# Supporting Information

# Structures of Mixed Manganese Ruthenium Oxides $(Mn_{1-x}Ru_x)O_2$ Crystallised Under Acidic Hydrothermal Conditions

## S1: Thermogravimetric analysis

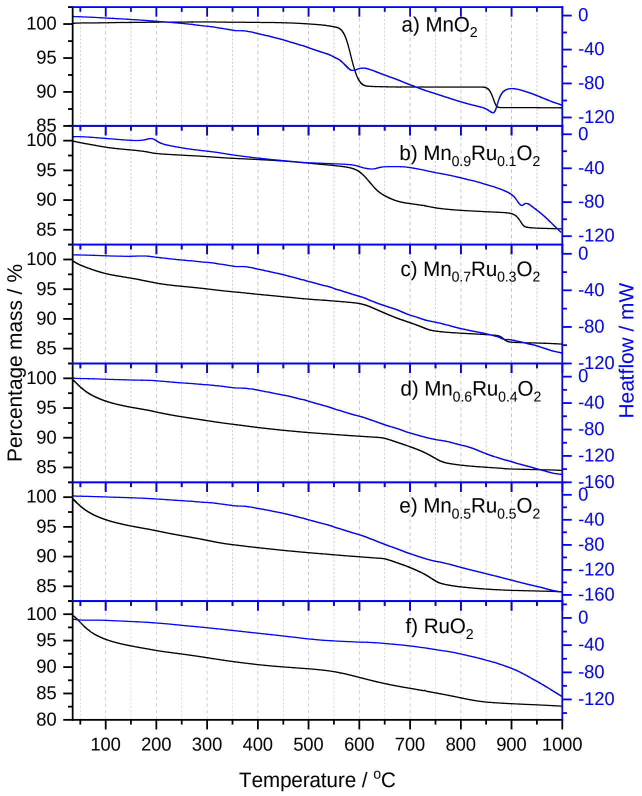


*Figure S1: TGA-DSC of $Mn_{1-x}Ru_xO_2$ materials on heating in air at 10 ℃ $min^{-1}$*

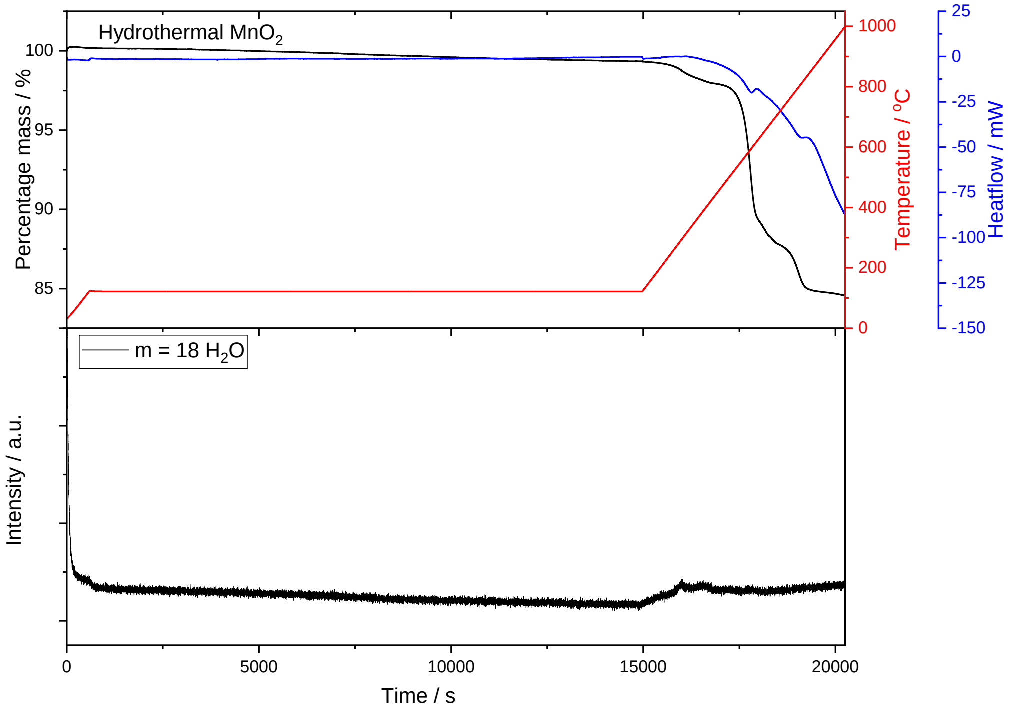


*Figure S2: TGA-DSC-MS of hydrothermally made $MnO_2$, showing evolution of mass = 18 ($H_2O$) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.*

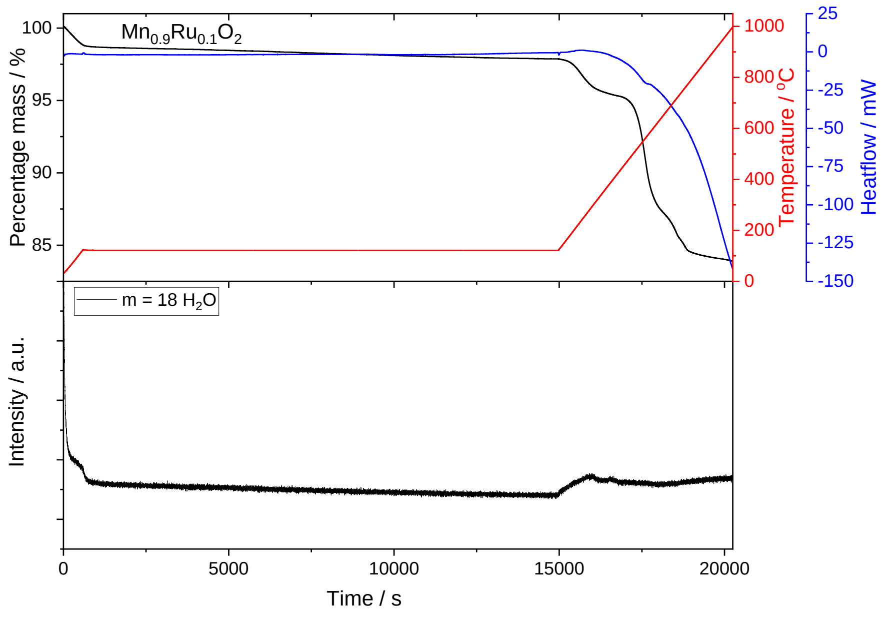


*Figure S3: TGA-MS of $Mn_{0.9}Ru_{0.1}O_2$, showing evolution of mass = 18 ($H_2O$) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.*

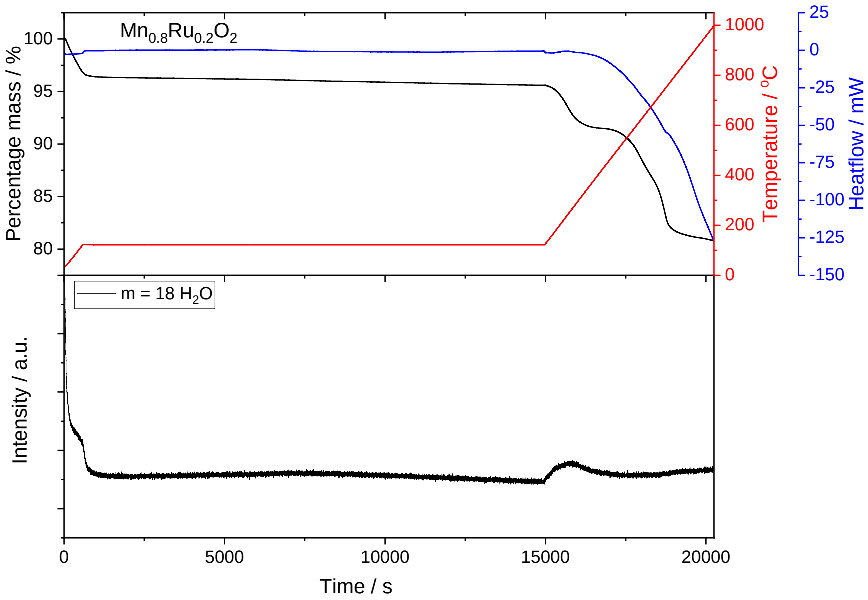


*Figure S4: TGA-MS of $Mn_{0.8}Ru_{0.2}O_2$, showing evolution s in mass 18 ($H_2O$) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.*

