner as in $Na_2Ni[PO_4]F$. This indicates that the structural transition from LiNaNi[$PO_4$]F to $Na_2Mn[PO_4]F$ is due to the $PO_4$ tilts and the permutation of atomic positions between the transition-metal and alkali-metal atoms.

#### *3.3.5. Na$_2$Mn[PO$_4$]F-Na$_2$Ni[PO$_4$]F structural relationship*

The structural transformations of $Na_2Ni[PO_4]F$ and $Na_2Mn[PO_4]F$ described in sections 3.3.3. and 3.3.4., respectively, confirm that the atomic positions in both structures are the same (Fig. S4a, b and Table S7). By comparison to $Na_2Ni[PO_4]F$, the $Na_2Mn[PO_4]F$ formula can be rewritten as $(Na,Mn)_2(Mn,Na)[PO_4]F$, since 3/4 of the transition metal atoms permute their atomic positions with those of sodium atoms (these atoms are highlighted in green on Table S7). This permutation is at the origin of the symmetry change from $P2_1/a$-$Na_2Ni[PO_4]F$ ($P2_1/a$, $a$ = 13.6978, $b$ = 5.1991, $c$ = 13.4581Å, $\beta$ = 120.58 °) to $P2_1/c$-$Na_2Mn[PO_4]F$ ($P2_1/c$, $a$ = 13.6830, $b$ = 5.3170, $c$ = 13.7683Å, $\beta$ = 120.04 °) and the transformation of the infinite chains of corner sharing dimer units (Fig. S6d) to corner-sharing octahedra (Fig. S6a). Given these close relationships to their crystal structures, $(Na,Mn)_2(Mn,Na)[PO_4]F$ can be viewed as a layered structure (Fig. S6b) similar to $Na_2Ni[PO_4]F$ (Fig. S6d) and $(Na,Ni)_2(Ni,Na)[PO_4]F$ as a 3D-structure (Fig. S6c) similar to $Na_2Mn[PO_4]F$ (Fig. S6a).

**Table S1.** Crystallographic data and structure refinements for $LiNaMg[PO_4]F$.

| | |
|---|---|
| Chemical formula | $LiNaMg[PO_4]F$ |
| Crystal color | colorless needle |
| Crystal size mm | 0.280×0.065×0.058 |
| $M$, g mol$^{-1}$ | 168.2 |
| Crystal system | monoclinic (twinned) |
| Space group | $P2_1/c$ |
| $a$, Å | 6.8179(7) |
| $b$, Å | 11.2234(12) |
| $c$ , Å | 5.0222(5) |
| $\beta$, ° | 90.00(1) |
| $V$, Å$^3$ | 384.30(7) |
| $Z$ | 4 |
| Density calcd., g cm$^{-3}$ | 2.91 |
| Temperature, K | 293 (1) |
| $F(000)$, $e$ | 328 |
| Diffractometer | SMART APEX |
| Monochromator | graphite |
| Radiation Å | Mo$K\alpha$ , 0.71069 |
| Scan mode | multi-scan |
| $h$ $k$ $l$ range | ±8, -14≤ $k$ ≤13, ±6 |
| $\theta_{min,}$ $\theta_{max,}$ ° | 2.99, 27.9 |
| Linear absorption coeff., mm$^{-1}$ | 0.911 |
| Absorption correction | Gaussian |
| $T_{min}/T_{max}$ | 0.8429 / 0.9592 |
| No. of reflections | 3026 |
| No. of independent reflections | 850 |
| Reflections used | all |
| $R_{int}$ | 0.03 |
| Refinement | $F^2$ |
| No. of refined parameters | 83 |
| $R$ factors $R(F)$ / $wR(F^2)$ [$I \geq 0\sigma(I)$] | 0.0298 / 0.0797 |
| g. o. f. | 1.19 |
| Weighting scheme | $w = 1/(\sigma^2(I) + 0.001156I^2)$ |
| Twin ratio | 0.434(3) |
| Diff. Fourier residues, $e^-$ Å$^{-3}$ | -0.21/ +0.26 |

**Table S2.** Anisotropic ADPs (Å$^2$) for $LiNaMg[PO_4]F$. 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 | 0.0089(19) | 0.007(2) | 0.0041(19) | 0.0000(13) | 0.001(2) | -0.0031(12) |
| Na | 0.0203(6) | 0.0204(7) | 0.0189(7) | -0.0026(4) | 0.0013(8) | -0.0003(6) |
| Mg | 0.0091(4) | 0.0089(5) | 0.0066(4) | 0.0001(3) | -0.0004(5) | 0.0009(4) |
| P | 0.0070(3) | 0.0076(3) | 0.0079(3) | -0.0004(2) | 0.0004(4) | 0.00062(18) |
| O1 | 0.0100(8) | 0.0145(9) | 0.0184(9) | 0.0014(7) | 0.0003(9) | -0.0015(7) |
| O2 | 0.0176(9) | 0.0152(9) | 0.0102(9) | -0.0056(7) | 0.0038(7) | 0.0003(7) |
| O3 | 0.0136(9) | 0.0166(9) | 0.0076(9) | -0.0017(7) | 0.0007(8) | 0.0000(6) |
| O4 | 0.0132(8) | 0.0118(8) | 0.0106(8) | 0.0009(7) | -0.0003(7) | -0.0013(7) |
| F | 0.0132(7) | 0.0179(8) | 0.0100(7) | -0.0028(6) | 0.0026(6) | -0.0034(5) |

