# Supporting information

# Antimicrobial and cell friendly properties of cobalt and nickel-doped tricalcium phosphate ceramics

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Table S1. Main crystallographic and experimental data on $Ca_{10.5-x}Ni_x(PO_4)_7$ and $Ca_{10.5-x}Co_x(PO_4)_7$.

| Sample | TCP | 0.33Ni-TCP | 0.67Ni-TCP | 1.00Ni-TCP | 1.33Ni-TCP | 0.33Co-TCP | 0.50Co-TCP | 0.67Co-TCP | 1.00Co-TCP |
|---|---|---|---|---|---|---|---|---|---|
| Temperature, K | 293 | | | | | | | | |
| Crystal system, space group | Trigonal, *R*3*c* | | | | | | | | |
| Radiation type | Cu *K*α | | | | | | | | |
| Diffractometer | Rigaku SmartLab SE | | | | | | | | |
| *θ*-Range | 3.000- 80.000, step size (°) 0.02 | | | | | | | | |
| $R_p$ | 7.39 | 6.25 | 6.53 | 5.92 | 6.29 | 6.60 | 6.39 | 6.16 | 5.27 |
| $R_{wp}$ | 10.21 | 8.08 | 8.22 | 7.68 | 8.41 | 8.74 | 8.75 | 8.22 | 7.29 |
| $R_{Bragg}$ | 3.71 | 3.36 | 3.36 | 3.42 | 2.94 | 3.34 | 3.07 | 3.08 | 2.71 |
| Goodness of fit (ChiQ) | 2.75 | 2.40 | 2.45 | 2.24 | 2.86 | 2.62 | 2.85 | 2.67 | 2.69 |
| Max./min. residual density ($e\times Å^{-3}$) | 0.39/-0.29 | 0.52/-0.45 | 0.58/-0.64 | 1.76/-1.24 | 1.78/-1.35 | 0.59/-0.68 | 0.66/-1.17 | 0.58/-0.97 | 0.59/-1.17 |
| No. of parameters | 93 | 87 | 66 | 88 | 87 | 81 | 91 | 89 | 91 |

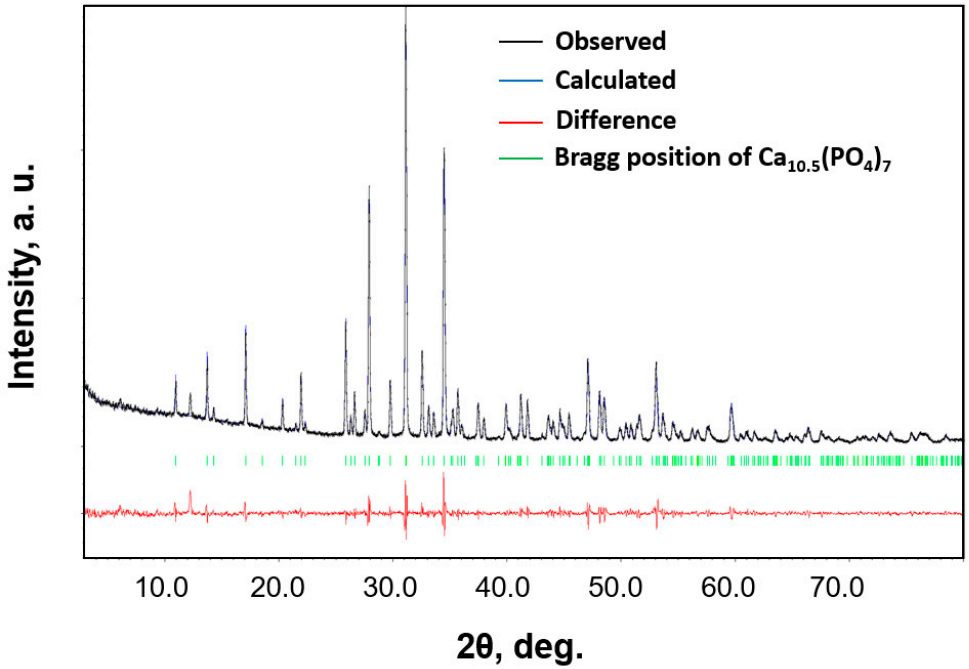


Figure S1 Intensity profiles for the powder X-ray Rietveld refinement of $Ca_{10.5}(PO_4)_7$. The observed and calculated profiles are represented in black and blue lines, respectively. The difference in the profile is plotted at the bottom (red line). Vertical bars indicate the positions of the Bragg reflections (green bars).

Table S2. Atomic coordinates, displacement parameters (Å$^2$) and site-occupancy factors (SOFs) in the structure of $Ca_{10.5}(PO_4)_7$.

| Atom | Wyckoff site | *x* | *y* | *z* | $U_{iso}$, Å$^2$ | SOF |
|---|---|---|---|---|---|---|
| M1 | 18b | 0.7241(9) | 0.8555(5) | 0.1670(6) | 0.0183(8) | $Ca_{1.0}$ |
| M2 | 18b | 0.6208(6) | 0.8196(8) | -0.0324(1) | 0.0171(1) | $Ca_{1.0}$ |
| M3 | 18b | 0.7279(3) | 0.8506(4) | 0.0617(1) | 0.0268(1) | $Ca_{1.0}$ |
| M4 | 6a | 0 | 0 | -0.0841(4) | 0.0960(1) | $Ca_{0.5}$ |
| M5 | 6a | 0 | 0 | 0.7354(1) | 0.0434(1) | $Ca_{1.0}$ |
| P1 | 6a | 0 | 0 | -0.0003(2) | 0.0185(7) | $P_{1.0}$ |
| P2 | 18b | 0.6889(4) | 0.8694(7) | 0.8700(4) | 0.0183(1) | $P_{1.0}$ |
| P3 | 18b | 0.6509(6) | 0.8400(6) | 0.7681(5) | 0.0208(1) | $P_{1.0}$ |
| O1 | 6a | 0.7305(3) | -0.0962(3) | -0.0952(6) | 0.0083 | $O_{1.0}$ |
| O2 | 6a | 0.7678(5) | 0.7860(9) | 0.8572(9) | 0.0083 | $O_{1.0}$ |
| O3 | 18b | 0.7278(4) | 0.0099(2) | 0.8441(7) | 0.0083 | $O_{1.0}$ |
| O4 | 18b | 0.5280(6) | 0.7512(5) | 0.8614(0) | 0.0083 | $O_{1.0}$ |
| O5 | 18b | 0.5975(0) | -0.0452(5) | 0.7793(6) | 0.0083 | $O_{1.0}$ |
| O6 | 6a | 0.5716(3) | 0.6867(5) | 0.7862(2) | 0.0083 | $O_{1.0}$ |
| O7 | 18b | 0.0778(3) | 0.8967(5) | 0.7767(5) | 0.0083 | $O_{1.0}$ |
| O8 | 18b | 0.6309(5) | 0.8307(0) | 0.7272(8) | 0.0083 | $O_{1.0}$ |
| O9 | 18b | 0.0055(7) | 0.8639(5) | -0.0208(7) | 0.0083 | $O_{1.0}$ |
| O10 | 18b | 0 | 0 | 0.0408(4) | 0.0083 | $O_{1.0}$ |