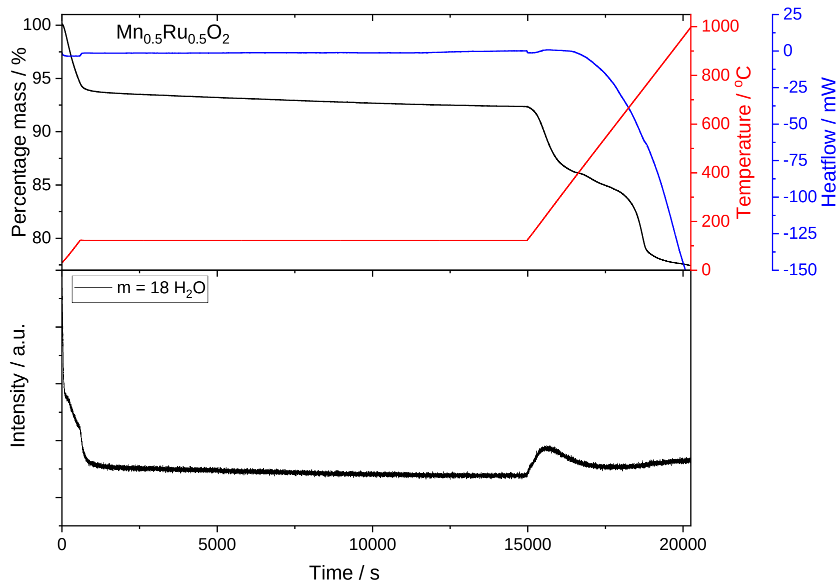


*Figure S5: TGA-MS of $Mn_{0.5}Ru_{0.5}O_2$, showing changes in mass 18 ($H_2O$) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.*

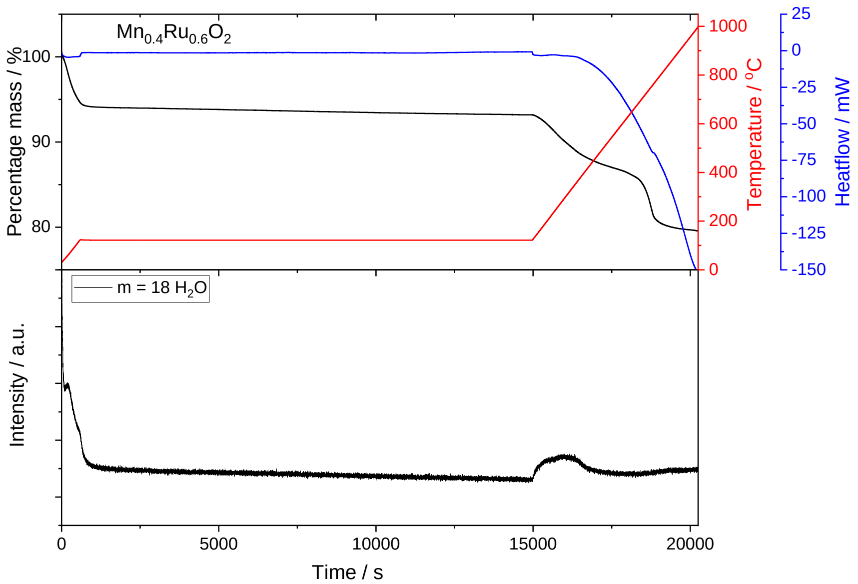


*Figure S6: TGA-MS of $Mn_{0.4}Ru_{0.6}O_2$, showing changes in mass 18 ($H_2O$) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.*

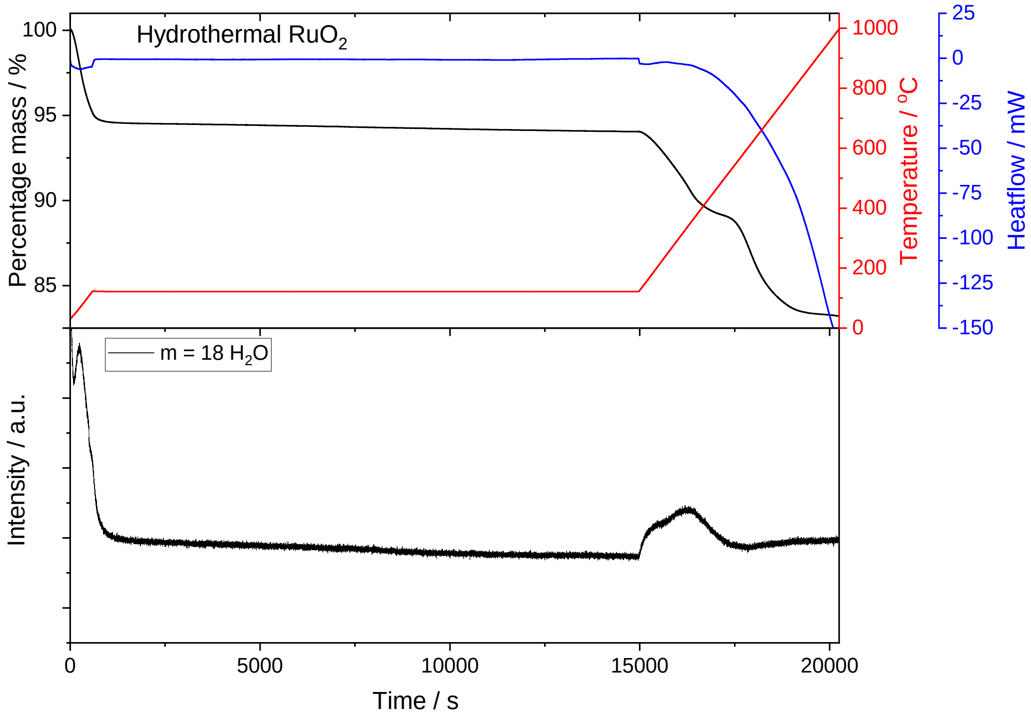


*Figure S7: TGA-MS of hydrothermally made $RuO_2$, showing changes in mass 18 ($H_2O$) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.*