**Table S3.** Crystallographic data of the $A_2M[TO_4]X$ compounds classified by structural type. The transformations of the original unit cells into orthorhombic subcells have been carried out using the geometric relationships given in Fig. 5q.

| | | *Original cells* | | | | | | *Transformation to orthorhombic subcells* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Chemical formula** | **S. G.** | ***a*** | ***b*** | ***c*** | ***β* (°)** | ***V* (Å$^3$)** | **Ref.** | ***a′*** | ***b′*** | ***c′*** | ***V* (Å$^3$)** |
| **$Na_2Co[PO_4]F$-type** | | | | | | | | | | | |
| $Na_2Co[PO_4]F$ | *Pbcn* | 5.2475 | 13.795 | 11.6890 | | 846.16 | 29 | 6.8975 | 5.2475 | 11.689 | 423.08 |
| $Na_2Mg[PO_4]F$ | *Pbcn* | 5.2230 | 13.818 | 11.7490 | | 847.94 | 23 | 6.909 | 5.2230 | 11.7490 | 423.97 |
| $Na_2Fe[PO_4]OH$ | *Pbcn* | 5.2270 | 13.861 | 11.7740 | | 853.04 | 31 | 6.9305 | 5.227 | 11.774 | 426.52 |
| $Na_2Fe[PO_4]F$ | *Pbcn* | 5.2200 | 13.854 | 11.7792 | | 851.85 | 32 | 6.927 | 5.22 | 11.7792 | 425.92 |
| **$Na_2Mn[PO_4]F$-type** | | | | | | | | | | | |
| $Na_2Mn[PO_4]F$ | $P2_1/c$ | 13.6830 | 5.3170 | 13.7683 | 120.04 | 867.10 | 30 | 6.8415 | 5.317 | 11.918 | 433.55 |
| $Li_2Mn[PO_4]F$ | $P2_1/c$ | 13.21 | 5.10 | 13.37 | 121.43 | 768.59 | 9 | 6.605 | 5.1 | 11.4083 | 384.30 |
| $Na_2Zr[GeO_4]O$ | $P2_1/c$ | 13.9913 | 5.5600 | 13.8800 | 119.22 | 942.35 | 33 | 6.9956 | 5.56 | 12.1138 | 471.17 |
| $Na_2Zr[SiO_4]O$ | $P2_1/c$ | 13.8113 | 5.4600 | 13.7000 | 119.21 | 901.74 | 34 | 6.9056 | 5.46 | 11.9578 | 450.87 |
| *β*-$\square_2Nb[PO_4]O$ | $P2_1/c$ | 13.0900 | 5.2890 | 13.2560 | 120.68 | 789.30 | 35 | 6.545 | 5.289 | 11.4000 | 394.65 |
| *β*-$\square_2Ta[PO_4]O$ | $P2_1/c$ | 13.0700 | 5.2810 | 13.2400 | 120.42 | 788.06 | 35 | 6.535 | 5.281 | 11.4173 | 394.03 |
| $Na_2Ni[PO_4]F$ | $P2_1/a$ | 13.6978 | 5.1991 | 13.4581 | 120.58 | 825.14 | 12 | 6.8489 | 5.1991 | 11.5863 | 412.57 |
| $\square_2Nb[PO_4]O$ | *Pnma* | 11.3040 | 5.3160 | 6.6400 | | 399.01 | 36 | 6.6400 | 5.3160 | 11.3040 | 399.01 |
| $\square_2Nb[VO_4]O$ | *Pnma* | 11.8860 | 5.5290 | 6.9340 | | 455.69 | 39 | 6.9340 | 5.5290 | 11.8860 | 455.69 |
| $\square_2Ta[VO_4]O$ | *Pnma* | 11.8940 | 5.5296 | 6.9529 | | 457.29 | 39 | 6.9529 | 5.5296 | 11.8940 | 457.29 |
| *β*-$\square_2Ta[AsO_4]O$ | *Pnma* | 11.5700 | 5.3100 | 6.6600 | | 409.17 | 38 | 6.6600 | 5.3100 | 11.5700 | 409.17 |
| $\square_2Ti[SO_4]O$ | *Pnma* | 10.9530 | 5.1520 | 6.4260 | | 362.62 | 40 | 6.4260 | 5.1520 | 10.9530 | 362.62 |
| $\square_2W[PO_4]O$ | $Pna2_1$ | 11.1740 | 6.5500 | 5.2280 | | 382.64 | 41 | 6.5500 | 5.2280 | 11.1740 | 382.64 |
| $\square_2Nb[PO_4]O$ | $Pna2_1$ | 11.2875 | 6.6296 | 5.2871 | | 395.64 | 37 | 6.6296 | 5.2871 | 11.2875 | 395.64 |
| **$Ca_2Na[SiO_4]F$-type** | | | | | | | | | | | |
| $Ca_2Ca[SiO_4]O$ | $P6_3/mmc$ | 7.0990 | 7.0990 | 5.6870 | | 248.20 | 26 | 7.099 | 5.687 | 12.296 | 496.40 |
| $Ca_2Na[SiO_4]F$ | *Pnma* | 5.3388 | 7.1542 | 12.4116 | | 474.05 | 44 | 7.1542 | 5.3388 | 12.4166 | 474.05 |
| $Ca_2Na[GeO_4]F$ | *Pnma* | 5.3620 | 7.3280 | 12.6810 | | 498.27 | 42 | 7.3280 | 5.3620 | 12.6810 | 498.27 |
| $LiNaNi[PO_4]F$ | $P2_1/c^*$ | 6.772 | 11.154 | 5.021 | 90.00 | 379.26 | 12 | 6.772 | 5.021 | 11.154 | 379.26 |
| $LiNaMg[PO_4]F$ | $P2_1/c^*$ | 6.8179 | 11.223 | 5.0222 | 90.00 | 384.30 | | 6.8179 | 5.0222 | 11.223 | 384.30 |
| **$Na_2Sc[GeO_4]OH$-type** | | | | | | | | | | | |
| $Na_2Sc[GeO_4]OH$ | $Pca2_1$ | 13.7800 | 5.5300 | 12.3400 | | 940.35 | 43 | | | | |