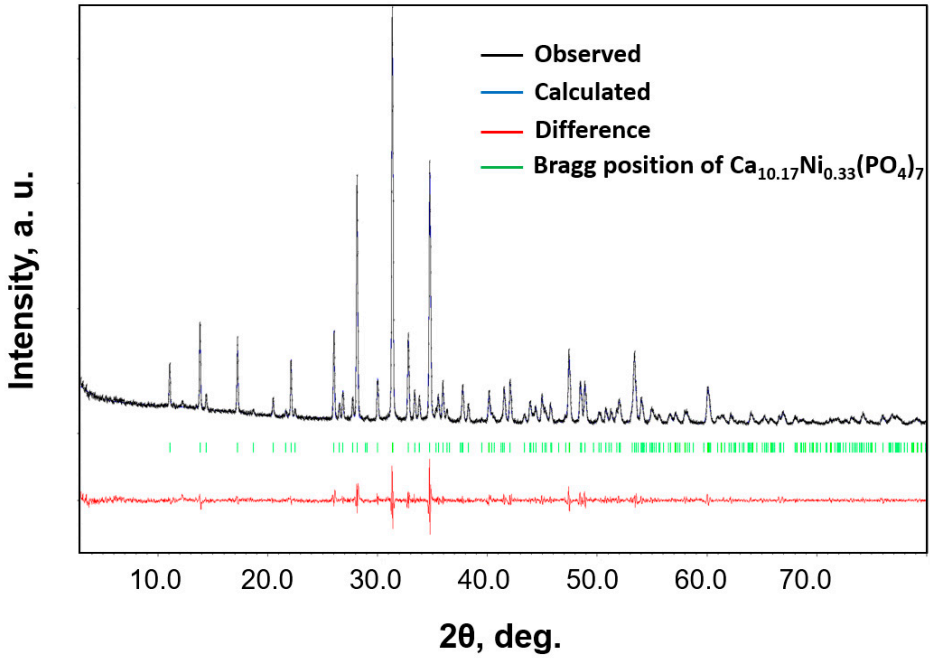


Figure S2. Intensity profiles for the powder X-ray Rietveld refinement of $Ca_{10.17}Ni_{0.33}(PO_4)_7$. The observed and calculated profiles are represented in black and blue lines, respectively. The difference in the profile is plotted at the bottom (red line). Vertical bars indicate the positions of the Bragg reflections (green bars).

Table S3. Atomic coordinates, displacement parameters (Å$^2$) and site-occupancy factors (SOFs) in the structure of $Ca_{10.17}Ni_{0.33}(PO_4)_7$.

| Atom | Wyckoff site | *x* | *y* | *z* | $U_{iso}$, Å$^2$ | SOF |
|---|---|---|---|---|---|---|
| M1 | 18b | 0.7240(9) | 0.8548(3) | 0.1681(4) | 0.0146(1) | $Ca_{1.0}$ |
| M2 | 18b | 0.6221(2) | 0.8211(5) | -0.0320(1) | 0.0316(1) | $Ca_{1.0}$ |
| M3 | 18b | 0.7261(4) | 0.8488(7) | 0.0619(1) | 0.0142(2) | $Ca_{1.0}$ |
| M4 | 6a | 0 | 0 | -0.0771(0) | 0.0056(7) | $Ca_{0.5}$ |
| M5 | 6a | 0 | 0 | 0.7381(7) | 0.0108(7) | $Ca_{0.67}$+$Ni_{0.33}$ |
| P1 | 6a | 0 | 0 | 0.0011(9) | 0.0172(9) | $P_{1.0}$ |
| P2 | 18b | 0.6911(9) | 0.8623(5) | 0.8704(4) | 0.0352(8) | $P_{1.0}$ |
| P3 | 18b | 0.6514(3) | 0.8486(2) | 0.7674(9) | 0.0133(1) | $P_{1.0}$ |
| O1 | 6a | 0.7418(9) | -0.0911(1) | -0.0940(7) | 0.0083 | $O_{1.0}$ |
| O2 | 6a | 0.7582(0) | 0.7658(2) | 0.8584(5) | 0.0083 | $O_{1.0}$ |
| O3 | 18b | 0.7416(0) | 0.0088(0) | 0.8466(9) | 0.0083 | $O_{1.0}$ |
| O4 | 18b | 0.5225(7) | 0.7585(9) | 0.8651(1) | 0.0083 | $O_{1.0}$ |
| O5 | 18b | 0.6105(9) | -0.0358(9) | 0.7835(7) | 0.0083 | $O_{1.0}$ |
| O6 | 6a | 0.5588(5) | 0.6993(7) | 0.7872(1) | 0.0083 | $O_{1.0}$ |
| O7 | 18b | 0.0763(2) | 0.8975(3) | 0.7742(8) | 0.0083 | $O_{1.0}$ |
| O8 | 18b | 0.6189(3) | 0.8116(8) | 0.7272(9) | 0.0083 | $O_{1.0}$ |
| O9 | 18b | 0.0013(4) | 0.8629(3) | -0.0188(3) | 0.0083 | $O_{1.0}$ |
| O10 | 18b | 0 | 0 | 0.0425(6) | 0.0083 | $O_{1.0}$ |