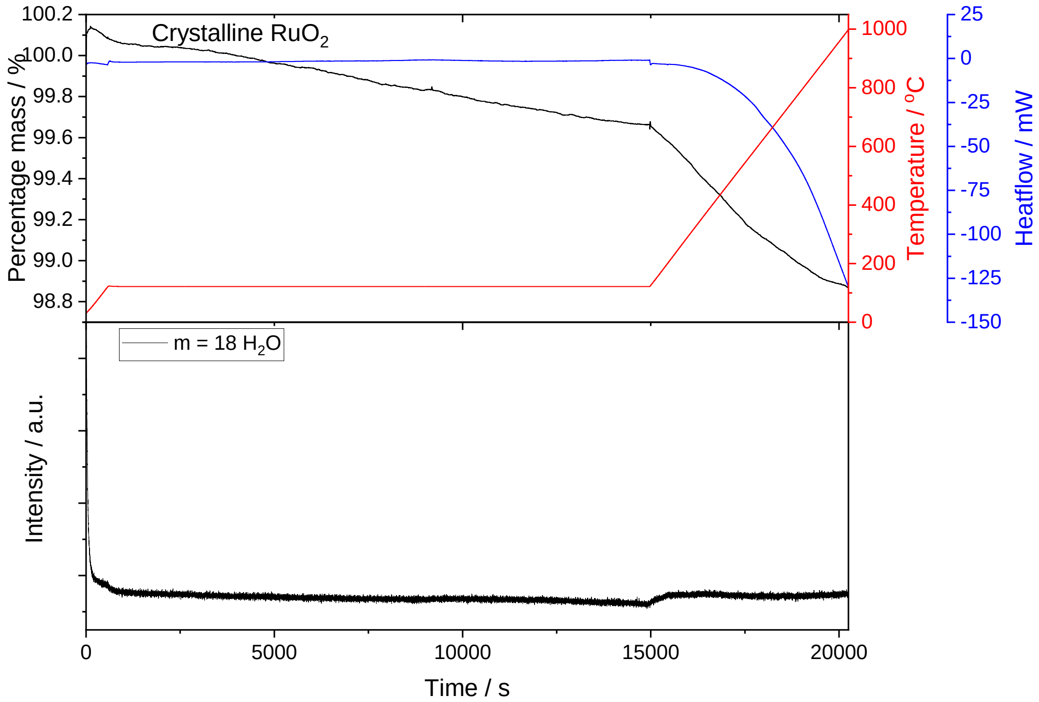


*Figure S8: TGA-MS of crystalline $RuO_2$, showing changes in mass 18 ($H_2O$) as the material is heated to 120 °C and held for 4 hours, and then heated to 1000 °C at 10 °C/min.*

## S2: XANES of reference materials

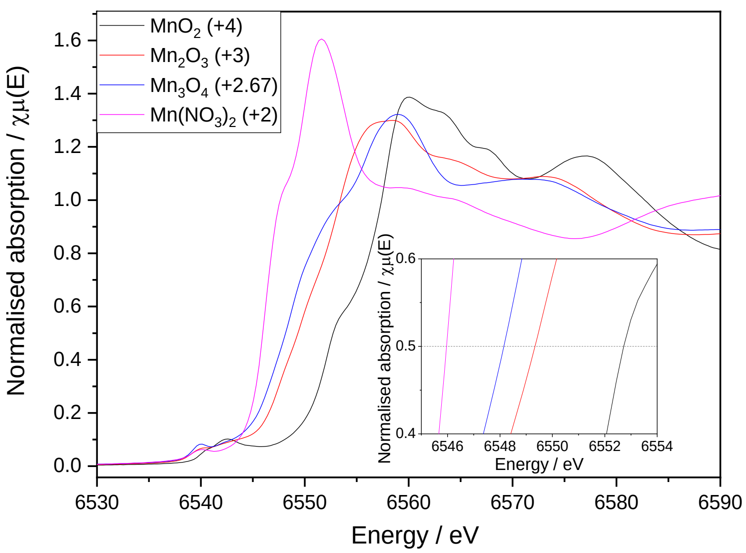


*Figure S9: Mn K edge XANES data of the reference materials for manganese from B18 Diamond Light Source.*

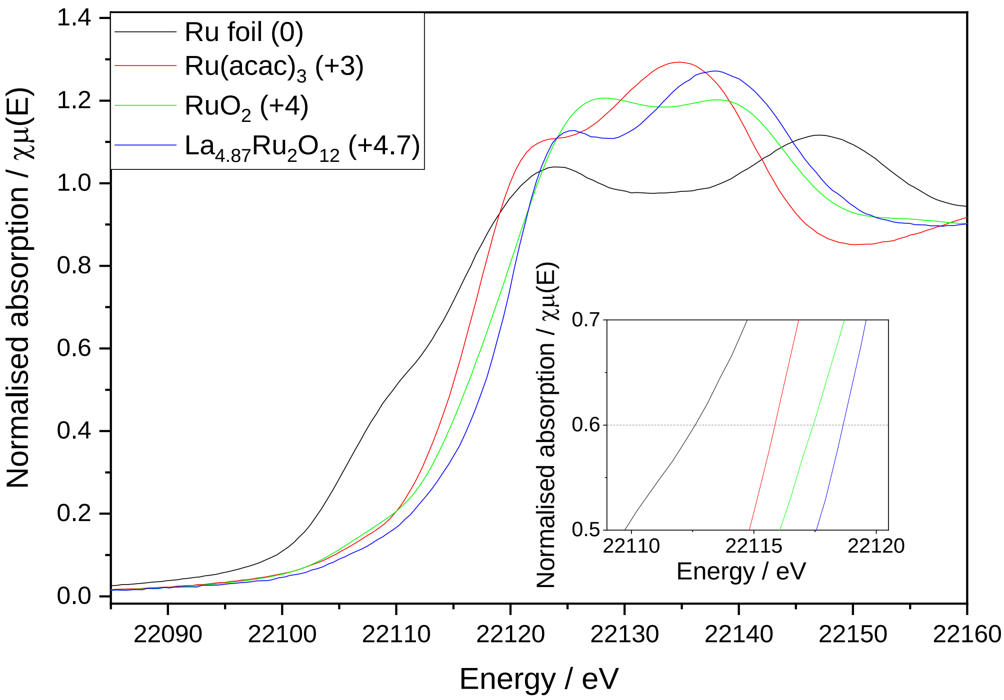


*Figure S10: Ru K edge XANES data of the reference materials for ruthenium from B18 Diamond Light Source.*

## S3: Additional EXAFS analysis

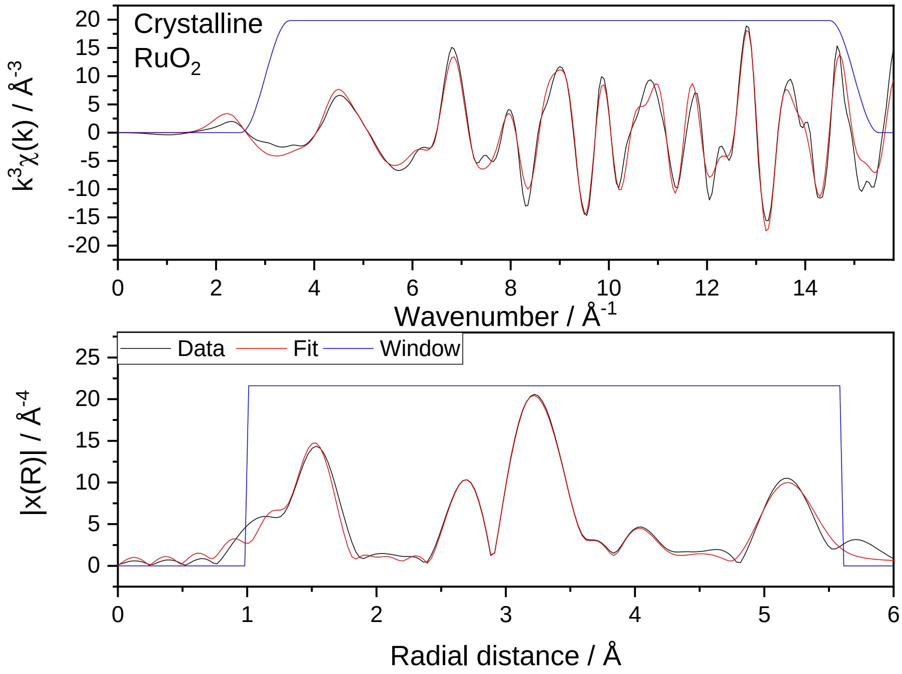


*Figure S11: Crystalline $RuO_2$ EXAFS fitting in k-space and R-space, fitted to literature $RuO_2$.*

