Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


**Supplementary**

Tables summarizing the main characteristics distances of FCNO versus temperature. Rietveld calculations were made using the SXRPD data; from 70K down to 50K the structure is refined in the trigonal space group and in the monoclinic one for 25 and 12K.

**Table S.I:** Dependence versus temperature (K) of the average $M_A$-O distance (Å), volume of the $M_AO_6$ octahedra (Å$^3$) and $M_A$-O distances (Å)

| T | <$M_A$-O> | V- $M_AO_6$ | $M_A$-O2 | $M_A$-O2 | $M_A$-O2 | $M_A$-O2 | $M_A$-O2 | $M_A$-O2 |
|---|---|---|---|---|---|---|---|---|
| 70 | 2.1291 | 12.7012 | 2.06(1) | 2.06(1) | 2.06(1) | 2.194(8) | 2.194(8) | 2.194(8) |
| 65 | 2.1227 | 12.6016 | 2.05(1) | 2.05(1) | 2.05(1) | 2.199(8) | 2.199(8) | 2.199(8) |
| 60 | 2.1257 | 12.6518 | 2.05(1) | 2.05(1) | 2.05(1) | 2.199(8) | 2.199(8) | 2.199(8) |
| 55 | 2.1242 | 12.6245 | 2.06(1) | 2.06(1) | 2.06(1) | 2.193(7) | 2.193(7) | 2.193(7) |
| 50 | 2.1257 | 12.6412 | 2.06(1) | 2.06(1) | 2.06(1) | 2.193(8) | 2.193(8) | 2.193(8) |
| 25 | 2.1246 | 12.5869 | 2.19(3) | 2.11(3) | 2.23(3) | 2.11(3) | 2.08(3) | 2.03(3) |
| 12 | 2.1216 | 12.5292 | 2.18(3) | 2.12(3) | 2.22(3) | 2.09(3) | 2.08(3) | 2.05(3) |

**Table S.II:** Dependence versus temperature (K) of the average $M_B$-O distance (Å), volume of the $M_BO_6$ octahedra (Å$^3$) and $M_B$-O distances (Å)

| T | <$M_B$-O> | V- $M_BO_6$ | $M_B$-O1 | $M_B$-O1 | $M_B$-O1 | $M_B$-O2 | $M_B$-O2 | $M_B$-O2 |
|---|---|---|---|---|---|---|---|---|
| 70 | 2.1522 | 12.6343 | 2.045(6) | 2.045(6) | 2.045(6) | 2.259(7) | 2.259(7) | 2.259(7) |
| 65 | 2.1609 | 12.7853 | 2.047(6) | 2.047(6) | 2.047(6) | 2.275(7) | 2.275(7) | 2.275(7) |
| 60 | 2.1603 | 12.7689 | 2.049(6) | 2.049(6) | 2.049(6) | 2.271(7) | 2.271(7) | 2.271(7) |
| 55 | 2.157 | 12.7225 | 2.044(6) | 2.044(6) | 2.044(6) | 2.270(7) | 2.270(7) | 2.270(7) |
| 50 | 2.1549 | 12.6814 | 2.041(6) | 2.041(6) | 2.041(6) | 2.268(7) | 2.268(7) | 2.268(7) |
| 25 | 2.1585 | 12.6852 | 2.02(3) | 2.00(3) | 2.11(3) | 2.36(3) | 2.22(3) | 2.25(3) |
| 12 | 2.1534 | 12.6093 | 2.04(3) | 1.96(2) | 2.11(3) | 2.34(3) | 2.20(3) | 2.27(3) |