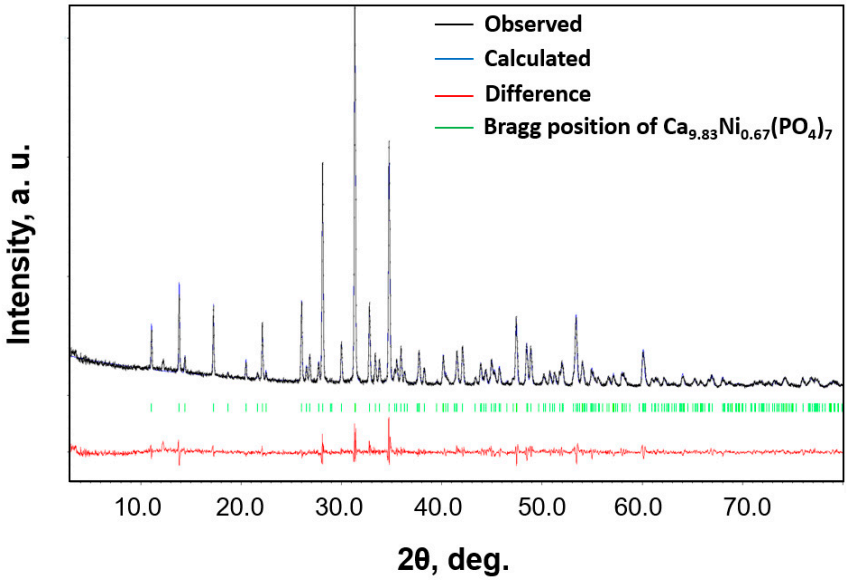


Figure S3. Intensity profiles for the powder X-ray Rietveld refinement of $Ca_{9.83}Ni_{0.67}(PO_4)_7$. The observed and calculated profiles are represented in black and blue lines, respectively. The difference in the profile is plotted at the bottom (red line). Vertical bars indicate the positions of the Bragg reflections (green bars).

Table S4. Atomic coordinates, displacement parameters (Å$^2$) and site-occupancy factors (SOFs) in the structure of $Ca_{9.83}Ni_{0.67}(PO_4)_7$.

| Atom | Wyckoff site | *x* | *y* | *z* | $U_{iso}$, Å$^2$ | SOF |
|---|---|---|---|---|---|---|
| M1 | 18b | 0.7255(7) | 0.8561(1) | 0.1674(4) | 0.0166(6) | $Ca_{1.0}$ |
| M2 | 18b | 0.6184(3) | 0.8175(7) | -0.0326(1) | 0.0226(8) | $Ca_{1.0}$ |
| M3 | 18b | 0.7257(3) | 0.8488(9) | 0.0615(1) | 0.0196(9) | $Ca_{1.0}$ |
| M4 | 6a | 0 | 0 | -0.0793(4) | 0.0851(0) | $Ca_{0.5}$ |
| M5 | 6a | 0 | 0 | 0.7361(5) | 0.0221(1) | $Ca_{0.33}$+$Ni_{0.67}$ |
| P1 | 6a | 0 | 0 | -0.0007(3) | 0.0328(9) | $P_{1.0}$ |
| P2 | 18b | 0.6900(0) | 0.8625(0) | 0.8705(2) | 0.0088(7) | $P_{1.0}$ |
| P3 | 18b | 0.6546(6) | 0.8500(4) | 0.7667(7) | 0.0083 | $P_{1.0}$ |
| O1 | 6a | 0.7389(5) | -0.0861(1) | -0.0936(4) | 0.0083 | $O_{1.0}$ |
| O2 | 6a | 0.7587(1) | 0.7674(5) | 0.8584(7) | 0.0083 | $O_{1.0}$ |
| O3 | 18b | 0.7314(5) | -0.0021(8) | 0.8453(9) | 0.0083 | $O_{1.0}$ |
| O4 | 18b | 0.5216(6) | 0.7531(1) | 0.8663(1) | 0.0083 | $O_{1.0}$ |
| O5 | 18b | 0.6018(2) | -0.0342(4) | 0.7825(2) | 0.0083 | $O_{1.0}$ |
| O6 | 6a | 0.5656(3) | 0.7005(5) | 0.7866(9) | 0.0083 | $O_{1.0}$ |
| O7 | 18b | 0.0729(9) | 0.8948(1) | 0.7757(3) | 0.0083 | $O_{1.0}$ |
| O8 | 18b | 0.6190(8) | 0.8135(1) | 0.7266(5) | 0.0083 | $O_{1.0}$ |
| O9 | 18b | -0.0016(1) | 0.8546(6) | -0.0145(3) | 0.0083 | $O_{1.0}$ |
| O10 | 18b | 0 | 0 | 0.0406(4) | 0.0083 | $O_{1.0}$ |