*Table S1: Fitting parameters for crystalline $RuO_2$ EXAFS data with R-factor=0.05736, $S_0^2$=1.1(2) and $E_0$=-4.7 eV, where $R_{eff}$ is effective path length.*

| Name | *N* | $\sigma^2$ / Å$^2$ | $R_{eff}$ / Å | *R* / Å |
|---|---|---|---|---|
| O1.1 | 6 | 0.0038(14) | 1.9713 | 1.967(14) |
| Ru1.1 | 2 | 0.0028(13) | 3.1049 | 3.110(16) |
| Ru1.2 | 8 | 0.0035(14) | 3.5385 | 3.5417(13) |
| O1.3 | 4 | 0.02(16) | 3.4123 | 3.6(7) |
| O1.4 | 4 | 0.00(3) | 3.6620 | 3.8(3) |
| Ru1.3 | 4 | 0.005(3) | 4.4968 | 4.49(3) |
| O1.2O1.7 | 16 | 0.005(10) | 4.6882 | 4.42(9) |
| O1.2O1.2 | 4 | 0.008(3) | 3.9715 | 3.963(3) |
| O1.2 | 4 | 0.008(3) | 3.9715 | 3.963(3) |
| O1.5 | 8 | 0.004(9) | 4.03610 | 3.94(11) |
| Ru1.5 | 8 | 0.004(3) | 5.63930 | 5.47(3) |
| O1.2Ru1.5 | 16 | 0.005(3) | 5.64350 | 5.63(3) |

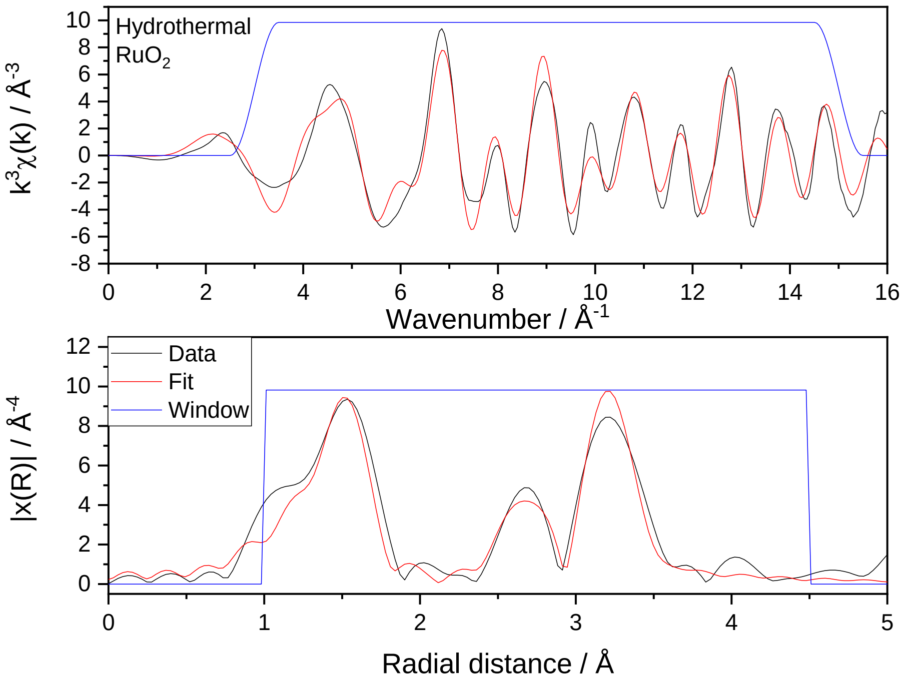


*Figure S12: Hydrothermally made $RuO_2$ EXAFS fitting in k space and R space, fitted to literature $RuO_2$.*[29]

*Table S2: Structural parameters fitted against the Ru K edge EXAFS of hydrothermal $RuO_2$, with R-factor=0.13086 $S_0^2$=0.77(12) and $E_0$=-3.9 eV, where $R_{eff}$ is effective path length.*

| Name | *N* | $\sigma^2$ / Å$^2$ | $R_{eff}$ / Å | *R* / Å |
|---|---|---|---|---|
| O1.1 | 6 | 0.0045(12) | 1.9713 | 1.971(10) |
| Ru1.1 | 2 | 0.0043(10) | 3.1049 | 3.102(12) |
| Ru1.2 | 8 | 0.0058(8) | 3.53850 | 3.548(10) |

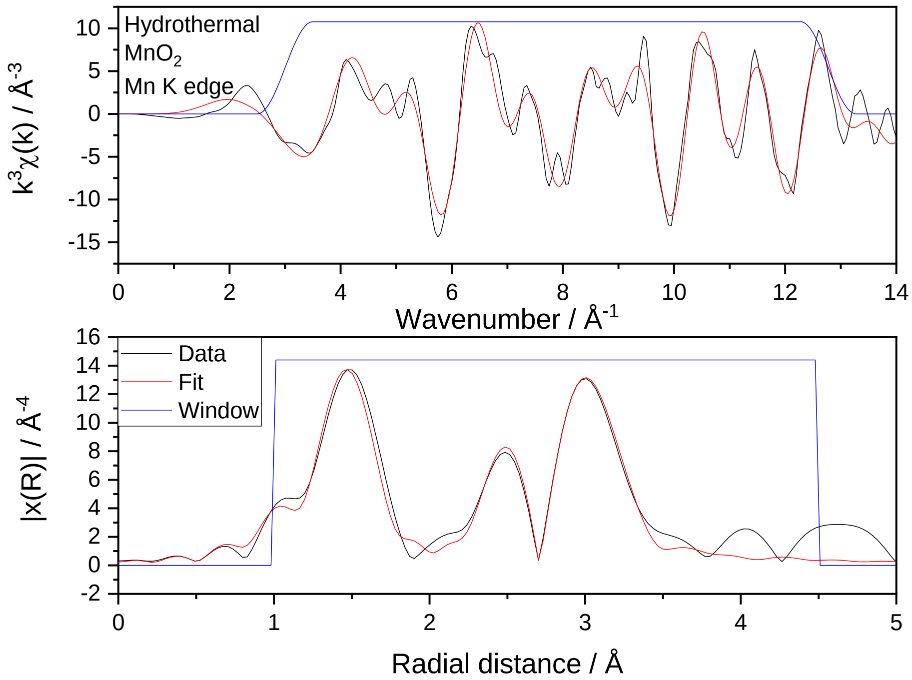


*Figure S13: Hydrothermally made $MnO_2$ Mn K edge EXAFS fitting in k space and R space, to literature $MnO_2$.*[28]

*Table S3: Structural parameters fitted against the Mn K edge EXAFS of hydrothermal $MnO_2$, with R-factor=0.09786, $S_0^2$=0.66(13) and $E_0$=-6.0 eV, where $R_{eff}$ is effective path length.*

| Name | *N* | $\sigma^2$ / Å$^2$ | $R_{eff}$ / Å | *R* / Å |
|---|---|---|---|---|
| O1.1 | 6 | 0.0021(14) | 1.88840 | 1.883(10) |
| Mn1.1 | 2 | 0.0018(16) | 2.8765 | 2.880(16) |
| Mn1.2 | 8 | 0.0034(12) | 3.4303 | 3.436(13) |