*: pseudomerohedrally twinned $LiNaNi[PO_4]F$ structures

**Table S4.** The atomic positions of $Na_2Co[PO_4]F$ ($P\bar{1}$, $a_2$ = 13.7950, $b_2$ = 11.6890, and $c_2$ = 5.2475 Å, $\alpha = \beta = \gamma$ = 90 °) and $LiNaNi[PO_4]F$ ($P\bar{1}$, $a_1$ = 13.545, $b_1$ = 11.154, $c_1$ = 5.021 Å, $\alpha = \beta = \gamma$ = 90 °) after the transformations.

| $Na_2Co[PO_4]F$ | | | | $LiNaNi[PO_4]F$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Atom** | **x2** | **y2** | **z2** | **Atom** | **x1** | **y1** | **z1** | **x2-x1** | **y2-y1** | **z2-z1** |
| Na1 | 0.25480 | 0.17130 | 0.73790 | Na1 | 0.25493 | 0.16529 | 0.74795 | -0.00013 | 0.00601 | -0.01005 |
| Na2 | 0.75480 | 0.17130 | 0.76210 | Na2 | 0.75493 | 0.16529 | 0.74795 | -0.00013 | 0.00601 | 0.01415 |
| Na3 | 0.74520 | 0.67130 | 0.73790 | Na3 | 0.74507 | 0.66529 | 0.75205 | 0.00013 | 0.00601 | -0.01415 |
| Na4 | 0.24520 | 0.67130 | 0.76210 | Na4 | 0.24507 | 0.66529 | 0.75205 | 0.00013 | 0.00601 | 0.01005 |
| Na5 | 0.87630 | 0.08310 | 0.25540 | Li1 | 0.87314 | 0.08225 | 0.23437 | 0.00316 | 0.00085 | 0.02103 |
| Na6 | 0.37630 | 0.08310 | 0.24460 | Li2 | 0.37314 | 0.08225 | 0.23437 | 0.00316 | 0.00085 | 0.01023 |
| Na7 | 0.12370 | 0.58310 | 0.25540 | Li3 | 0.12686 | 0.58225 | 0.26563 | -0.00316 | 0.00085 | -0.01023 |
| Na8 | 0.62370 | 0.58310 | 0.24460 | Li4 | 0.62686 | 0.58225 | 0.26563 | -0.00316 | 0.00085 | -0.02103 |
| Co1 | 0.98880 | 0.17440 | 0.72180 | Ni1 | 0.99018 | 0.17231 | 0.76617 | -0.00138 | 0.00209 | -0.04437 |
| Co2 | 0.48880 | 0.17440 | 0.77820 | Ni2 | 0.49018 | 0.17231 | 0.76617 | -0.00138 | 0.00209 | 0.01203 |
| Co3 | 0.01120 | 0.67440 | 0.72180 | Ni3 | 0.00982 | 0.67231 | 0.73383 | 0.00138 | 0.00209 | -0.01203 |
| Co4 | 0.51120 | 0.67440 | 0.77820 | Ni4 | 0.50982 | 0.67231 | 0.73383 | 0.00138 | 0.00209 | 0.04437 |
| P1 | 0.11810 | 0.41210 | 0.79480 | P1 | 0.12106 | 0.41794 | 0.77416 | -0.00296 | -0.00584 | 0.02064 |
| P2 | 0.61810 | 0.41210 | 0.70520 | P2 | 0.62106 | 0.41794 | 0.77416 | -0.00296 | -0.00584 | -0.06896 |
| P3 | 0.88190 | 0.91210 | 0.79480 | P3 | 0.87894 | 0.91794 | 0.72584 | 0.00296 | -0.00584 | 0.06896 |
| P4 | 0.38190 | 0.91210 | 0.70520 | P4 | 0.37894 | 0.91794 | 0.72584 | 0.00296 | -0.00584 | -0.02064 |
| O1 | 0.71610 | 0.13100 | 0.20880 | O1 | 0.72694 | 0.12388 | 0.23717 | -0.01084 | 0.00712 | -0.02837 |
| O2 | 0.21610 | 0.13100 | 0.29120 | O2 | 0.22694 | 0.12388 | 0.23717 | -0.01084 | 0.00712 | 0.05403 |
| O3 | 0.28390 | 0.63100 | 0.20880 | O3 | 0.27306 | 0.62388 | 0.26283 | 0.01084 | 0.00712 | -0.05403 |
| O4 | 0.78390 | 0.63100 | 0.29120 | O4 | 0.77306 | 0.62388 | 0.26283 | 0.01084 | 0.00712 | 0.02837 |
| O5 | 0.03620 | 0.34730 | 0.64990 | O5 | 0.05146 | 0.32913 | 0.63644 | -0.01526 | 0.01817 | 0.01346 |
| O6 | 0.53620 | 0.34730 | 0.85010 | O6 | 0.55146 | 0.32913 | 0.63644 | -0.01526 | 0.01817 | 0.21366 |
| O7 | 0.96380 | 0.84730 | 0.64990 | O7 | 0.94854 | 0.82913 | 0.86356 | 0.01526 | 0.01817 | -0.21366 |
| O8 | 0.46380 | 0.84730 | 0.85010 | O8 | 0.44854 | 0.82913 | 0.86356 | 0.01526 | 0.01817 | -0.01346 |
| O9 | 0.10890 | 0.96020 | 0.26730 | O9 | 0.09685 | 0.07442 | 0.57453 | 0.01205 | 0.88578 | -0.30723 |
| O10 | 0.60370 | 0.10630 | 0.58630 | O10 | 0.59685 | 0.07442 | 0.57453 | 0.00685 | 0.03188 | 0.01177 |
| O11 | 0.89630 | 0.60630 | 0.91370 | O11 | 0.90315 | 0.57442 | 0.92547 | -0.00685 | 0.03188 | -0.01177 |
| O12 | 0.39110 | 0.46020 | 0.23270 | O12 | 0.40315 | 0.57442 | 0.92547 | -0.01205 | -0.11422 | -0.69277 |
| O13 | 0.10370 | 0.10630 | 0.91370 | O13 | 0.10800 | 0.95895 | 0.14449 | -0.0043 | -0.85265 | 0.76921 |
| O14 | 0.60890 | 0.96020 | 0.23270 | O14 | 0.60800 | 0.95895 | 0.14449 | 0.0009 | 0.00125 | 0.08821 |
| O15 | 0.89110 | 0.46020 | 0.26730 | O15 | 0.89200 | 0.45895 | 0.35551 | -0.0009 | 0.00125 | -0.08821 |
| O16 | 0.39630 | 0.60630 | 0.58630 | O16 | 0.39200 | 0.45895 | 0.35551 | 0.0043 | 0.14735 | 0.23079 |
| F1 | 0.87460 | 0.25000 | 0.50000 | F1 | 0.89521 | 0.21364 | 0.46517 | -0.02061 | 0.03636 | 0.03483 |
| F2 | 0.40380 | 0.25000 | 0.50000 | F2 | 0.39521 | 0.21364 | 0.46517 | 0.00859 | 0.03636 | 0.03483 |
| F3 | 0.09620 | 0.75000 | 0.00000 | F3 | 0.10479 | 0.71364 | 0.03483 | -0.00859 | 0.03636 | -0.03483 |
| F4 | 0.62540 | 0.75000 | 0.00000 | F4 | 0.60479 | 0.71364 | 0.03483 | 0.02061 | 0.03636 | -0.03483 |