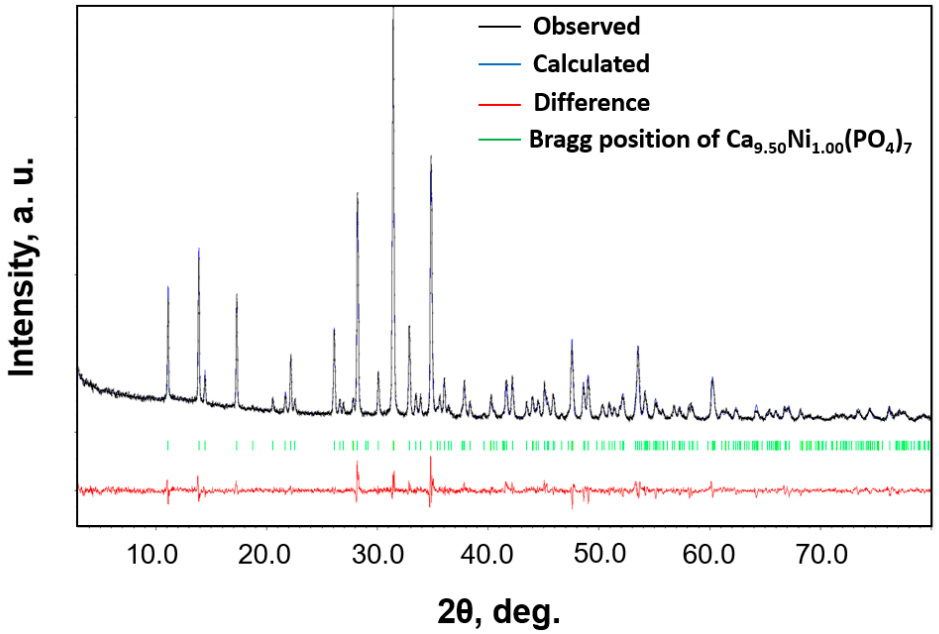


Figure S4. Intensity profiles for the powder X-ray Rietveld refinement of $Ca_{9.50}Ni_{1.00}(PO_4)_7$. The observed and calculated profiles are represented in black and blue lines, respectively. The difference in the profile is plotted at the bottom (red line). Vertical bars indicate the positions of the Bragg reflections (green bars).

Table S5. Atomic coordinates, displacement parameters (Å$^2$) and site-occupancy factors (SOFs) in the structure of $Ca_{9.50}Ni_{1.00}(PO_4)_7$.

| Atom | Wyckoff site | *x* | *y* | *z* | $U_{iso}$, Å$^2$ | SOF |
|---|---|---|---|---|---|---|
| M1 | 18b | 0.7167(9) | 0.8453(3) | 0.1688(0) | 0.0113(7) | $Ca_{1.0}$ |
| M2 | 18b | 0.6273(0) | 0.8233(0) | -0.0338(9) | 0.0213(3) | $Ca_{1.0}$ |
| M3 | 18b | 0.7225(3) | 0.8523(8) | 0.0608(2) | 0.0253(9) | $Ca_{1.0}$ |
| M4 | 6a | 0 | 0 | -0.0828(7) | 0.0228(8) | $Ca_{0.5}$ |
| M5 | 6a | 0 | 0 | 0.7329(3) | 0.0244(6) | $Ni_{1.00}$ |
| P1 | 6a | 0 | 0 | 0.0029(2) | 0.0155(3) | $P_{1.0}$ |
| P2 | 18b | 0.6766(8) | 0.8548(5) | 0.8690(4) | 0.0009(1) | $P_{1.0}$ |
| P3 | 18b | 0.6338(9) | 0.8288(1) | 0.7649(8) | 0.0083 | $P_{1.0}$ |
| O1 | 6a | 0.7450(1) | -0.0884(9) | -0.0893(4) | 0.0083 | $O_{1.0}$ |
| O2 | 6a | 0.7722(2) | 0.8148(5) | 0.8515(8) | 0.0083 | $O_{1.0}$ |
| O3 | 18b | 0.7206(0) | -0.0081(6) | 0.8453(1) | 0.0083 | $O_{1.0}$ |
| O4 | 18b | 0.5141(2) | 0.7461(4) | 0.8683(5) | 0.0083 | $O_{1.0}$ |
| O5 | 18b | 0.6162(9) | -0.0359(5) | 0.7738(1) | 0.0083 | $O_{1.0}$ |
| O6 | 6a | 0.5875(5) | 0.6779(0) | 0.7834(8) | 0.0083 | $O_{1.0}$ |
| O7 | 18b | 0.0753(8) | 0.8900(5) | 0.7729(7) | 0.0083 | $O_{1.0}$ |
| O8 | 18b | 0.6208(1) | 0.8206(9) | 0.7266(8) | 0.0083 | $O_{1.0}$ |
| O9 | 18b | -0.0090(2) | 0.8730(6) | -0.0256(7) | 0.0083 | $O_{1.0}$ |
| O10 | 18b | 0 | 0 | 0.0433(7) | 0.0083 | $O_{1.0}$ |

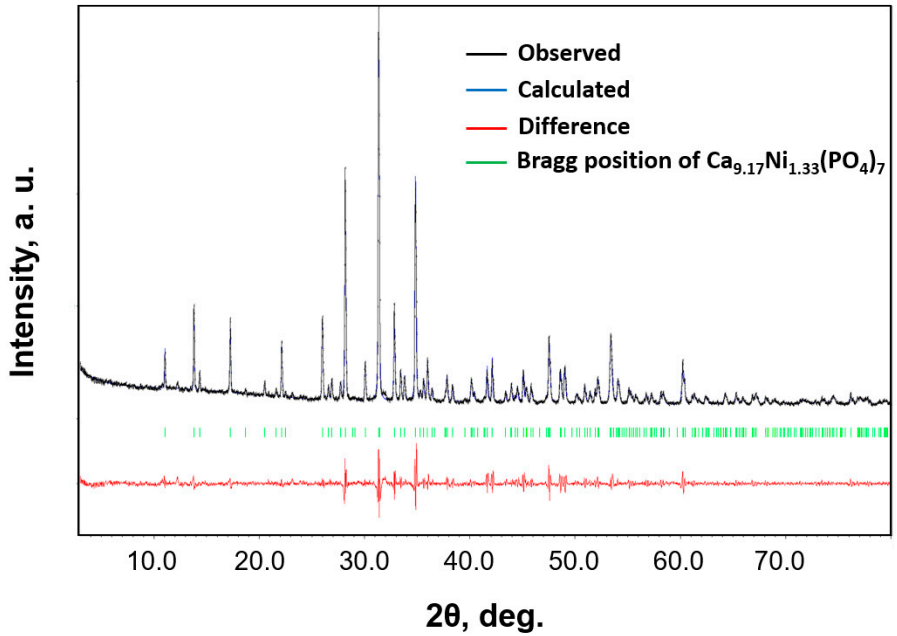


Figure S5. Intensity profiles for the powder X-ray Rietveld refinement of $Ca_{9.17}Ni_{1.33}(PO_4)_7$. The observed and calculated profiles are represented in black and blue lines, respectively. The difference in the profile is plotted at the bottom (red line). Vertical bars indicate the positions of the Bragg reflections (green bars).

