**SUPPORTING INFORMATION**

# Structure - property relationships in α-, β′- and γ-modifications of $Mn_3(PO_4)_2$

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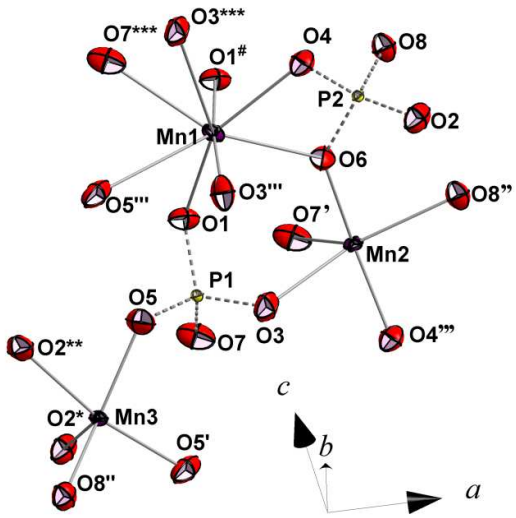


Figure S1. Basic structural units with atom labeling scheme. Displacement ellipsoids are presented at the 90% probability level. Symmetry codes: (') x, 0.5–y, z; (") x, –0.5+y, 0.5–z; ("') x, 0.5–y, 0.5+z; (*) –1+x, y, –1+z; (**) –1+x, 0.5–y, –0.5+z; (***) x, y, 1+z; (’) –x, 1–y, –z; (’’) 1–x, 1–y, 1–z; (’’’) x, y, –1+z; (#) –x, 1–y, 1–z.

**Table S1.** Atomic coordinates and equivalent isotropic displacement factors

| Atom | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Mn1 | 0.05946(5) | 0.38328(3) | 0.65290(7) | 0.01341(11) |
| Mn2 | 0.27859(5) | 0.42414(4) | 0.16837(6) | 0.01225(11) |
| Mn3 | -0.36141(5) | 0.19331(3) | -0.12618(6) | 0.00983(11) |
| P1 | -0.08718(7) | 0.36169(6) | 0.11111(10) | 0.00656(13) |
| P2 | 0.39467(8) | 0.41261(6) | 0.69253(10) | 0.00643(13) |
| O1 | -0.0726(2) | 0.43197(16) | 0.3233(3) | 0.0109(4) |
| O2 | 0.5211(2) | 0.32356(16) | 0.6678(3) | 0.0116(4) |
| O3 | 0.0649(2) | 0.29824(16) | 0.0975(3) | 0.0128(4) |
| O4 | 0.3022(2) | 0.37199(16) | 0.8673(3) | 0.0113(4) |
| O5 | -0.2141(2) | 0.27030(17) | 0.1250(3) | 0.0134(4) |
| O6 | 0.2735(2) | 0.41707(16) | 0.4873(3 | 0.0115(4) |
| O7 | -0.1294(2) | 0.43494(16 | -0.0940(3) | 0.0136(4) |
| O8 | 0.4668(2) | 0.53439(15) | 0.7442(3) | 0.0107(4) |

**Table S2.** Selected bond distances (Å)

| Atom | Bond | Atom | Bond |
|---|---|---|---|
| $Mn1O_{6+2}$ | | | |
| Mn1–O3 | 2.108(2) | Mn1–O6 | 2.319(2) |
| Mn1–O1 | 2.122(2) | Mn1–O4 | 2.342(2) |
| Mn1–O1 | 2.271(2) | Mn1–O7 | 2.537(2) |
| Mn1–O3 | 2.938(2) | Mn1–O2 | 2.964(2) |
| average 2.232; 2.450 | | | |
| $Mn2O_5$ | | | |
| Mn2–O6 | 2.002(2) | Mn2–O8 | 2.272(2) |
| Mn2–O4 | 2.016(2) | Mn2–O3 | 2.355(2) |
| Mn2–O7 | 2.086(2) | | |

| | | | |
|---|---|---|---|
| average 2.146 | | | |
| $Mn3O_5$ | | | |
| Mn3–O5 | 2.071(2) | Mn3–O5 | 2.214(2) |
| Mn3–O8 | 2.121(2) | Mn3–O2 | 2.253(2) |
| Mn3–O2 | 2.130(2) | | |
| average 2.158 | | | |
| $P1O_4$ | | $P2O_{1+4}$ | |
| P1–O7 | 1.529(2) | P2–O4 | 1.533(2) |
| P1–O3 | 1.537(2) | P2–O2 | 1.534(2) |
| P1–O1 | 1.539(2) | P2–O6 | 1.536(2) |
| P1–O5 | 1.543(2) | P2–O8 | 1.545(2) |
| average 1.537 | | average 1.537 | |

**Table S3.** Local bond valences in the α-$Mn_3(PO_4)_2$ crystal structure

| | Mn1 | Mn2 | Mn3 | P1 | P2 | Σ |
|---|---|---|---|---|---|---|
| O1 | 0.408;0.272 | | | 1.233 | | 1.913 |
| O2 | | | 0.399; 0.286 | | 1.250 | 1.935 |
| O3 | 0.423; 0.045 | 0.217 | | 1.241 | | 1.926 |
| O4 | 0.225 | 0.544 | | | 1.256 | 2.025 |
| O5 | 0.042 | | 0.468; 0.318 | 1.223 | | 2.051 |
| O6 | 0.240 | 0.563 | | | 1.244 | 2.047 |
| O7 | 0.133 | 0.449 | | 1.270 | | 1.852 |
| O8 | | 0.272 | 0.409 | | 1.216 | 1.897 |
| Σ | 1.788 | 2.045 | 1.880 | 4.967 | 4.966 | |