

## Supporting Information

### Enumeration as a tool for structure solution – a materials genomic approach to solving the cation-ordered structure of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$

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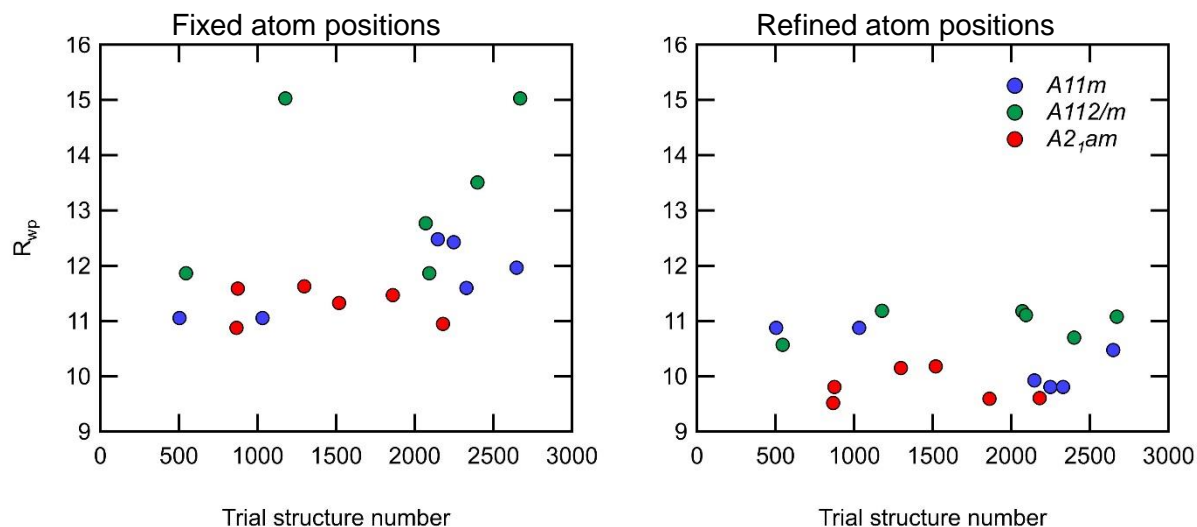