Table S6. Atomic coordinates, displacement parameters (Å$^2$) and site-occupancy factors (SOFs) in the structure of $Ca_{9.17}Ni_{1.33}(PO_4)_7$.

| Atom | Wyckoff site | *x* | *y* | *z* | $U_{iso}$, Å$^2$ | SOF |
|---|---|---|---|---|---|---|
| M1 | 18b | 0.7119(9) | 0.8606(2) | 0.1712(1) | 0.0247(2) | Ca+Ni |
| M2 | 18b | 0.6127(1) | 0.8224(5) | -0.0309(9) | 0.0167(5) | $Ca_{1.0}$ |
| M3 | 18b | 0.7237(6) | 0.8459(8) | 0.0635(7) | 0.0270(3) | Ca+Ni |
| M4 | 6a | 0 | 0 | -0.0779(3) | 0.0307(6) | $Ca_{0.5}$ |
| M5 | 6a | 0 | 0 | 0.7392(8) | 0.0144(1) | $Ni_{1.00}$ |
| P1 | 6a | 0 | 0 | 0.0002(3) | 0.0615(1) | $P_{1.0}$ |
| P2 | 18b | 0.6847(0) | 0.8546(5) | 0.8707(6) | 0.0164(5) | $P_{1.0}$ |
| P3 | 18b | 0.6561(7) | 0.8621(4) | 0.7681(6) | 0.0833(9) | $P_{1.0}$ |
| O1 | 6a | 0.7886(5) | -0.0415(6) | -0.0843(5) | 0.0083 | $O_{1.0}$ |
| O2 | 6a | 0.7475(3) | 0.7576(8) | 0.8558(8) | 0.0083 | $O_{1.0}$ |
| O3 | 18b | 0.7408(8) | -0.0314(5) | 0.8518(4) | 0.0083 | $O_{1.0}$ |
| O4 | 18b | 0.5136(9) | 0.7881(6) | 0.8720(1) | 0.0083 | $O_{1.0}$ |
| O5 | 18b | 0.6078(4) | -0.0241(5) | 0.7695(5) | 0.0083 | $O_{1.0}$ |
| O6 | 6a | 0.5613(4) | 0.7048(1) | 0.7847(1) | 0.0083 | $O_{1.0}$ |
| O7 | 18b | 0.0673(2) | 0.8837(4) | 0.7818(6) | 0.0083 | $O_{1.0}$ |
| O8 | 18b | 0.6205(9) | 0.8223(0) | 0.7277(0) | 0.0083 | $O_{1.0}$ |
| O9 | 18b | -0.0255(1) | 0.9040(2) | -0.0287(5) | 0.0083 | $O_{1.0}$ |
| O10 | 18b | 0 | 0 | 0.0416(9) | 0.0083 | $O_{1.0}$ |

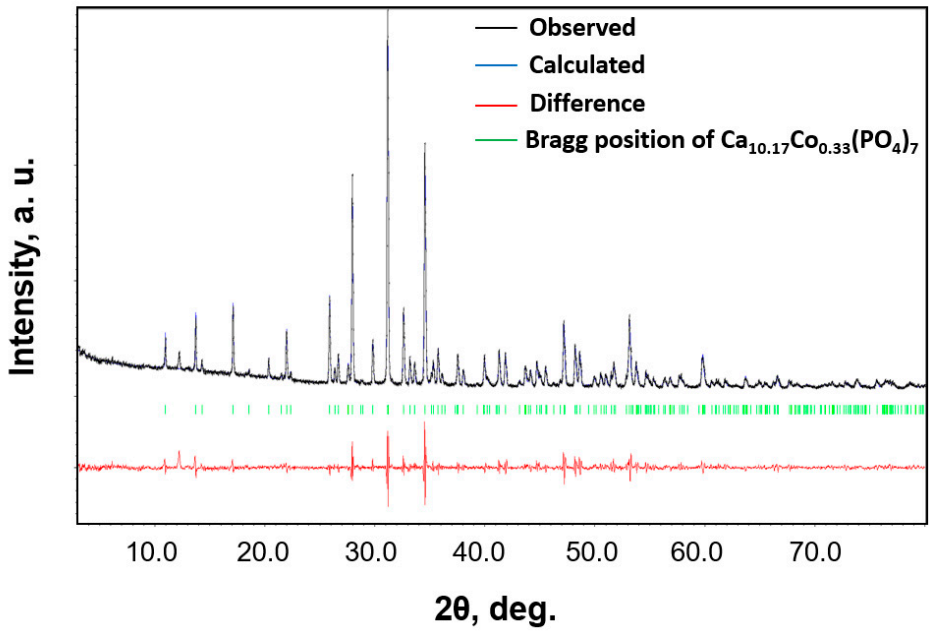


Figure S6. Intensity profiles for the powder X-ray Rietveld refinement of $Ca_{10.17}Co_{0.33}(PO_4)_7$. The observed and calculated profiles are represented in black and blue lines, respectively. The difference in the profile is plotted at the bottom (red line). Vertical bars indicate the positions of the Bragg reflections (green bars).