**Table S.III:** Dependence versus temperature (K) of the average Nb-O distance (Å), volume of the $NbO_6$ octahedra (Å$^3$) and Nb-O distances (Å)

| T | <Nb-O> | V- $NbO_6$ | Nb-O1 | Nb-O1 | Nb-O1 | Nb-O2 | Nb-O2 | Nb-O2 |
|---|---|---|---|---|---|---|---|---|
| 70 | 2.0061 | 10.2031 | 2.113(7) | 2.113(7) | 2.113(7) | 1.899(6) | 1.899(6) | 1.899(6) |
| 65 | 2.0069 | 10.2221 | 2.107(7) | 2.107(7) | 2.107(7) | 1.907(6) | 1.907(6) | 1.907(6) |
| 60 | 2.0038 | 10.1648 | 2.105(7) | 2.105(7) | 2.105(7) | 1.903(6) | 1.903(6) | 1.903(6) |
| 55 | 2.0076 | 10.2417 | 2.113(7) | 2.113(7) | 2.113(7) | 1.903(6) | 1.903(6) | 1.903(6) |
| 50 | 2.0077 | 10.2533 | 2.114(7) | 2.114(7) | 2.114(7) | 1.901(6) | 1.901(6) | 1.901(6) |
| 25 | 2.0075 | 10.2376 | 2.07(4) | 2.14(3) | 2.14(4) | 1.95(3) | 1.83(3) | 1.92(2) |
| 12 | 2.0138 | 10.365 | 2.07(4) | 2.12(4) | 2.19(3) | 1.92(3) | 1.87(3) | 1.92(2) |

**Table S.IV:** Dependence versus temperature (K) of selected cation-cation distances (Å)

| T | $M_A$-$M_A$ | $M_A$-$M_A$ | $M_A$-$M_A$ | $M_B$-$M_B$ | $M_B$-$M_B$ | $M_B$-$M_B$ | $M_A$-$M_B$ |
|---|---|---|---|---|---|---|---|
| 70 | 3.0235(8) | 3.0235(8) | 3.0235(8) | 3.405(2) | 3.405(2) | 3.405(2) | 2.926(5) |
| 65 | 3.0235(8) | 3.0235(8) | 3.0235(8) | 3.401(2) | 3.401(2) | 3.401(2) | 2.929(5) |
| 60 | 3.0235(8) | 3.0235(8) | 3.0235(8) | 3.401(2) | 3.401(2) | 3.401(2) | 2.929(5) |
| 55 | 3.0228(8) | 3.0228(8) | 3.0228(8) | 3.404(2) | 3.404(2) | 3.404(2) | 2.923(5) |
| 50 | 3.0238(8) | 3.0238(8) | 3.0238(8) | 3.403(2) | 3.403(2) | 3.403(2) | 2.928(5) |
| 25 | 2.98(2) | 3.10(1) | 2.99(1) | 3.30(2) | 3.45(1) | | 2.928(4) |
| 12 | 3.00(2) | 3.08(1) | 3.00(1) | 3.30(1) | 3.45(1) | | 2.930(4) |
| | | | | | | | |
| T | Nb-Nb | Nb-$M_B$ | Nb-$M_B$ | Nb-$M_B$ | Nb-$M_A$ | Nb-$M_A$ | Nb-$M_A$ |
| 70 | 3.053(3) | 3.0838(8) | 3.0838(8) | 3.0838(8) | 3.507(2) | 3.507(2) | 3.507(2) |
| 65 | 3.046(3) | 3.0839(8) | 3.0839(8) | 3.0839(8) | 3.508(2) | 3.508(2) | 3.508(2) |
| 60 | 3.048(3) | 3.0842(8) | 3.0842(8) | 3.0842(8) | 3.508(2) | 3.508(2) | 3.508(2) |
| 55 | 3.048(3) | 3.0836(8) | 3.0836(8) | 3.0836(8) | 3.509(2) | 3.509(2) | 3.509(2) |
| 50 | 3.044(3) | 3.0833(8) | 3.0833(8) | 3.0833(8) | 3.508(2) | 3.508(2) | 3.508(2) |
| 25 | 3.048(3) | 3.08(1) | 3.04(1) | 3.14(1) | 3.546(9) | 3.454(9) | 3.53(1) |
| 12 | 3.047(2) | 3.08(1) | 3.05(1) | 3.13(1) | 3.54(1) | 3.46(1) | 3.53(1) |