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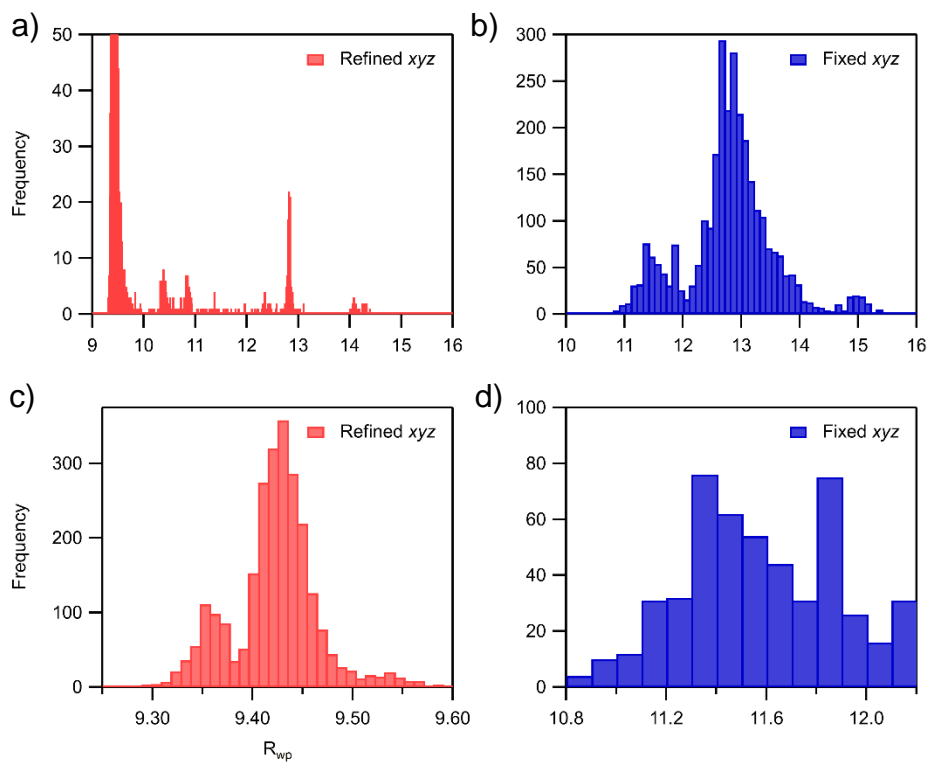
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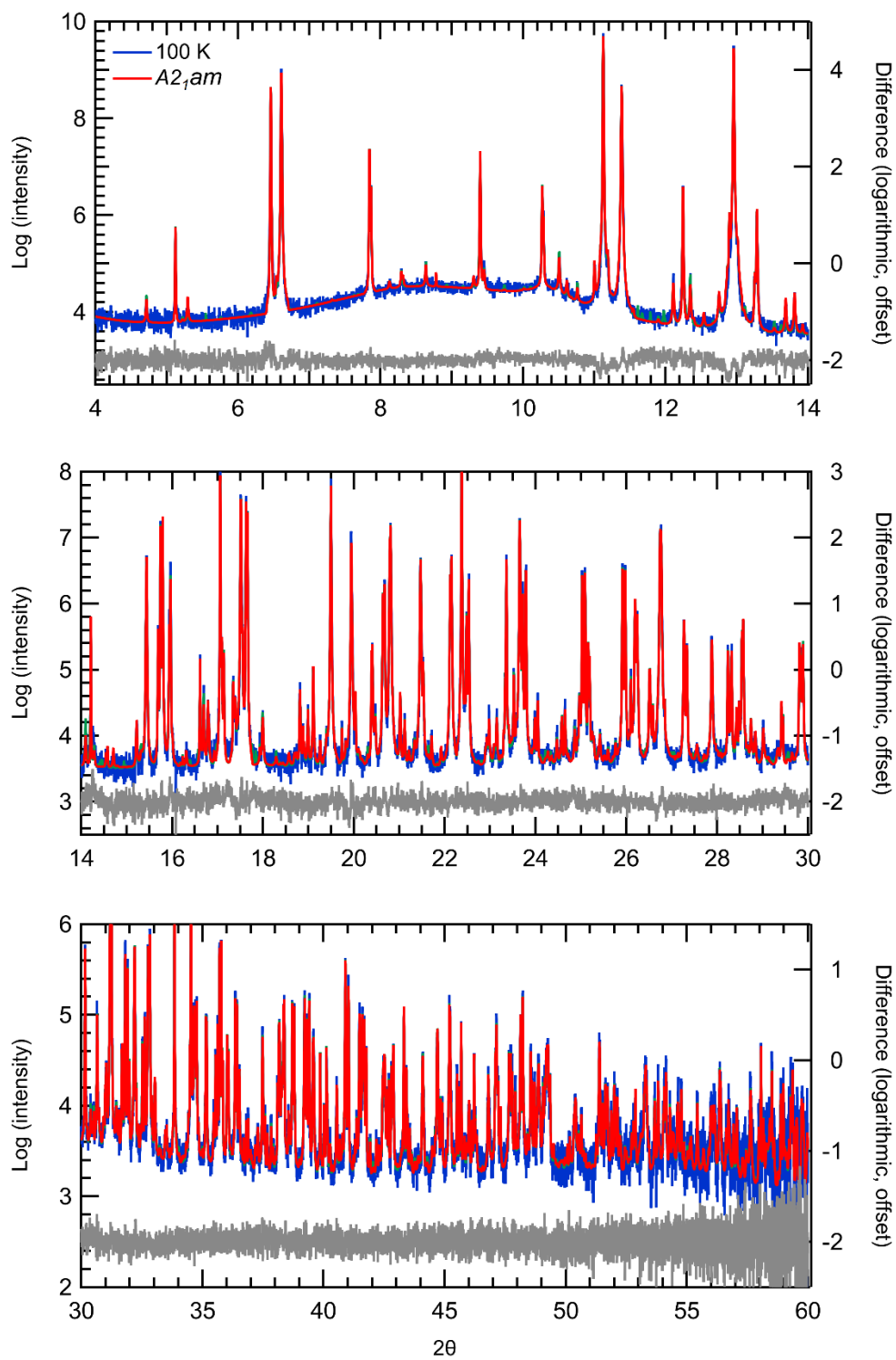
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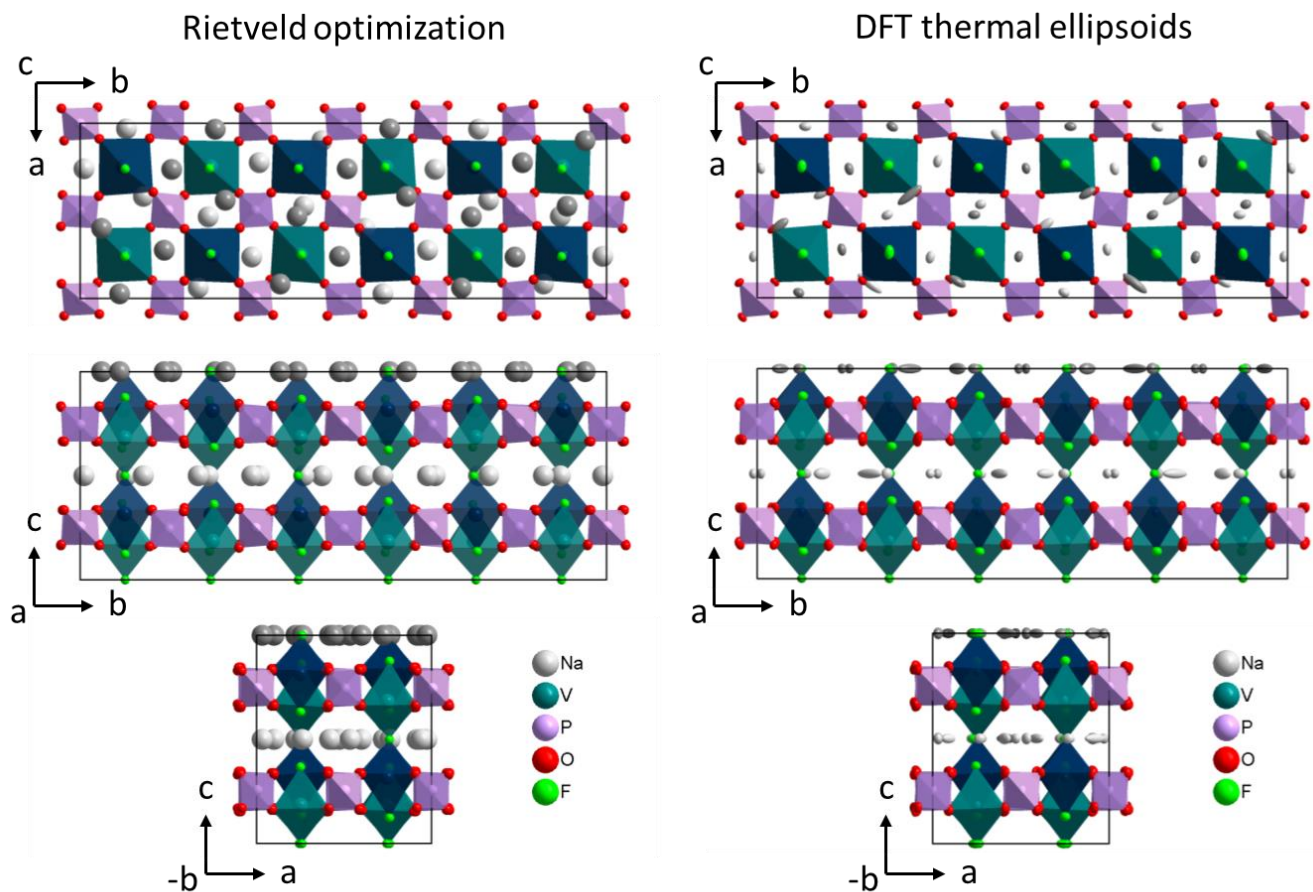
**Figure S1.** Comparison of  $R_{wp}$  values obtained after Rietveld refinements in which atom positions were fixed (left) or were freely refined (right), here shown only for the three space group symmetries with centered lattices (complete data is shown in Figure 5).