**Table S5.** The atomic positions of $Na_2Ni[PO_4]F$ ($P\bar{1}$, $a$ = 13.6978(16) Å, $b$ = 5.1991(3) Å, $c$ = 13.4581(8) Å, $\alpha = \gamma$ = 90 °, $\beta$ = 120.58(1) °) and $LiNaNi[PO_4]F$ ($P\bar{1}$, $a$ = 13.545(7) Å, $b$ = 5.021(3) Å, $c$ = 13.049(5) Å, $\alpha = \gamma$ = 90 °, $\beta$ = 121.27(3) °) after the transformations.

| $Na_2Ni[PO_4]F$ | | | | $LiNaNi[PO_4]F$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Atom** | **x2** | **y2** | **z2** | **Atom** | **x1** | **y1** | **z1** | **x2-x1** | **y2-y1** | **z2-z1** |
| Na1 | 0.3385 | 0.7602 | 0.67 | Na1 | 0.33755 | 0.752 | 0.6653 | 0.00095 | 0.0082 | 0.0047 |
| Na2 | 0.8385 | 0.7398 | 0.67 | Na2 | 0.83755 | 0.752 | 0.6653 | 0.00095 | -0.0122 | 0.0047 |
| Na3 | 0.0806 | 0.7387 | 0.1704 | Na3 | 0.07775 | 0.748 | 0.1653 | 0.00285 | -0.0093 | 0.0051 |
| Na4 | 0.5806 | 0.7613 | 0.1704 | Na4 | 0.57775 | 0.748 | 0.1653 | 0.00285 | 0.0133 | 0.0051 |
| Na5 | 0.9176 | 0.2421 | 0.5811 | Li1 | 0.91425 | 0.2656 | 0.5823 | 0.00335 | -0.0235 | -0.0012 |
| Na6 | 0.4176 | 0.2579 | 0.5811 | Li2 | 0.41425 | 0.2656 | 0.5823 | 0.00335 | -0.0077 | -0.0012 |
| Na7 | 0.4118 | 0.2296 | 0.0812 | Li3 | 0.41805 | 0.2344 | 0.0823 | -0.00625 | -0.0048 | -0.0011 |
| Na8 | 0.9118 | 0.2704 | 0.0812 | Li4 | 0.91805 | 0.2344 | 0.0823 | -0.00625 | 0.036 | -0.0011 |
| Ni1 | 0.07515 | 0.77672 | 0.67689 | Ni1 | 0.07635 | 0.7338 | 0.6723 | -0.0012 | 0.04292 | 0.00459 |
| Ni2 | 0.57515 | 0.72328 | 0.67689 | Ni2 | 0.57635 | 0.7338 | 0.6723 | -0.0012 | -0.01052 | 0.00459 |
| Ni3 | 0.85096 | 0.78356 | 0.17655 | Ni3 | 0.84595 | 0.7662 | 0.1723 | 0.00501 | 0.01736 | 0.00425 |
| Ni4 | 0.64904 | 0.28356 | 0.82345 | Ni4 | 0.65405 | 0.2338 | 0.8277 | -0.00501 | 0.04976 | -0.00425 |
| P1 | 0.323 | 0.7015 | 0.9126 | P1 | 0.33005 | 0.7258 | 0.9179 | -0.00705 | -0.0243 | -0.0053 |
| P2 | 0.823 | 0.7985 | 0.9126 | P2 | 0.83005 | 0.7258 | 0.9179 | -0.00705 | 0.0727 | -0.0053 |
| P3 | 0.3385 | 0.7919 | 0.4117 | P3 | 0.33785 | 0.7742 | 0.4179 | 0.00065 | 0.0177 | -0.0062 |
| P4 | 0.8385 | 0.7081 | 0.4117 | P4 | 0.83785 | 0.7742 | 0.4179 | 0.00065 | -0.0661 | -0.0062 |