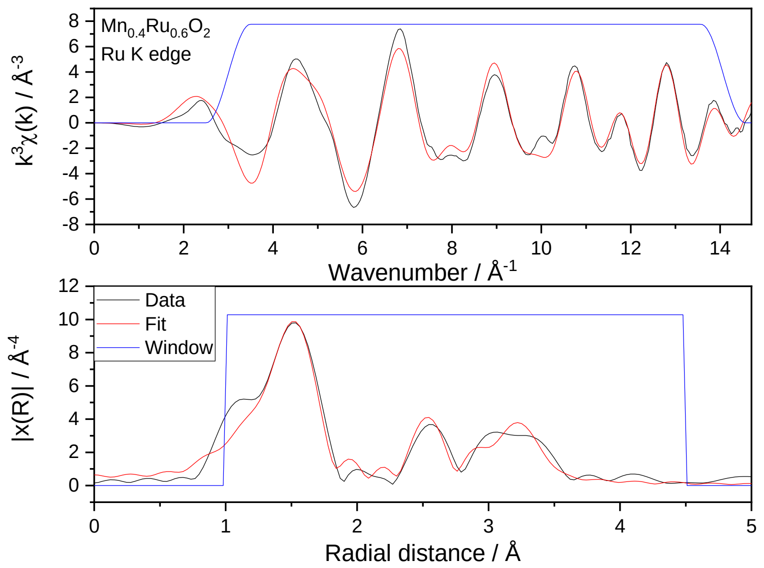


*Figure S14: $Mn_{0.4}Ru_{0.6}O_2$ Ru K edge EXAFS fitting in k space and R space.*

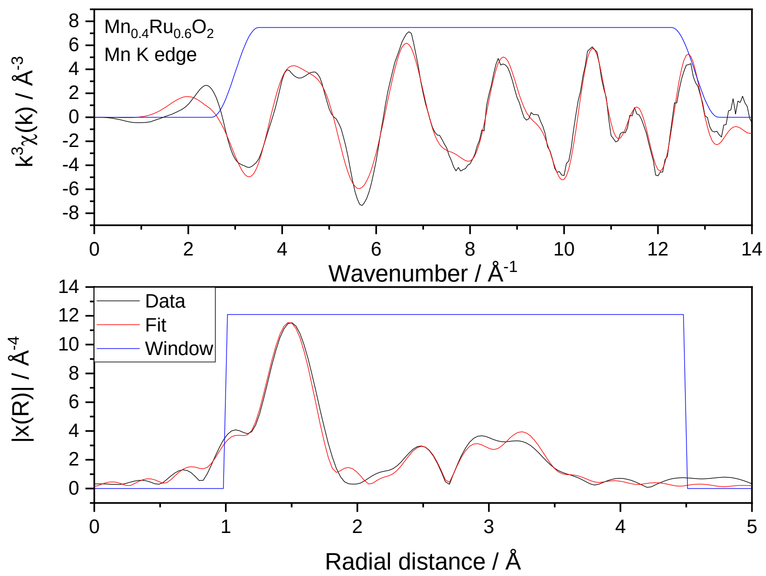


*Figure S15: $Mn_{0.4}Ru_{0.6}O_2$ Mn K edge EXAFS fitting in k space and R space.*

*Table S4: Structural parameters fitted against the Mn K edge and Ru K edge EXAFS of $Mn_{0.4}Ru_{0.6}O_2$ with an R-factor=0.07619, where $R_{eff}$ is effective path length.*

| Name | *N* | $\sigma^2$ / Å$^2$ | $R_{eff}$ / Å | *R* / Å |
|---|---|---|---|---|
| Ru K edge ($S_0^2$=0.82(8) and $E_0$=-1.48 eV) | | | | |
| Ru-O | 6 | 0.0046(8) | 1.97130 | 1.972(7) |
| Ru-Ru | 1.18 | 0.0049(12) | 3.10490 | 3.067(16) |
| Mn-Ru | 0.82 | 0.0049(12) | | 2.99(3) |
| Ru-Ru | 4.72 | 0.0062(11) | 3.53850 | 3.535(8) |
| Mn-Ru | 3.28 | 0.0062(11) | | 3.512(17) |
| Mn K edge ($S_0^2$=0.62(18) and $E_0$=-4.73 eV) | | | | |
| Mn-O | 6 | 0.003(2) | (1.88840) | 1.900(16) |
| Mn-Mn | 0.82 | 0.0049(12) | (2.87650) | 2.94(8) |
| Mn-Ru | 1.18 | 0.0049(12) | | 2.99(3) |
| Mn-Mn | 3.28 | 0.0062(11) | (3.4303) | 3.48(5) |
| Mn-Ru | 4.72 | 0.0062(11) | | 3.512(17) |

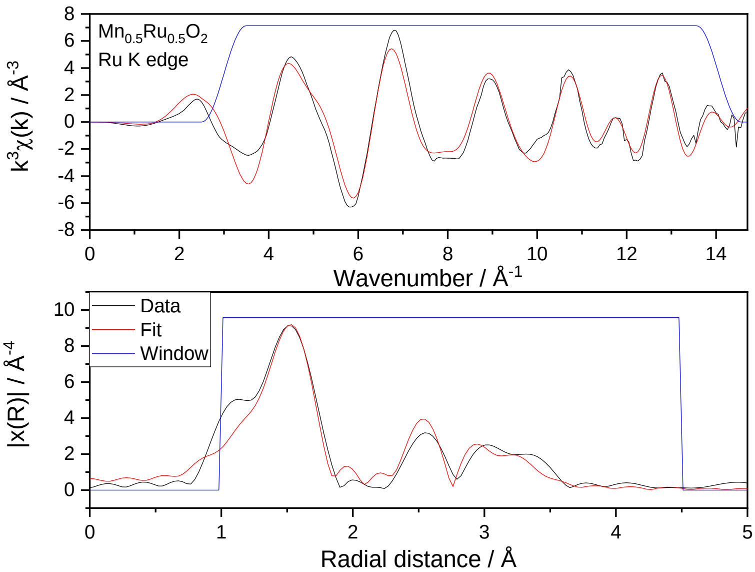


*Figure S16: $Mn_{0.5}Ru_{0.5}$ $O_2$ Ru K edge EXAFS fitting in k space and R space, to edited literature $RuO_2$.*[29]

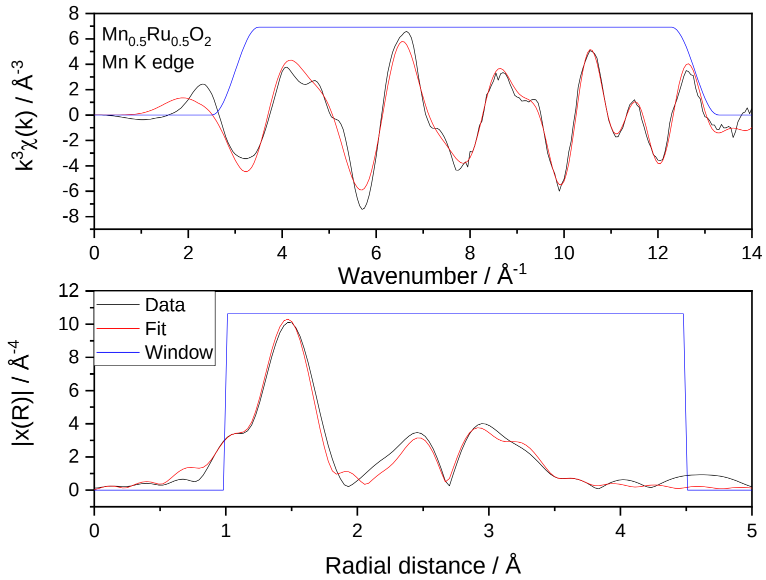


*Figure S17: $Mn_{0.5}Ru_{0.5}O_2$ Mn K edge EXAFS fitting in k space and R space.*