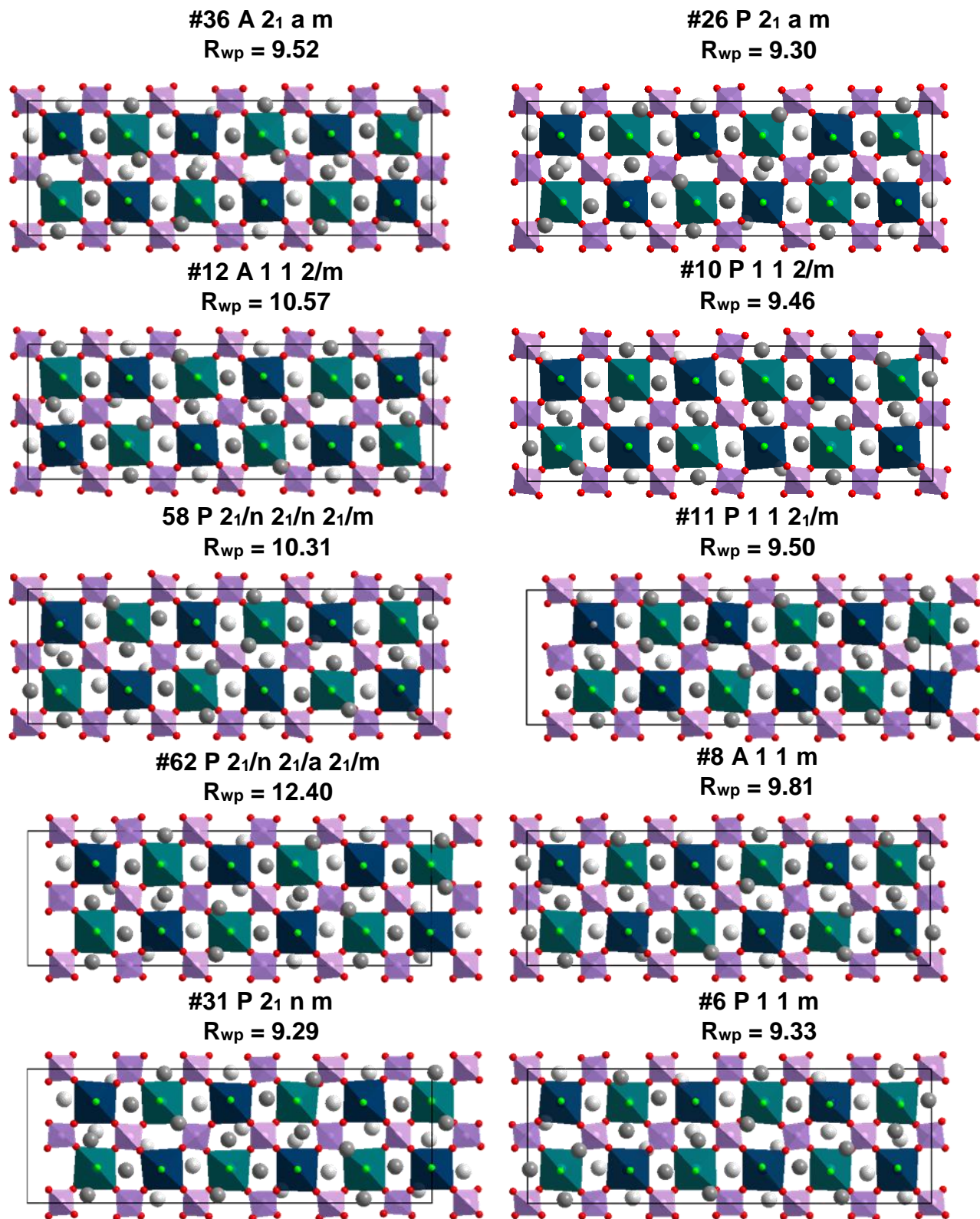
**Figure S2.** Histogram of  $R_{wp}$  values for Rietveld refinements for the 2,940 trial structures generated by enumeration performed using refined atomic coordinates (a and c, shown in red) and fixed atomic coordinates (b and d, shown in blue). The upper plots show the data over the full width of  $R_{wp}$  values while the lower plots show a zoom of the first peak in the histogram.