| O1 | 0.7812 | 0.2835 | 0.6311 | O1 | 0.78885 | 0.2628 | 0.6239 | -0.00765 | 0.0207 | 0.0072 |
| O2 | 0.2812 | 0.2165 | 0.6311 | O2 | 0.28885 | 0.2628 | 0.6239 | -0.00765 | -0.0463 | 0.0072 |
| O3 | 0.5964 | 0.2172 | 0.1303 | O3 | 0.58505 | 0.2372 | 0.1239 | 0.01135 | -0.02 | 0.0064 |
| O4 | 0.0964 | 0.2828 | 0.1303 | O4 | 0.08505 | 0.2372 | 0.1239 | 0.01135 | 0.0456 | 0.0064 |
| O5 | 0.2081 | 0.8422 | 0.8461 | O5 | 0.21605 | 0.8636 | 0.8291 | -0.00795 | -0.0214 | 0.017 |
| O6 | 0.7081 | 0.6578 | 0.8461 | O6 | 0.71605 | 0.8636 | 0.8291 | -0.00795 | -0.2058 | 0.017 |
| O7 | 0.3862 | 0.6489 | 0.3452 | O7 | 0.36305 | 0.6364 | 0.3291 | 0.02315 | 0.0125 | 0.0161 |
| O8 | 0.8862 | 0.8511 | 0.3452 | O8 | 0.86305 | 0.6364 | 0.3291 | 0.02315 | 0.2147 | 0.0161 |
| O9 | 0.0884 | 0.2314 | 0.4589 | O9 | 0.1341 | -0.0745 | 0.5744 | -0.0457 | 0.3059 | -0.1155 |
| O10 | 0.654 | 0.9148 | 0.6059 | O10 | 0.6341 | 0.9255 | 0.5744 | 0.0199 | -0.0107 | 0.0315 |
| O11 | 0.8767 | 0.7378 | 1.0416 | O11 | 0.8097 | 0.4255 | 0.9256 | 0.067 | 0.3123 | 0.116 |
| O12 | 0.7016 | 0.5922 | 0.1076 | O12 | 0.6903 | 0.5745 | 0.0744 | 0.0113 | 0.0177 | 0.0332 |
| O13 | 0.5884 | 0.2686 | 0.4589 | O13 | 0.58745 | 0.3555 | 0.4589 | 0.00095 | -0.0869 | 0 |
| O14 | 0.154 | 0.5852 | 0.6059 | O14 | 0.08745 | 0.3555 | 0.4589 | 0.06655 | 0.2297 | 0.147 |
| O15 | 0.7984 | 1.0922 | 0.8924 | O15 | 0.8785 | 0.8555 | 1.041 | -0.0801 | 0.2367 | -0.1486 |
| O16 | 0.6233 | 0.2378 | 0.9584 | O16 | 0.6215 | 0.1445 | 0.959 | 0.0018 | 0.0933 | -0.0006 |
| F1 | 0.0019 | -0.0043 | 0.7527 | F1 | 0.002 | 0.0348 | 0.7136 | -0.0001 | -0.0391 | 0.0391 |
| F2 | 0.5296 | 0.0047 | 0.7484 | F2 | 0.502 | 0.0348 | 0.7136 | 0.0276 | -0.0301 | 0.0348 |
| F3 | 0.4981 | 0.4957 | 0.2473 | F3 | 0.4616 | 0.4652 | 0.2136 | 0.0365 | 0.0305 | 0.0337 |
| F4 | 0.9704 | 0.5047 | 0.2516 | F4 | 0.9616 | 0.4652 | 0.2136 | 0.0088 | 0.0395 | 0.038 |

**Table S6.** The atomic positions of $Na_2Mn[PO_4]F$ ($P\bar{1}$, $a$ = 13.6830, $b$ = 5.3170, $c$ = 13.7683Å, and $\beta$ = 120.04 °) and $LiNaNi[PO_4]F$ ($P\bar{1}$, $a$ = 13.545(7) Å, $b$ = 5.021(3) Å, $c$ = 13.049(5) Å, $\alpha = \gamma$ = 90 °, and $\beta$ = 121.27(3) °) after the transformations.

