Supporting Information

Expanding the ambient-pressure phase space of CaFe$_2$O$_4$-type sodium post-spinel host–guest compounds

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### Table S1 Compositions that did not form a CF structure

| Target compound     | Starting materials             | Applied temperature (s) (°C) | Atmosphere | Major phases                                                                 |
|---------------------|--------------------------------|-----------------------------|------------|-----------------------------------------------------------------------------|
| NaYZrO4             | NaHCO3, Y2O3, ZrO2             | 1050 1200                   | Air        | Na2ZrO3, Y2O3, cubic Y-substituted ZrO2                                      |
| NaInZrO4            | NaHCO3, In2O3, ZrO2             | 950 1100                    | Air        | NaInO2, ZrO2, NaInO3, In2O3, ZrO2                                           |
| NaScRuO4            | NaHCO3, Sc2O3, RuO2             | 950                          | Air        | Na2xSc3RuO9 (Sc-substituted?), Sc2O3                                        |
| NaMnRuO4            | NaHCO3, Mn2O3, RuO2             | 950                          | Air        | RuO2, Na3Mn2O2, NaMn2O2                                                    |
| NaRhRuO4            | NaHCO3, Rh2O3, RuO2             | 950                          | Air        | RuO2, unknown- possibly Na3(Rh,Ru)O2                                        |
| NaAlSnO4            | NaHCO3, Al2O3, SnO2             | 950                          | Air        | SnO2, NaAlO2                                                               |
| NaGaSnO4            | NaHCO3, Ga2O3, SnO2             | 950 1200                    | Air        | NaGaO2, SnO2, NaGaO2, SnO2, NaGaO2, SnO2                                    |
| NaYSnO4             | NaHCO3, Y2O3, SnO2              | 1200                         | Air        | Y2Sn2O7, Y2O3                                                              |
| NaRhSnO4            | NaRhO2, SnO2                    | 1000                         | Air        | SnO2, NaRhO2                                                               |
| NaMn0.5Ti1.5O4      | NaHCO3, MnO, TiO2               | 875 950                      | Argon      | Na2TiO7, MnTiO3, unknown                                                   |
| NaCu0.5Ti1.5O4      | NaHCO3, CuO, TiO2               | 925                          | Air        | Na2TiO7, NaCu2,5Ti6,5O18, CuO                                              |
| NaZn0.5Ti1.5O4      | NaHCO3, ZnO, TiO2               | 900                          | Air        | Na2TiO7, ZnO                                                              |
| NaMn0.5Zr1.5O4      | NaHCO3, MnO, ZrO2               | 1000                         | Argon      | ZrO2, MnO, Na2ZrO3                                                         |
| NaCo0.5Zr1.5O4      | NaHCO3, Co3O4, ZrO2             | 950                          | Air        | ZrO2, Na2ZrO3, CoO                                                         |
| NaCd0.5Zr1.5O4      | NaHCO3, CdO, ZrO2               | 1000                         | Air        | Na2ZrO3, ZrO2, CdO                                                        |
| NaNi0.5Ru1.5O4      | NaHCO3, NiO, RuO2               | 950                          | Air        | RuO2, unknown- possibly mixture of Na3(Ni,Ru)O2 phases                     |
| NaCr1.5Sb0.5O4      | NaHCO3, Cr2O3, NaSbO3           | 900 950                      | Argon      | Na0.58Cr0.79Sb0.21O2, NaSbO3                                               |
| NaMn1.5Sb0.5O4      | NaHCO3, Mn2O3, Sb2O3            | 1000                         | Air        | NaSbO3, unknown                                                           |
| NaRh1.5Sb0.5O4      | NaHCO3, Rh2O3, Sb2O3            | 950                          | Air        | NaSbO3, unknown                                                           |
| NaSc1.5Ta0.5O4      | NaHCO3, Sc2O3, Ta2O5           | 950                          | Air        | NaTaO3, Sc2O3                                                             |
| NaCoSbO4            | NaHCO3, Co3O4, Sb2O3            | 1200                         | Air        | NaSbO3, Co2,3Sb0.67O4                                                      |
Figure S1 Rietveld refinement for NaCrTiO$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, and the red tick marks indicate the location of the CF-NaCrTiO$_4$ peaks.

Figure S2 Rietveld refinement for NaRhTiO$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, and the red tick marks indicate the location of the CF-NaRhTiO$_4$ peaks.
Figure S3 Rietveld refinement for NaCrSnO$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, the red tick marks indicate the location of the CF-NaCrSnO$_4$ peaks, and the magenta tick marks indicate the location of NaCrO$_2$ peaks.

Figure S4 Rietveld refinement for NaMnSnO$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, and the red tick marks indicate the location of the CF-NaMnSnO$_4$ peaks. The inset is included to show that the peak at 3.7° is an unknown impurity and too far away from the calculated angle of the (1 0 1) peak. Thus, cation site preference is either very weak or nonexistent in NaMnSnO$_4$. 
Figure S5 Rietveld refinement for NaInSnO$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, and the red tick marks indicate the location of the CF-NaInSnO$_4$ peaks.