**Figure S3.** Rietveld fit to the optimal  $A2_1am$  structural model (red) compared to the experimental data (blue) with the difference pattern shown in gray. The close agreement across hundreds of peaks indicates that this structural model very closely matches the true structure.

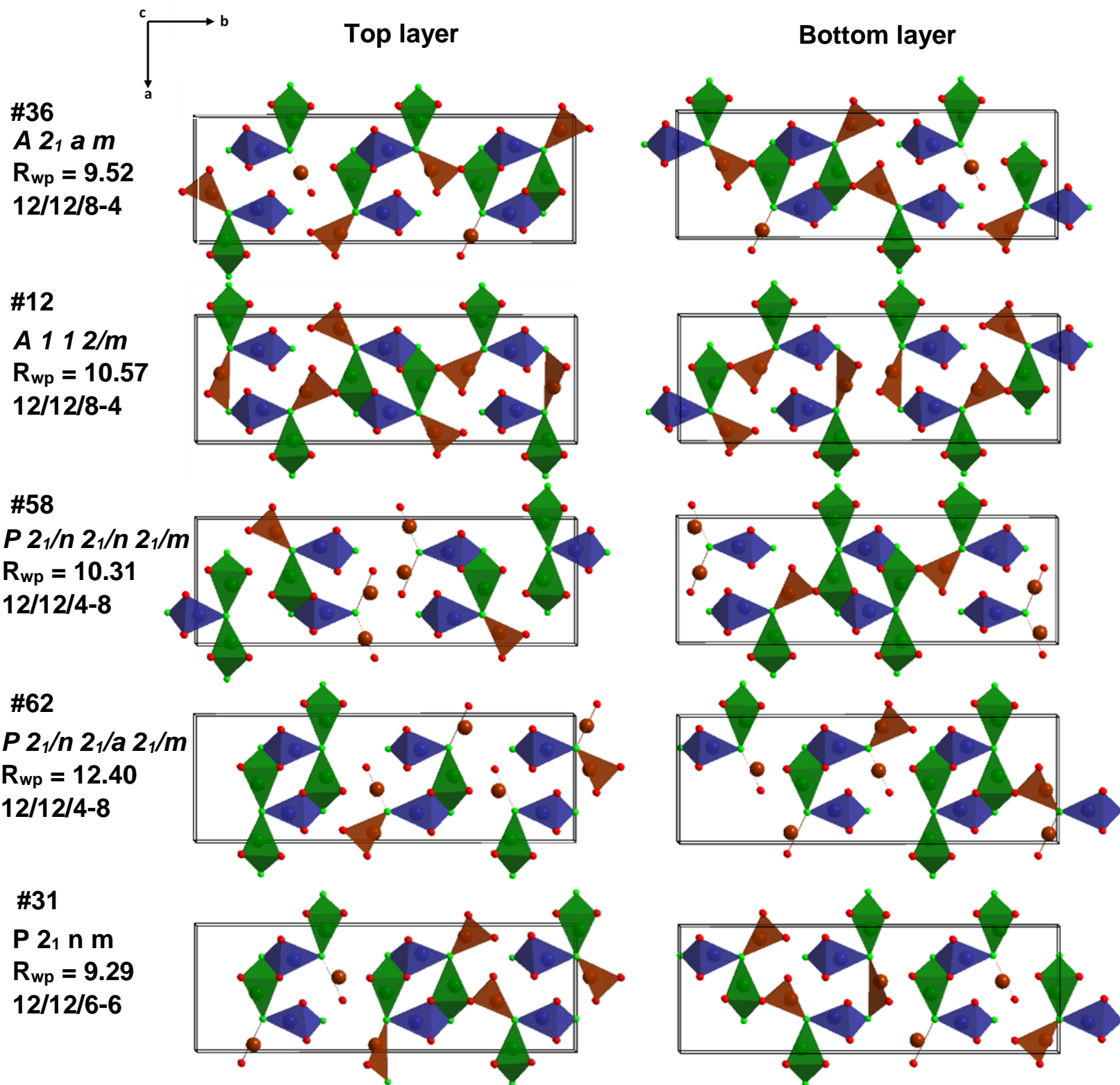


**Figure S4.** Axial views showing cation polyhedral representation of optimal  $A2_1am$  structure of LT-NVPF obtained after Rietveld refinement (left) and as obtained from the DFT calculation of atomic displacement parameters with the thermal ellipsoids drawn at the 90% level (right). The  $VO_6$  octahedra are shown in dark blue when the apical F is in the Na plane and in teal otherwise, and the  $PO_4$  tetrahedra are shown in mauve. Na atoms are shown in dark grey in the upper layer and light grey in the lower layer, O are shown in red, and F are shown in green.