| $Na_2Mn[PO_4]F$ | | | | $LiNaNi[PO_4]F$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Atom** | **x2** | **y2** | **z2** | **Atom** | **x1** | **y1** | **z1** | **x2-x1** | **y2-y1** | **z2-z1** |
| Na1 | 0.33392 | 0.7586 | 0.6632 | Na1 | 0.33755 | 0.752 | 0.6653 | -0.00363 | 0.0066 | -0.0021 |
| Na2 | 0.83455 | 0.737 | 0.67191 | Na2 | 0.83755 | 0.752 | 0.6653 | -0.003 | -0.015 | 0.00661 |
| Na3 | 0.07984 | 0.7383 | 0.1665 | Na3 | 0.07775 | 0.748 | 0.1653 | 0.00209 | -0.0097 | 0.0012 |
| Mn1 | 0.5761 | 0.77224 | 0.17666 | Na4 | 0.57775 | 0.748 | 0.1653 | -0.00165 | 0.02424 | 0.01136 |
| Mn2 | 0.92356 | 0.22901 | 0.60041 | Li1 | 0.91425 | 0.2656 | 0.5823 | 0.00931 | -0.03659 | 0.01811 |
| Na4 | 0.41977 | 0.2562 | 0.58675 | Li2 | 0.41425 | 0.2656 | 0.5823 | 0.00552 | -0.0094 | 0.00445 |
| Na5 | 0.41977 | 0.2438 | 0.08675 | Li3 | 0.41805 | 0.2344 | 0.0823 | 0.00172 | 0.0094 | 0.00445 |
| Mn3 | 0.92356 | 0.27099 | 0.10041 | Li4 | 0.91805 | 0.2344 | 0.0823 | 0.00551 | 0.03659 | 0.01811 |
| Na6 | 0.07984 | 0.7617 | 0.6665 | Ni1 | 0.07635 | 0.7338 | 0.6723 | 0.00349 | 0.0279 | -0.0058 |
| Mn4 | 0.5761 | 0.72776 | 0.67666 | Ni2 | 0.57635 | 0.7338 | 0.6723 | -0.00025 | -0.00604 | 0.00436 |
| Na7 | 0.83455 | 0.763 | 0.17191 | Ni3 | 0.84595 | 0.7662 | 0.1723 | -0.0114 | -0.0032 | -0.00039 |
| Na8 | 0.66608 | 0.2586 | 0.8368 | Ni4 | 0.65405 | 0.2338 | 0.8277 | 0.01203 | 0.0248 | 0.0091 |
| P1 | 0.33795 | 0.7144 | 0.91529 | P1 | 0.33005 | 0.7258 | 0.9179 | 0.0079 | -0.0114 | -0.00261 |
| P2 | 0.83782 | 0.7835 | 0.92335 | P2 | 0.83005 | 0.7258 | 0.9179 | 0.00777 | 0.0577 | 0.00545 |
| P3 | 0.33795 | 0.7856 | 0.41529 | P3 | 0.33785 | 0.7742 | 0.4179 | 1E-04 | 0.0114 | -0.00261 |
| P4 | 0.83782 | 0.7165 | 0.42335 | P4 | 0.83785 | 0.7742 | 0.4179 | -3E-05 | -0.0577 | 0.00545 |
| O1 | 0.7875 | 0.2799 | 0.6352 | O1 | 0.78885 | 0.2628 | 0.6239 | -0.00135 | 0.0171 | 0.0113 |
| O2 | 0.2881 | 0.2214 | 0.6517 | O2 | 0.28885 | 0.2628 | 0.6239 | -0.00075 | -0.0414 | 0.0278 |
| O3 | 0.614 | 0.1466 | 0.149 | O3 | 0.58505 | 0.2372 | 0.1239 | 0.02895 | -0.0906 | 0.0251 |
| O4 | 0.0963 | 0.2981 | 0.1348 | O4 | 0.08505 | 0.2372 | 0.1239 | 0.01125 | 0.0609 | 0.0109 |
| O5 | 0.2125 | 0.7799 | 0.8648 | O5 | 0.21605 | 0.8636 | 0.8291 | -0.00355 | -0.0837 | 0.0357 |
| O6 | 0.7119 | 0.7214 | 0.8483 | O6 | 0.71605 | 0.8636 | 0.8291 | -0.00415 | -0.1422 | 0.0192 |
| O7 | 0.386 | 0.6466 | 0.351 | O7 | 0.36305 | 0.6364 | 0.3291 | 0.02295 | 0.0102 | 0.0219 |
| O8 | 0.9037 | 0.7981 | 0.3652 | O8 | 0.86305 | 0.6364 | 0.3291 | 0.04065 | 0.1617 | 0.0361 |
| O9 | 0.1166 | 0.1465 | 0.4638 | O9 | 0.1341 | -0.0745 | 0.5744 | -0.0175 | 0.221 | -0.1106 |
| O10 | 0.6515 | 0.9261 | 0.5963 | O10 | 0.6341 | 0.9255 | 0.5744 | 0.0174 | 0.0006 | 0.0219 |
| O11 | 0.8834 | 0.6465 | 1.0362 | O11 | 0.8097 | 0.4255 | 0.9256 | 0.0737 | 0.221 | 0.1106 |
| O12 | 0.6515 | 0.5739 | 0.0963 | O12 | 0.6903 | 0.5745 | 0.0744 | -0.0388 | -0.0006 | 0.0219 |
| O13 | 0.5973 | 0.2855 | 0.4601 | O13 | 0.58745 | 0.3555 | 0.4589 | 0.00985 | -0.07 | 0.0012 |
| O14 | 0.1489 | 0.5717 | 0.5558 | O14 | 0.08745 | 0.3555 | 0.4589 | 0.06145 | 0.2162 | 0.0969 |
| O15 | 0.8511 | 1.0717 | 0.9442 | O15 | 0.8785 | 0.8555 | 1.041 | -0.0274 | 0.2162 | -0.0968 |
| O16 | 0.5973 | 0.2145 | 0.9601 | O16 | 0.6215 | 0.1445 | 0.959 | -0.0242 | 0.07 | 0.0011 |
| F1 | -0.0003 | -0.0004 | 0.7632 | F1 | 0.002 | 0.0348 | 0.7136 | -0.0023 | -0.0352 | 0.0496 |
| F2 | 0.5073 | 0.0016 | 0.7414 | F2 | 0.502 | 0.0348 | 0.7136 | 0.0053 | -0.0332 | 0.0278 |
| F3 | 0.5073 | 0.4984 | 0.2414 | F3 | 0.4616 | 0.4652 | 0.2136 | 0.0457 | 0.0332 | 0.0278 |
| F4 | 0.9997 | 0.5004 | 0.2632 | F4 | 0.9616 | 0.4652 | 0.2136 | 0.0381 | 0.0352 | 0.0496 |