Table S7. Atomic coordinates, displacement parameters (Å$^2$) and site-occupancy factors (SOFs) in the structure of $Ca_{10.17}Co_{0.33}(PO_4)_7$.

| Atom | Wyckoff site | *x* | *y* | *z* | $U_{iso}$, Å$^2$ | SOF |
|---|---|---|---|---|---|---|
| M1 | 18b | 0.7292(3) | 0.8573(9) | 0.1684(8) | 0.0280(1) | $Ca_{1.0}$ |
| M2 | 18b | 0.6216(8) | 0.8251(7) | -0.0318(8) | 0.0091(1) | $Ca_{1.0}$ |
| M3 | 18b | 0.7259(6) | 0.8571(0) | 0.0624(7) | 0.0596(2) | $Ca_{1.0}$ |
| M4 | 6a | 0 | 0 | -0.0805(9) | 0.0415(6) | $Ca_{0.5}$ |
| M5 | 6a | 0 | 0 | 0.7374(2) | 0.0387(1) | $Ca_{0.67}$+$Co_{0.33}$ |
| P1 | 6a | 0 | 0 | -0.0039(4) | 0.0563(0) | $P_{1.0}$ |
| P2 | 18b | 0.6978(5) | 0.8673(2) | 0.8701(0) | 0.0437(5) | $P_{1.0}$ |
| P3 | 18b | 0.6587(6) | 0.8479(7) | 0.7664(6) | 0.0063(8) | $P_{1.0}$ |
| O1 | 6a | 0.7203(6) | -0.0952(4) | -0.0859(6) | 0.0083(0) | $O_{1.0}$ |
| O2 | 6a | 0.7694(8) | 0.7726(0) | 0.8609(6) | 0.0083(0) | $O_{1.0}$ |
| O3 | 18b | 0.7375(0) | 0.0079(3) | 0.8514(4) | 0.0083(0) | $O_{1.0}$ |
| O4 | 18b | 0.5275(3) | 0.7725(4) | 0.8669(2) | 0.0083(0) | $O_{1.0}$ |
| O5 | 18b | 0.5975(7) | -0.0438(6) | 0.7852(1) | 0.0083(0) | $O_{1.0}$ |
| O6 | 6a | 0.5759(6) | 0.7216(1) | 0.7901(8) | 0.0083(0) | $O_{1.0}$ |
| O7 | 18b | 0.0826(5) | 0.9060(1) | 0.7788(2) | 0.0083(0) | $O_{1.0}$ |
| O8 | 18b | 0.6091(1) | 0.7985(2) | 0.7330(1) | 0.0083(0) | $O_{1.0}$ |
| O9 | 18b | -0.0140(6) | 0.8438(0) | -0.0216(9) | 0.0083(0) | $O_{1.0}$ |
| O10 | 18b | 0 | 0 | 0.0373(1) | 0.0083(0) | $O_{1.0}$ |

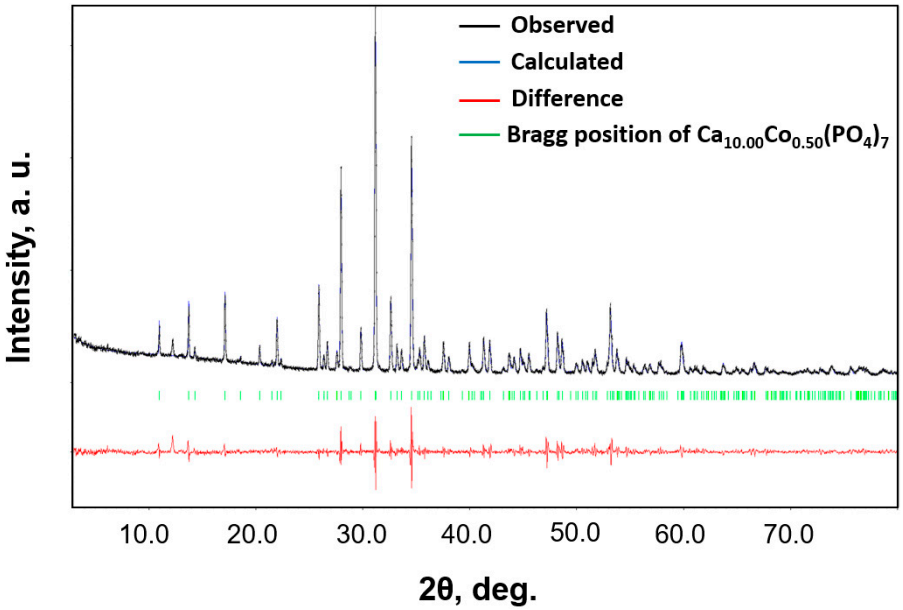


Figure S7. Intensity profiles for the powder X-ray Rietveld refinement of $Ca_{10.00}Co_{0.50}(PO_4)_7$. The observed and calculated profiles are represented in black and blue lines, respectively. The difference in the profile is plotted at the bottom (red line). Vertical bars indicate the positions of the Bragg reflections (green bars).

Table S8. Atomic coordinates, displacement parameters (Å$^2$) and site-occupancy factors (SOFs) in the structure of $Ca_{10.00}Co_{0.50}(PO_4)_7$.