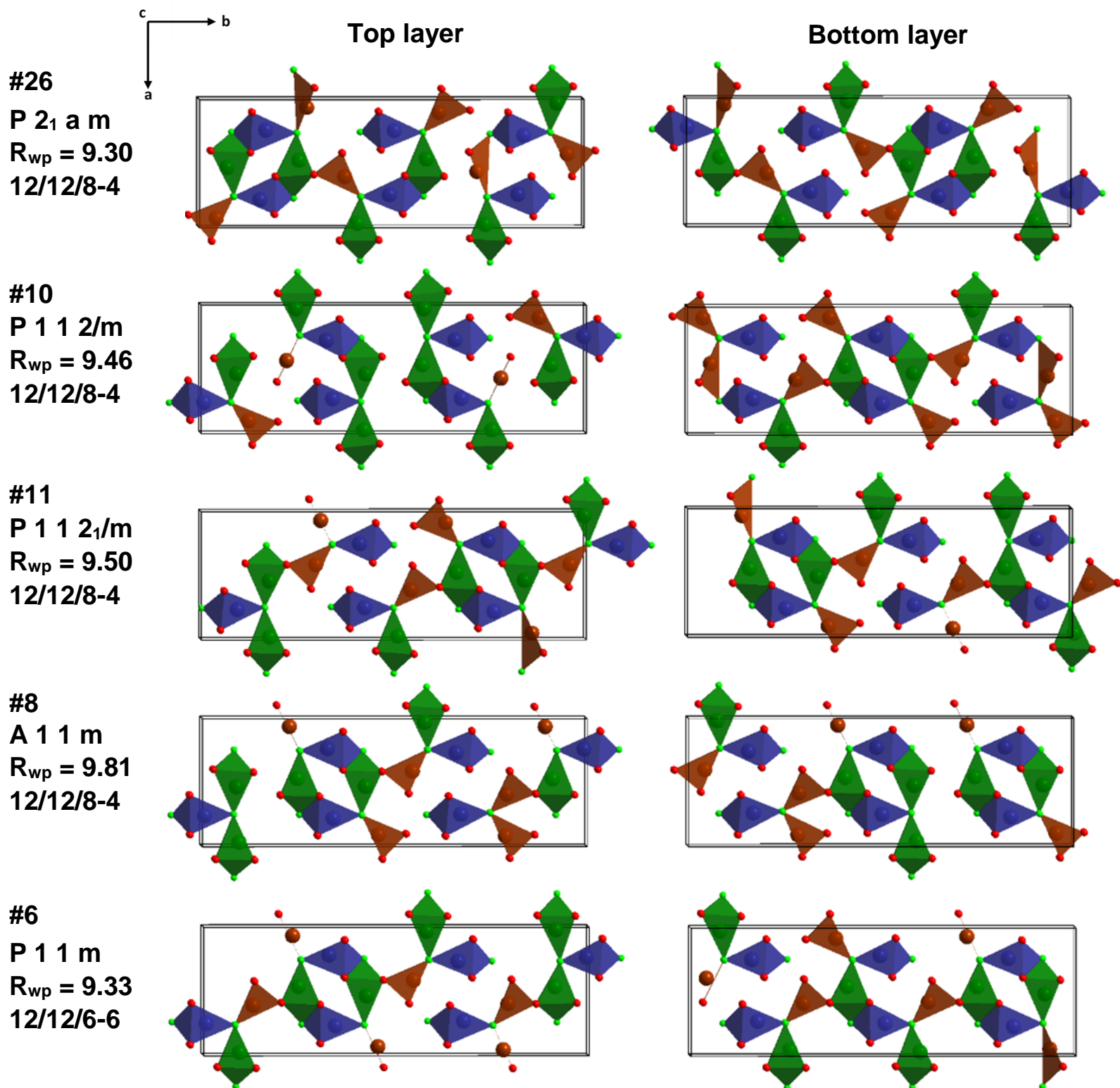


**Figure S5.** Cation polyhedral environments for the best fitting structural model for each of the ten trial space groups for LT-NVPF. The VO<sub>6</sub> are shown in dark blue when the apical F is in the Na plane and in teal otherwise, and PO<sub>4</sub> tetrahedra are shown in mauve. Na atoms are shown in dark grey in the upper layer and light grey in the lower layer, O atoms are shown in red, and F atoms in green.





**Figure S6.** Na-ion coordination environments for the best fitting structural model for each of the ten trial space groups for LT-NVPF. Coordination polyhedra are color-coded based on their correspondence to that of the Na1 site (blue), Na2 site (green), or Na3 site (brown) in the RT-NVPF structure. Labels specify the space group number and name, the fit  $R_{wp}$ , and the number of Na ions of each Na1 / Na2 / Na3, with counts in the last category separated by a dash for CN = 6 and CN = 4 sites, respectively.



**Figure S6 (continued).** Na-ion coordination environments for the best fitting structural model for each of the ten trial space groups for LT-NVPF. Coordination polyhedra are color-coded based on their correspondence to that of the Na1 site (blue), Na2 site (green), or Na3 site (brown) in the RT-NVPF structure. Labels specify the space group number and name, the fit  $R_{wp}$ , and the number of Na ions of each Na1 / Na2 / Na3, with counts in the last category separated by a dash for CN = 6 and CN = 4 sites, respectively.