**Table S7.** The atomic positions of $Na_2Mn[PO_4]F$ ($P\bar{1}$, $a$ = 13.6830, $b$ = 5.3170, $c$ = 13.7683Å, and $\beta$ = 120.04 °) and $Na_2Ni[PO_4]F$ ($P\bar{1}$, $a$ = 13.6978(16) Å, $b$ = 5.1991(3) Å, $c$ = 13.4581(8) Å, $\alpha = \gamma$ = 90 °, $\beta$ = 120.58(1) °) after the transformations.

| $Na_2Mn[PO_4]F$ | | | | $Na_2Ni[PO_4]F$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Atom** | **x2** | **y2** | **z2** | **Atom** | **x2** | **y2** | **z2** | **x2-x1** | **y2-y1** | **z2-z1** |
| Na1 | 0.33392 | 0.7586 | 0.6632 | Na1 | 0.3385 | 0.7602 | 0.67 | -0.00458 | -0.0016 | -0.0068 |
| Na2 | 0.83455 | 0.737 | 0.67191 | Na2 | 0.8385 | 0.7398 | 0.67 | -0.00395 | -0.0028 | 0.00191 |
| Na3 | 0.07984 | 0.7383 | 0.1665 | Na3 | 0.0806 | 0.7387 | 0.1704 | -0.00076 | -0.0004 | -0.0039 |
| Mn1 | 0.5761 | 0.77224 | 0.17666 | Na4 | 0.5806 | 0.7613 | 0.1704 | -0.0045 | 0.01094 | 0.00626 |
| Mn2 | 0.92356 | 0.22901 | 0.60041 | Na5 | 0.9176 | 0.2421 | 0.5811 | 0.00596 | -0.01309 | 0.01931 |
| Na4 | 0.41977 | 0.2562 | 0.58675 | Na6 | 0.4176 | 0.2579 | 0.5811 | 0.00217 | -0.0017 | 0.00565 |
| Na5 | 0.41977 | 0.2438 | 0.08675 | Na7 | 0.4118 | 0.2296 | 0.0812 | 0.00797 | 0.0142 | 0.00555 |
| Mn3 | 0.92356 | 0.27099 | 0.10041 | Na8 | 0.9118 | 0.2704 | 0.0812 | 0.01176 | 0.00059 | 0.01921 |
| Na6 | 0.07984 | 0.7617 | 0.6665 | Ni1 | 0.07515 | 0.77672 | 0.67689 | 0.00469 | -0.01502 | -0.01039 |
| Mn4 | 0.5761 | 0.72776 | 0.67666 | Ni2 | 0.57515 | 0.72328 | 0.67689 | 0.00095 | 0.00448 | -0.00023 |
| Na7 | 0.83455 | 0.763 | 0.17191 | Ni3 | 0.85096 | 0.78356 | 0.17655 | -0.01641 | -0.02056 | -0.00464 |
| Na8 | 0.66608 | 0.2586 | 0.8368 | Ni4 | 0.64904 | 0.28356 | 0.82345 | 0.01704 | -0.02496 | 0.01335 |
| P1 | 0.33795 | 0.7144 | 0.91529 | P1 | 0.323 | 0.7015 | 0.9126 | 0.01495 | 0.0129 | 0.00269 |
| P2 | 0.83782 | 0.7835 | 0.92335 | P2 | 0.823 | 0.7985 | 0.9126 | 0.01482 | -0.015 | 0.01075 |
| P3 | 0.33795 | 0.7856 | 0.41529 | P3 | 0.3385 | 0.7919 | 0.4117 | -0.00055 | -0.0063 | 0.00359 |
| P4 | 0.83782 | 0.7165 | 0.42335 | P4 | 0.8385 | 0.7081 | 0.4117 | -0.00068 | 0.0084 | 0.01165 |
| O1 | 0.7875 | 0.2799 | 0.6352 | O1 | 0.7812 | 0.2835 | 0.6311 | 0.0063 | -0.0036 | 0.0041 |
| O2 | 0.2881 | 0.2214 | 0.6517 | O2 | 0.2812 | 0.2165 | 0.6311 | 0.0069 | 0.0049 | 0.0206 |
| O3 | 0.614 | 0.1466 | 0.149 | O3 | 0.5964 | 0.2172 | 0.1303 | 0.0176 | -0.0706 | 0.0187 |
| O4 | 0.0963 | 0.2981 | 0.1348 | O4 | 0.0964 | 0.2828 | 0.1303 | -0.0001 | 0.0153 | 0.0045 |
| O5 | 0.2125 | 0.7799 | 0.8648 | O5 | 0.2081 | 0.8422 | 0.8461 | 0.0044 | -0.0623 | 0.0187 |
| O6 | 0.7119 | 0.7214 | 0.8483 | O6 | 0.7081 | 0.6578 | 0.8461 | 0.0038 | 0.0636 | 0.0022 |
| O7 | 0.386 | 0.6466 | 0.351 | O7 | 0.3862 | 0.6489 | 0.3452 | -0.0002 | -0.0023 | 0.0058 |
| O8 | 0.9037 | 0.7981 | 0.3652 | O8 | 0.8862 | 0.8511 | 0.3452 | 0.0175 | -0.053 | 0.02 |
| O9 | 0.1166 | 0.1465 | 0.4638 | O9 | 0.0884 | 0.2314 | 0.4589 | 0.0282 | -0.0849 | 0.0049 |
| O10 | 0.6515 | 0.9261 | 0.5963 | O10 | 0.654 | 0.9148 | 0.6059 | -0.0025 | 0.0113 | -0.0096 |
| O11 | 0.8834 | 0.6465 | 1.0362 | O11 | 0.8767 | 0.7378 | 1.0416 | 0.0067 | -0.0913 | -0.0054 |
| O12 | 0.6515 | 0.5739 | 0.0963 | O12 | 0.7016 | 0.5922 | 0.1076 | -0.0501 | -0.0183 | -0.0113 |
| O13 | 0.5973 | 0.2855 | 0.4601 | O13 | 0.5884 | 0.2686 | 0.4589 | 0.0089 | 0.0169 | 0.0012 |
| O14 | 0.1489 | 0.5717 | 0.5558 | O14 | 0.154 | 0.5852 | 0.6059 | -0.0051 | -0.0135 | -0.0501 |
| O15 | 0.8511 | 1.0717 | 0.9442 | O15 | 0.7984 | 1.0922 | 0.8924 | 0.0527 | -0.0205 | 0.0518 |
| O16 | 0.5973 | 0.2145 | 0.9601 | O16 | 0.6233 | 0.2378 | 0.9584 | -0.026 | -0.0233 | 0.0017 |
| F1 | -0.0003 | -0.0004 | 0.7632 | F1 | 0.0019 | -0.0043 | 0.7527 | -0.0022 | 0.0039 | 0.0105 |
| F2 | 0.5073 | 0.0016 | 0.7414 | F2 | 0.5296 | 0.0047 | 0.7484 | -0.0223 | -0.0031 | -0.007 |
| F3 | 0.5073 | 0.4984 | 0.2414 | F3 | 0.4981 | 0.4957 | 0.2473 | 0.0092 | 0.0027 | -0.0059 |
| F4 | 0.9997 | 0.5004 | 0.2632 | F4 | 0.9704 | 0.5047 | 0.2516 | 0.0293 | -0.0043 | 0.0116 |