*Table S5: Structural parameters fitted against the Mn K edge and Ru K edge EXAFS of $Mn_{0.5}Ru_{0.5}O_2$ with an R-factor=0.08564, where $R_{eff}$ is effective path length.*

| Name | $N$ | $\sigma^2$ / Å$^2$ | $R_{eff}$ / Å | $R$ / Å |
|---|---|---|---|---|
| Ru K edge ($S_0^2$=0.78(9) and $E_0$=-1.43 eV) | | | | |
| Ru-O | 6 | 0.0048(9) | 1.97130 | 1.979(8) |
| Ru-Ru | 0.94 | 0.0052(11) | 3.10490 | 3.06(2) |
| Mn-Ru | 1.06 | 0.0052(11) | | 2.983(19) |
| Ru-Ru | 3.76 | 0.0066(12) | 3.53850 | 3.529(13) |
| Mn-Ru | 4.24 | 0.0066(12) | | 3.511(11) |
| Mn K edge ($S_0^2$=0.62(9) and $E_0$=-7.08 eV) | | | | |
| Mn-O | 6 | 0.0036(11) | (1.88840) | 1.89591 |
| Mn-Mn | 1.06 | 0.0052(11) | (2.87650) | 2.90(3) |
| Mn-Ru | 0.94 | 0.0052(11) | | 2.983(19) |
| Mn-Mn | 4.24 | 0.0066(12) | (3.4303) | 3.47(2) |
| Mn-Ru | 3.76 | 0.0066(12) | | 3.511(11) |

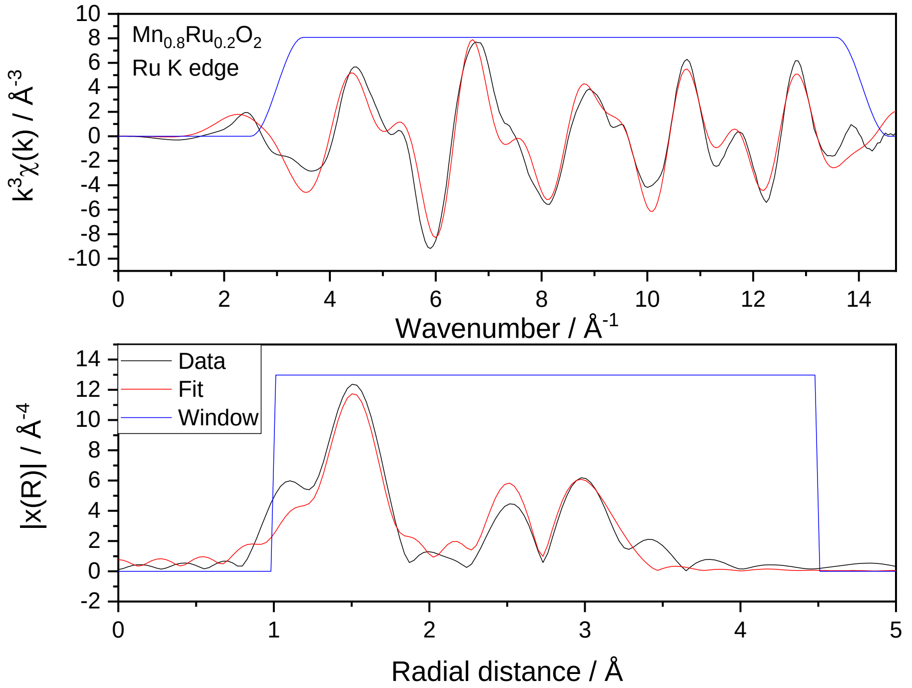


*Figure S18: $Mn_{0.8}Ru_{0.2}O_2$ Ru K edge EXAFS fitting in k space and R space, to edited literature $MnO_2$.*[28]

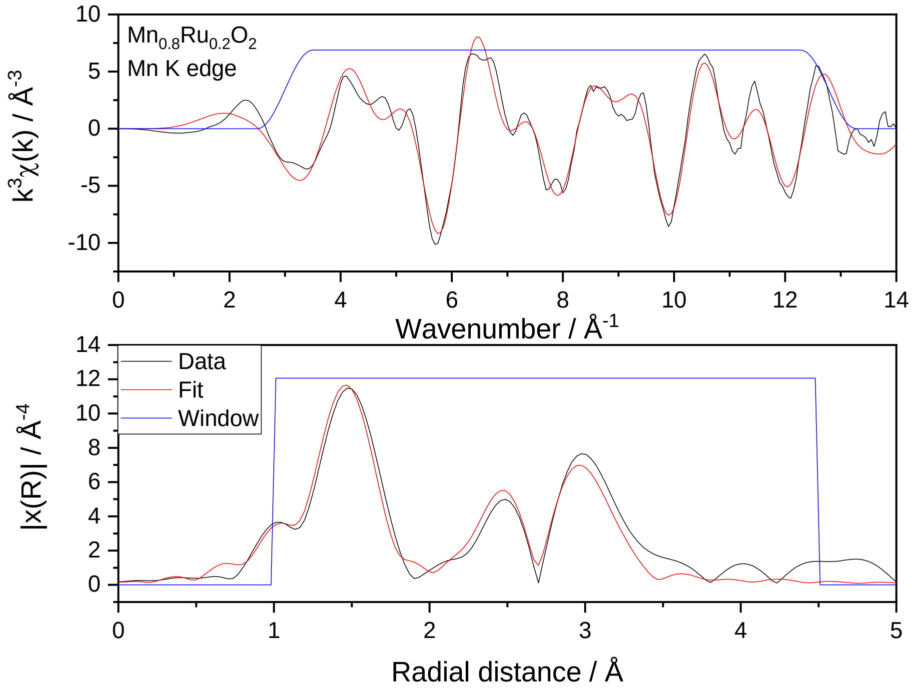


*Figure S19: $Mn_{0.8}Ru_{0.2}O_2$ Mn K edge EXAFS fitting in k space and R space, to edited literature $MnO_2$.*[28]

*Table S6: Structural parameters fitted against the Mn K edge and Ru K edge EXAFS of $Mn_{0.8}Ru_{0.2}O_2$ with an R-factor=0.10094, where $R_{eff}$ is effective path length.*

| Name | $N$ | $\sigma^2$ / Å$^2$ | $R_{eff}$ / Å | $R$ / Å |
|---|---|---|---|---|
| Ru K edge ($S_0^2$=0.73(9) and $E_0$=-1.75 eV) | | | | |
| Ru-O | 6 | 0.0025(8) | (1.97130) | 1.954(6) |
| Ru-Ru | 0.4 | 0.003(3) | (3.10490) | 2.86(9) |
| Mn-Ru | 1.6 | 0.003(3) | | 2.926(15) |
| Ru-Ru | 1.6 | 0.007(2) | (3.53850) | 3.51(7) |
| Mn-Ru | 6.4 | 0.007(2) | | 3.481(12) |
| Mn K edge ($S_0^2$=0.62(2) and $E_0$=-6.95 eV) | | | | |
| Mn-O | 6 | 0.003(2) | 1.88840 | 1.89(2) |
| Mn-Mn | 1.6 | 0.003(3) | 2.87650 | 2.89(4) |
| Mn-Ru | 0.4 | 0.003(3) | | 2.926(15) |
| Mn-Mn | 6.4 | 0.007(2) | 3.4303 | 3.46(3) |
| Mn-Ru | 1.6 | 0.007(2) | | 3.481(12) |