| Atom | Wyckoff site | *x* | *y* | *z* | $U_{iso}$, Å$^2$ | SOF |
|---|---|---|---|---|---|---|
| M1 | 18b | 0.7219(7) | 0.8550(9) | 0.1666(3) | 0.0568(7) | $Ca_{1.0}$ |
| M2 | 18b | 0.6153(9) | 0.8194(9) | -0.0335(1) | 0.0087(3) | $Ca_{1.0}$ |
| M3 | 18b | 0.7272(1) | 0.8519(7) | 0.0611(7) | 0.0489(9) | $Ca_{1.0}$ |
| M4 | 6a | 0 | 0 | -0.0796(3) | 0.0111(5) | $Ca_{0.5}$ |
| M5 | 6a | 0 | 0 | 0.7367(4) | 0.0212(9) | $Ca_{0.50}$+$Co_{0.50}$ |
| P1 | 6a | 0 | 0 | -0.0001(7) | 0.0121(1) | $P_{1.0}$ |
| P2 | 18b | 0.6959(4) | 0.8627(1) | 0.8693(9) | 0.0459(2) | $P_{1.0}$ |
| P3 | 18b | 0.6575(8) | 0.8515(2) | 0.7673(7) | 0.0059(1) | $P_{1.0}$ |
| O1 | 6a | 0.7288(4) | -0.0916(6) | -0.0930(1) | 0.0083 | $O_{1.0}$ |
| O2 | 6a | 0.7629(5) | 0.7657(9) | 0.8580(2) | 0.0083 | $O_{1.0}$ |
| O3 | 18b | 0.7417(9) | 0.0084(8) | 0.8467(6) | 0.0083 | $O_{1.0}$ |
| O4 | 18b | 0.5262(1) | 0.7653(1) | 0.8647(2) | 0.0083 | $O_{1.0}$ |
| O5 | 18b | 0.6158(3) | -0.0394(3) | 0.7834(8) | 0.0083 | $O_{1.0}$ |
| O6 | 6a | 0.5657(1) | 0.6991(8) | 0.7857(7) | 0.0083 | $O_{1.0}$ |
| O7 | 18b | 0.0750(3) | 0.8958(6) | 0.7764(3) | 0.0083 | $O_{1.0}$ |
| O8 | 18b | 0.6221(1) | 0.8162(5) | 0.7272(3) | 0.0083 | $O_{1.0}$ |
| O9 | 18b | -0.0049(3) | 0.8598(3) | -0.0195(5) | 0.0083 | $O_{1.0}$ |
| O10 | 18b | 0 | 0 | 0.0411(6) | 0.0083 | $O_{1.0}$ |

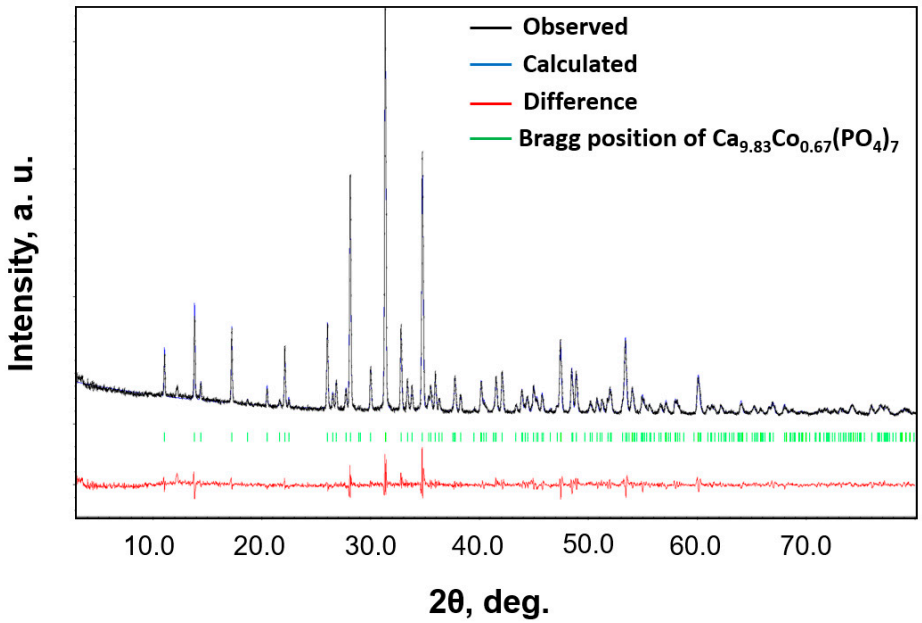


Figure S8. Intensity profiles for the powder X-ray Rietveld refinement of $Ca_{9.83}Co_{0.67}(PO_4)_7$. The observed and calculated profiles are represented in black and blue lines, respectively. The difference in the profile is plotted at the bottom (red line). Vertical bars indicate the positions of the Bragg reflections (green bars).

Table S9. Atomic coordinates, displacement parameters (Å$^2$) and site-occupancy factors (SOFs) in the structure of $Ca_{9.83}Co_{0.67}(PO_4)_7$.

| Atom | Wyckoff site | *x* | *y* | *z* | $U_{iso}$, Å$^2$ | SOF |
|---|---|---|---|---|---|---|
| M1 | 18b | 0.7262(5) | 0.8556(8) | 0.1670(8) | 0.0509(1) | $Ca_{1.0}$ |
| M2 | 18b | 0.6182(8) | 0.8201(9) | -0.0330(0) | 0.0028(0) | $Ca_{1.0}$ |
| M3 | 18b | 0.7255(5) | 0.8539(1) | 0.0607(4) | 0.0481(5) | $Ca_{1.0}$ |
| M4 | 6a | 0 | 0 | -0.0798(7) | 0.0107(9) | $Ca_{0.5}$ |
| M5 | 6a | 0 | 0 | 0.7371(2) | 0.0196(3) | $Ca_{0.33}$+$Co_{0.67}$ |
| P1 | 6a | 0 | 0 | 0.0010(1) | 0.0104(5) | $P_{1.0}$ |
| P2 | 18b | 0.6971(5) | 0.8681(6) | 0.8701(9) | 0.0290(3) | $P_{1.0}$ |
| P3 | 18b | 0.6599(4) | 0.8513(3) | 0.7669(9) | 0.0015(5) | $P_{1.0}$ |
| O1 | 6a | 0.7238(4) | -0.0918(7) | -0.0897(1) | 0.0083 | $O_{1.0}$ |
| O2 | 6a | 0.7670(8) | 0.7751(4) | 0.8577(5) | 0.0083 | $O_{1.0}$ |
| O3 | 18b | 0.7306(4) | 0.0056(3) | 0.8479(4) | 0.0083 | $O_{1.0}$ |
| O4 | 18b | 0.5289(1) | 0.7667(5) | 0.8638(0) | 0.0083 | $O_{1.0}$ |
| O5 | 18b | 0.6088(6) | -0.0409(6) | 0.7823(7) | 0.0083 | $O_{1.0}$ |
| O6 | 6a | 0.5751(3) | 0.7038(5) | 0.7878(3) | 0.0083 | $O_{1.0}$ |
| O7 | 18b | 0.0788(1) | 0.9048(1) | 0.7762(7) | 0.0083 | $O_{1.0}$ |
| O8 | 18b | 0.6159(9) | 0.8148(2) | 0.7272(4) | 0.0083 | $O_{1.0}$ |
| O9 | 18b | -0.0105(7) | 0.8541(5) | -0.0217(7) | 0.0083 | $O_{1.0}$ |
| O10 | 18b | 0 | 0 | 0.0423(7) | 0.0083 | $O_{1.0}$ |