Figure S6 Rietveld refinement for NaMg$_{0.5}$Sn$_{1.5}$O$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, and the red tick marks indicate the location of the CF-NaMg$_{0.5}$Sn$_{1.5}$O$_4$ peaks.
**Figure S7** Rietveld refinement for NaCo$_{0.5}$Sn$_{1.5}$O$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, the red tick marks indicate the location of the CF-NaCo$_{0.5}$Sn$_{1.5}$O$_4$ peaks, and the magenta tick marks indicate the location of SnO$_2$ peaks.

**Figure S8** Rietveld refinement for NaNi$_{0.5}$Sn$_{1.5}$O$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, the red tick marks indicate the location of the CF-NaNi$_{0.5}$Sn$_{1.5}$O$_4$ peaks, and the magenta tick marks indicate the location of SnO$_2$ peaks.
Figure S9 Rietveld refinement for NaCu$_{0.5}$Sn$_{1.5}$O$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, the red tick marks indicate the location of the CF-NaCu$_{0.5}$Sn$_{1.5}$O$_4$ peaks, and the magenta tick marks indicate the location of SnO$_2$ peaks.

Figure S10 Rietveld refinement for NaZn$_{0.5}$Sn$_{1.5}$O$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, and the red tick marks indicate the location of the CF-NaZn$_{0.5}$Sn$_{1.5}$O$_4$ peaks.
Figure S11 Rietveld refinement for “NaSc$_{1.5}$Sb$_{0.5}$O$_4$.” Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, the red tick marks indicate the location of the CF- NaSc$_{1.5}$Sb$_{0.5}$O$_4$ peaks, and the magenta tick marks indicate the location of Sc$_2$O$_3$ peaks.

Figure S12 Rietveld refinement for Na$_{1.16}$In$_{1.18}$Sb$_{0.66}$O$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, and the red tick marks indicate the location of the CF- Na$_{1.16}$In$_{1.18}$Sb$_{0.66}$O$_4$ peaks.
Figure S13 Rietveld refinement for NaFe$_{0.5}$Ti$_{1.5}$O$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, and the red tick marks indicate the location of the CF-NaFe$_{0.5}$Ti$_{1.5}$O$_4$ peaks.

Figure S14 Rietveld refinement for NaMn$_{0.5}$Sn$_{1.5}$O$_4$. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, and the red tick marks indicate the location of the CF-NaMn$_{0.5}$Sn$_{1.5}$O$_4$ peaks.
Figure S15 Rietveld refinement for NaFe\textsubscript{0.5}Sn\textsubscript{1.5}O\textsubscript{4}. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, the red tick marks indicate the location of the CF-NaFe\textsubscript{0.5}Sn\textsubscript{1.5}O\textsubscript{4} peaks, and the magenta tick marks indicate the location of SnO\textsubscript{2} peaks.

Figure S16 Rietveld refinement for NaCd\textsubscript{0.5}Sn\textsubscript{1.5}O\textsubscript{4}. Blue crosses are the observed intensities, the green curve is the fitted pattern, the black curve is the difference pattern, the red tick marks indicate the location of the CF-NaCd\textsubscript{0.5}Sn\textsubscript{1.5}O\textsubscript{4} peaks, and the magenta tick marks indicate the location of SnO\textsubscript{2} peaks.
Figure S17 $^{23}$Na Multiple-quantum MAS NMR spectrum of Na$_{1.16}$In$_{1.18}$Sb$_{0.66}$O$_4$ recorded with a z-filtered pulse sequence at 14 kHz MAS and 9.4 T. Cross sections, extracted parallel to $\delta_2$, are shown on the right. Distinct quadrupolar lineshape features are not visible for any of the sodium environments.
Table S2 Table of Na-O bond lengths for selected compounds

|                | Na$_{0.99}$Cr$_{0.99}$Ti$_{1.01}$O$_4$ | NaNi$_{0.5}$Sn$_{1.5}$O$_4$ | Na$_{0.96}$In$_{0.96}$Sn$_{1.04}$O$_4$ |
|----------------|-------------------------------------|----------------------------|-------------------------------------|
| Na1-O2 (×2)   | 2.378(1) Å                         | 2.444(2) Å                 | 2.472(2) Å                         |
| Na1-O4 (×2)   | 2.390(1) Å                         | 2.458(2) Å                 | 2.484(2) Å                         |
| Na1-O3        | 2.507(1) Å                         | 2.606(3) Å                 | 2.674(3) Å                         |
| Na1-O3        | 2.533(1) Å                         | 2.642(3) Å                 | 2.701(3) Å                         |
| Na1-O1 (×2)   | 2.568(1) Å                         | 2.644(2) Å                 | 2.728(3) Å                         |

Figure S18 $^{23}$Na Solid-state NMR of diamagnetic CF structures at 12.5 kHz MAS and 9.4 T.