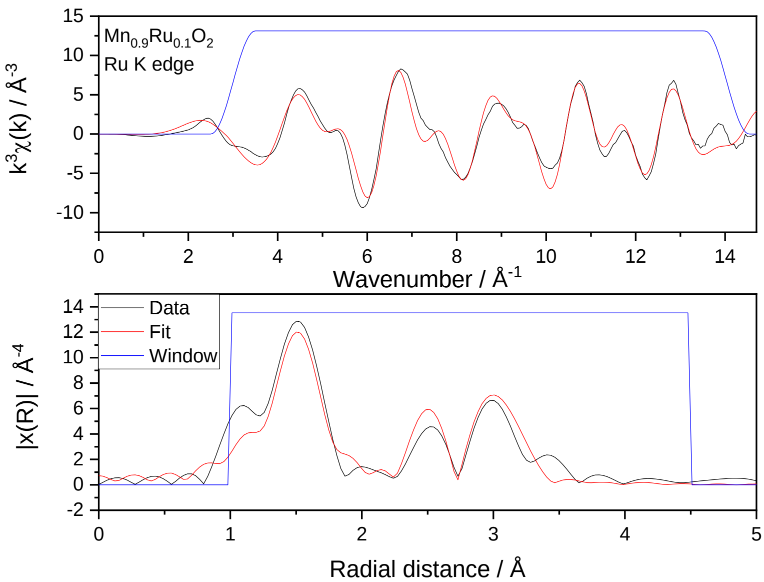


*Figure S20: $Mn_{0.9}Ru_{0.1}O_2$ Ru K edge EXAFS fitting in k space and R space*[28]

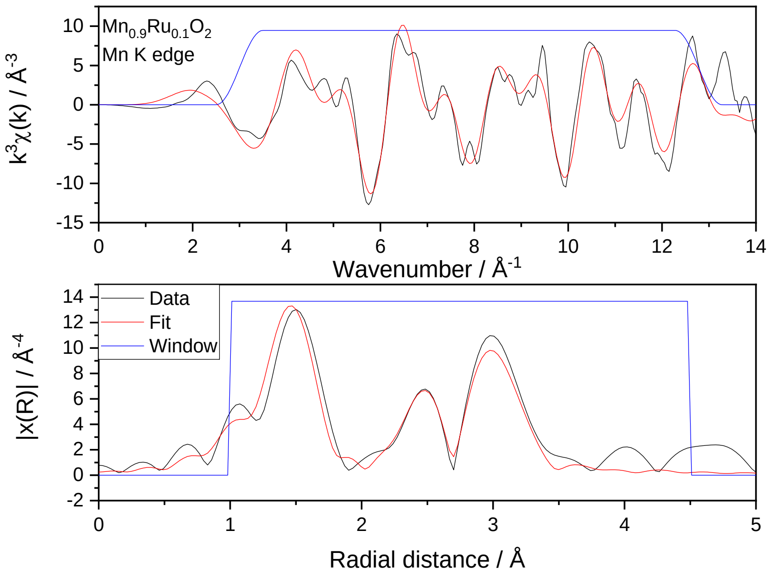


*Figure S21: $Mn_{0.9}Ru_{0.1}O_2$ Mn K edge EXAFS fitting in k space and R space.* [28]

*Table S7: Structural parameters fitted against the Mn K edge and Ru K edge EXAFS of $Mn_{0.9}Ru_{0.1}O_2$ with an R-factor=0.11774, where $R_{eff}$ is effective path length.*

| Name | *N* | $\sigma^2$ / Å$^2$ | $R_{eff}$ / Å | *R* / Å |
|---|---|---|---|---|
| Ru K edge ($S_0^2$=0.69(10) and $E_0$=-2.27 eV) | | | | |
| Ru-O | 6 | 0.0020(9) | (1.97130) | 1.951(9) |
| Ru-Ru | 0.15 | 0.0038(17) | (3.10490) | 2.48(9) |
| Mn-Ru | 1.85 | 0.0038(17) | | 2.95(3) |
| Ru-Ru | 0.6 | 0.0053(10) | (3.53850) | 3.04(9) |
| Mn-Ru | 7.4 | 0.0053(10) | | 3.461(16) |
| Mn K edge ($S_0^2$=0.78(14) and $E_0$=-6.21 eV) | | | | |
| Mn-O | 6 | 0.0034(16) | 1.88840 | 1.88739 |
| Mn-Mn | 1.85 | 0.0038(17) | 2.87650 | 2.88(2) |
| Mn-Ru | 0.15 | 0.0038(17) | | 2.95(3) |
| Mn-Mn | 7.4 | 0.0053(10) | 3.4303 | 3.438(17) |
| Mn-Ru | 0.6 | 0.0053(10) | | 3.461(16) |