**Table S8.** Basis vectors for the 4*e*(x,y,z) site of the $P2_1/c$*(14)* space group and the propagation vector k=(1/2,0,0). The atomic positions are Ni1 (x,y,z), Ni2 (-x,y+1/2,-z+1/2), Ni3(-x,-y,-z), and Ni4(x,-y+1/2,z+1/2). The ordering modes are A(+--+), C(++--), F(++++), and G(+-+-). The model providing the best agreement with the experimental NPD data is highlighted in bold font.

| IR | Basis vectors | Shubnikov group |
|---|---|---|
| **Γ1** | **GxFyGz** | **$P2_1$'/c** |
| Γ2 | AxCyAz | $P2_1$/c' |
| Γ3 | FxGyFz | $P2_1$'/c' |
| Γ4 | CxAyCz | $P2_1$/c |

**Table S9.** Crystal structural parameters for LiNaNi[$PO_4$]F based on the Rietveld refinement against NPD data collected at 3 K. Space group $P2_1/c$(#14), a = 6.7788(2) Å, b = 11.1702(3) Å, c = 5.01886(16) Å, β = 89.736(2), V = 380.03(2) Å$^3$, $B_{ov}$ = 0.14(8) Å$^2$.

| Atom | Wyckoff site | x | y | z | BVS |
|---|---|---|---|---|---|
| Li | 4e | -0.250(5) | 0.082(2) | 0.269(6) | 0.93(4) |
| Na | 4e | 0.516(2) | 0.1674(13) | 0.749(4) | 1.01(2) |
| Ni | 4e | -0.0200(10) | 0.1720(5) | 0.7624(13) | 2.08(3) |
| P | 4e | 0.2494(16) | 0.4194(9) | 0.762(2) | 5.01(3) |
| O1 | 4e | -0.5461(12) | 0.1248(6) | 0.237(2) | 2.12(6) |
| O2 | 4e | 0.0904(14) | 0.3269(10) | 0.6397(19) | 1.78(4) |
| O3 | 4e | 0.1961(14) | 0.0731(8) | 0.5688(18) | 1.82(5) |
| O4 | 4e | 0.2125(14) | -0.0395(9) | 0.1477(15) | 2.17(6) |
| F | 4e | -0.2033(16) | 0.2143(7) | 0.4594(20) | 1.16(3) |