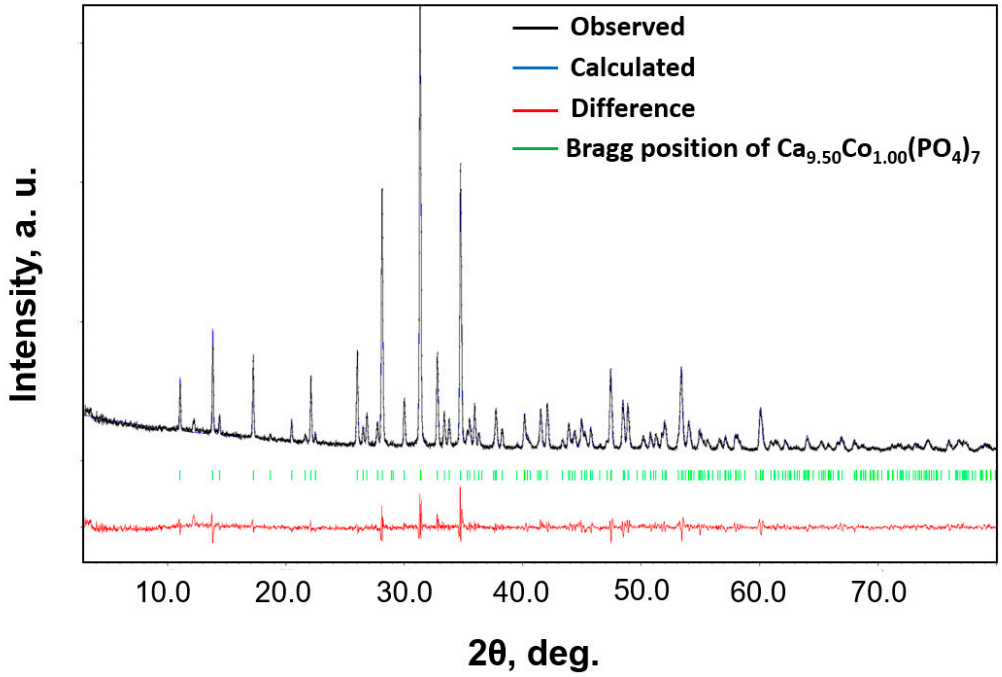


Figure S9. Intensity profiles for the powder X-ray Rietveld refinement of $Ca_{9.50}Co_{1.00}(PO_4)_7$. The observed and calculated profiles are represented in black and blue lines, respectively. The difference in the profile is plotted at the bottom (red line). Vertical bars indicate the positions of the Bragg reflections (green bars).

Table S10. Atomic coordinates, displacement parameters (Å$^2$) and site-occupancy factors (SOFs) in the structure of $Ca_{9.50}Co_{1.00}(PO_4)_7$.

| Atom | Wyckoff site | *x* | *y* | *z* | $U_{iso}$, Å$^2$ | SOF |
|---|---|---|---|---|---|---|
| M1 | 18b | 0.7293(5) | 0.8580(6) | 0.1681(8) | 0.0413(4) | $Ca_{1.0}$ |
| M2 | 18b | 0.6197(9) | 0.8219(7) | -0.0324(6) | 0.0066(3) | $Ca_{1.0}$ |
| M3 | 18b | 0.7273(6) | 0.8553(1) | 0.0620(9) | 0.0486(8) | $Ca_{1.0}$ |
| M4 | 6a | 0 | 0 | -0.0766(2) | 0.0716(4) | $Ca_{0.5}$ |
| M5 | 6a | 0 | 0 | 0.7387(7) | 0.0186(6) | $Co_{1.00}$ |
| P1 | 6a | 0 | 0 | 0.0012(1) | 0.0213(8) | $P_{1.0}$ |
| P2 | 18b | 0.6992(3) | 0.8624(7) | 0.8720(4) | 0.0507(1) | $P_{1.0}$ |
| P3 | 18b | 0.6586(0) | 0.8525(0) | 0.7676(8) | 0.0095(6) | $P_{1.0}$ |
| O1 | 6a | 0.7267(3) | -0.0867(3) | -0.0887(5) | 0.0083 | $O_{1.0}$ |
| O2 | 6a | 0.7675(1) | 0.7677(6) | 0.8593(3) | 0.0083 | $O_{1.0}$ |
| O3 | 18b | 0.7407(9) | 0.0027(2) | 0.8488(7) | 0.0083 | $O_{1.0}$ |
| O4 | 18b | 0.5288(2) | 0.7804(6) | 0.8664(6) | 0.0083 | $O_{1.0}$ |
| O5 | 18b | 0.6143(6) | -0.0364(2) | 0.7835(5) | 0.0083 | $O_{1.0}$ |
| O6 | 6a | 0.5701(3) | 0.7083(7) | 0.7898(4) | 0.0083 | $O_{1.0}$ |
| O7 | 18b | 0.0770(3) | 0.9076(8) | 0.7749(6) | 0.0083 | $O_{1.0}$ |
| O8 | 18b | 0.6109(8) | 0.8016(4) | 0.7285(5) | 0.0083 | $O_{1.0}$ |
| O9 | 18b | -0.0130(0) | 0.8502(6) | -0.0200(9) | 0.0083 | $O_{1.0}$ |
| O10 | 18b | 0 | 0 | 0.0426(8) | 0.0083 | $O_{1.0}$ |