## S4: XPS analysis

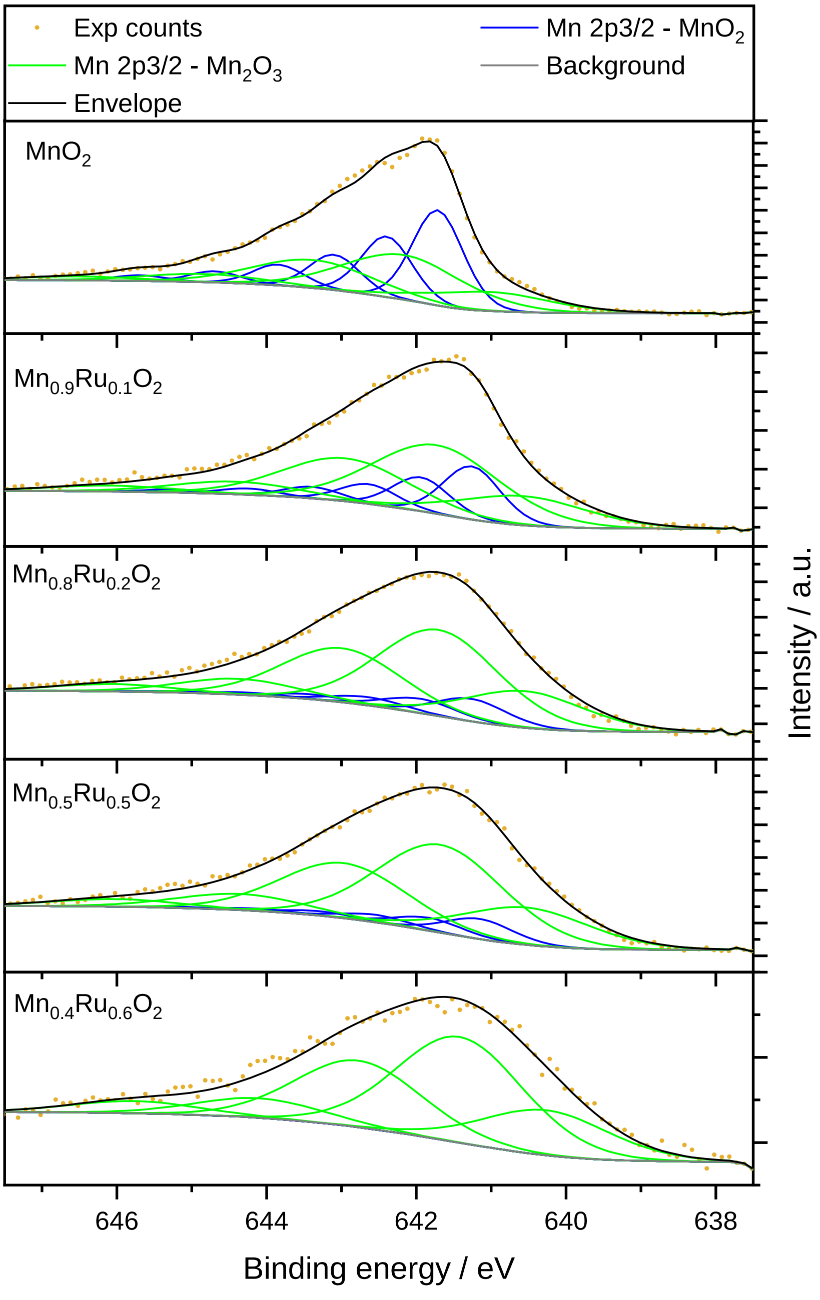


*Figure S22: Manganese 2p XPS of $Mn_{1-x}Ru_xO_2$ materials.*

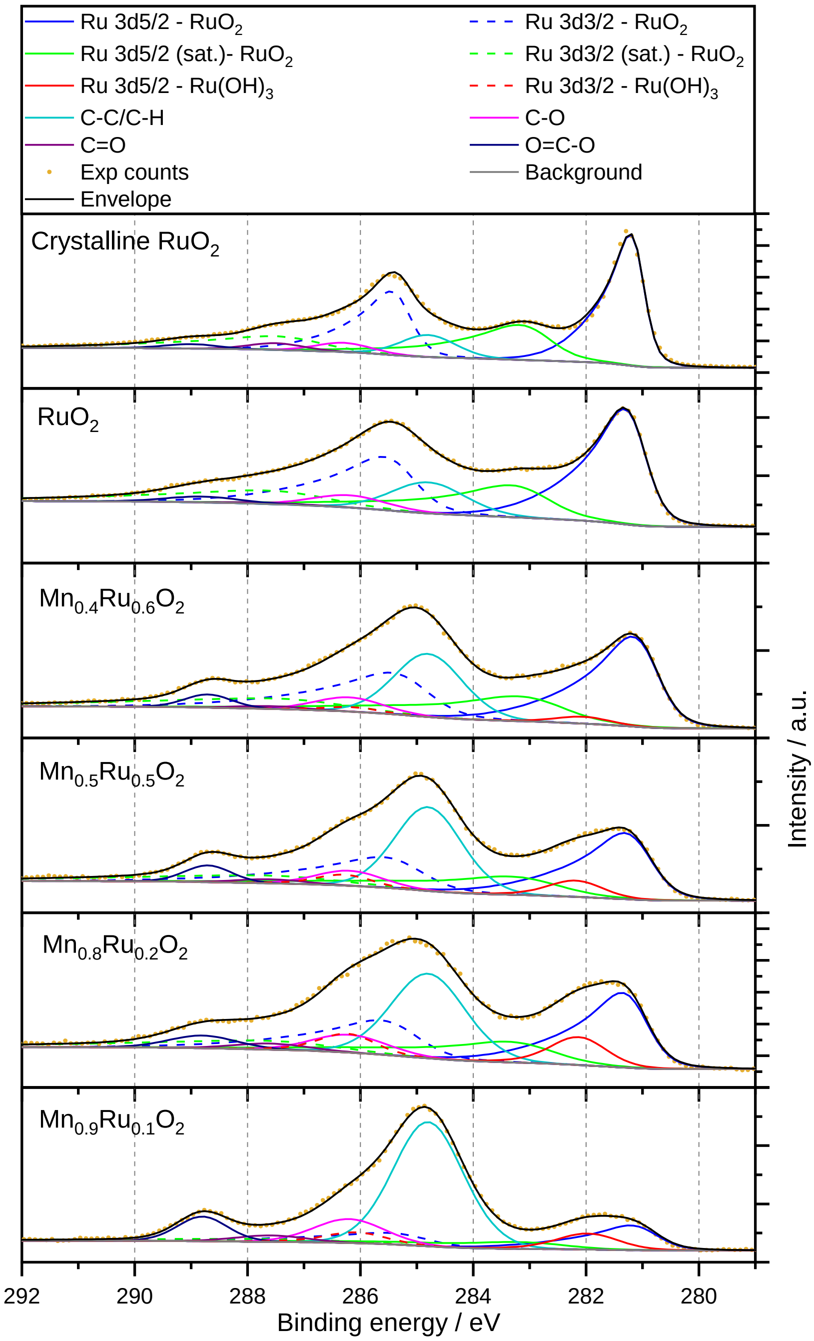


*Figure S23: Ruthenium 3d and carbon 1s XPS of $Mn_{1-x}Ru_xO_2$ materials compared to crystalline $RuO_2$.*

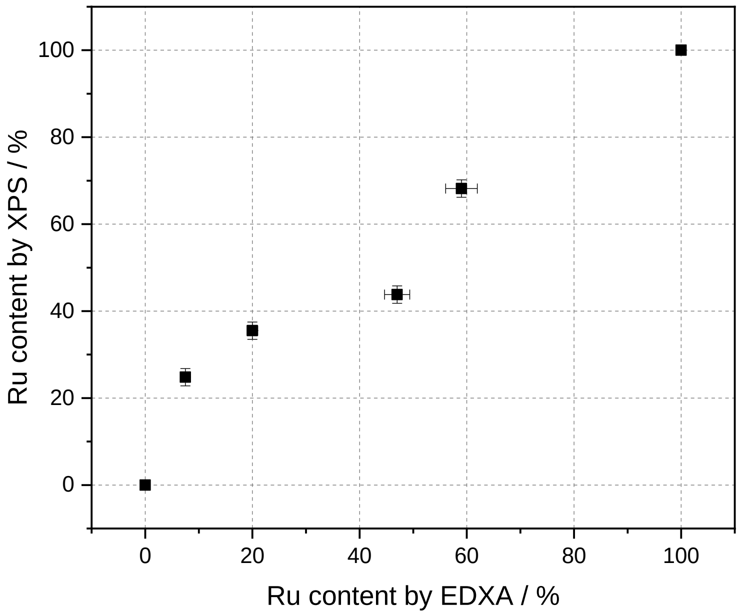


*Figure S24: Percentage ruthenium to manganese content by EDXA compared to XPS.*

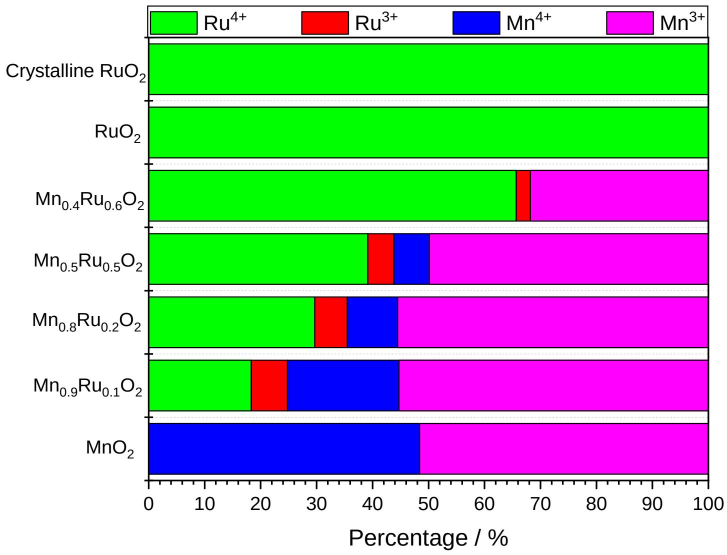


*Figure S25: Percentage content of $Ru^{4+}$, $Ru^{3+}$, $Mn^{3+}$ and $Mn^{4+}$, calculated from XPS.*