

Vacancy enhanced oxygen redox reversibility in P3-type magnesium doped sodium manganese oxide $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$

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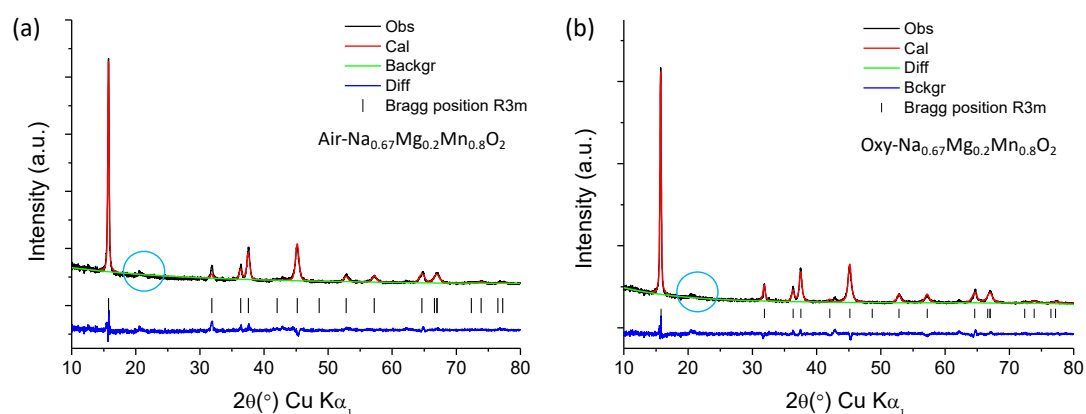


Figure S1. Profile fits for Le Bail refinement of as-synthesized (a) Air- $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$ and (b) Oxy- $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$ using the space group of $R3m$, respectively. Observed data points are shown in black, with fitted profile in red and the difference is shown in blue. Tick marks indicate allowed reflections.

Table S1. Rietveld refinement results for as-synthesized (a) Air-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ and (b) Oxy-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ using a superlattice model (space group *Cm*).

| (a) Pristine Air-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ | | | | | | |
|---|----------------|-----------|-----------|----------|--------------|------|
| R _{exp} = 1.08%, R _{wp} : 2.96 % , R _p = 2.24% Contains 1.2% MgO | | | | | | |
| Lattice parameters P3 Space group <i>Cm</i> <i>a</i> = 4.9997(7) Å <i>b</i> = 8.6473(12) Å <i>c</i> = 6.5811(7) Å β = 121.060(7)° | | | | | | |
| Cell volume = 243.74(6) Å ³ | | | | | | |
| atom | Wyckoff symbol | x/a | y/b | z/c | Occupancy | Biso |
| Mg1/Mn1 | 2a | 0 | 0 | 0 | 0.56/0.44(2) | 0.5 |
| Mn2 | 4b | 0.5 | 0.8291(7) | 0 | 0.99(1) | 0.5 |
| Na1 | 4b | 0.874(4) | 0.817(3) | 0.5 | 0.68(1) | 1.5 |
| Na1 | 2a | 0.371(11) | 0 | 0.5 | 0.48(3) | 1.5 |
| O1 | 4b | 0.265(9) | 0.835(4) | 0.150(4) | 1 | 0.6 |
| O2 | 2a | 0.791(13) | 0 | 0.169(8) | 1 | 0.6 |
| O3 | 4b | 0.707(11) | 0.167(4) | 0.796(4) | 1 | 0.6 |
| O4 | 2a | 0.183(19) | 0 | 0.777(9) | 1 | 0.6 |

| (b) Pristine Oxy-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ | | | | | | |
|---|----------------|-----------|-----------|----------|--------------|------|
| R _{exp} = 1.14%, R _{wp} : 3.25 % , R _p = 2.44% Contains 1.6% MgO | | | | | | |
| Lattice parameters P3 Space group <i>Cm</i> <i>a</i> = 4.9953(7) Å <i>b</i> = 8.6307(13) Å <i>c</i> = 6.5573(7) Å β = 120.899(8)° | | | | | | |
| Cell volume = 242.59(6) Å ³ | | | | | | |
| atom | Wyckoff symbol | x/a | y/b | z/c | Occupancy | Biso |
| Mg1/Mn1 | 2a | 0 | 0 | 0 | 0.59/0.41(2) | 0.5 |
| Mn2 | 4b | 0.5 | 0.8317(8) | 0 | 0.93(1) | 0.5 |
| Na1 | 4b | 0.883(4) | 0.803(2) | 0.5 | 0.75(2) | 1.5 |
| Na1 | 2a | 0.361(12) | 0 | 0.5 | 0.51(4) | 1.5 |
| O1 | 4b | 0.259(6) | 0.833(3) | 0.151(3) | 1 | 0.6 |
| O2 | 2a | 0.766(6) | 0 | 0.168(5) | 1 | 0.6 |
| O3 | 4b | 0.716(9) | 0.169(3) | 0.803(3) | 1 | 0.6 |
| O4 | 2a | 0.187(10) | 0 | 0.769(5) | 1 | 0.6 |

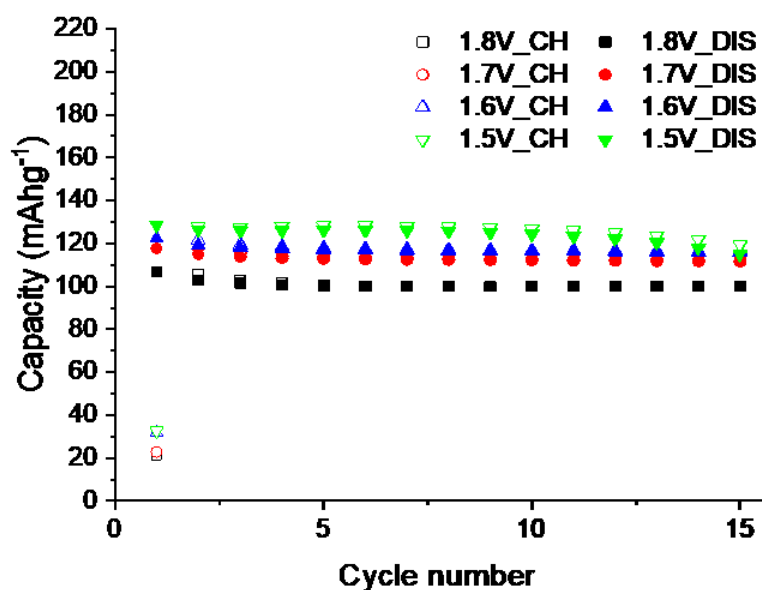


Figure S2. Galvanostatic cycling performance of Air- $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$ cycled at 30°C at a rate of 200 mA g^{-1} between 1.8 and 3.8 V in black, 1.7 and 3.8 V in red, 1.6 and 3.8 V in blue and 1.5 and 3.8 V in green. Empty and full symbols represent charge and discharge capacity, respectively.

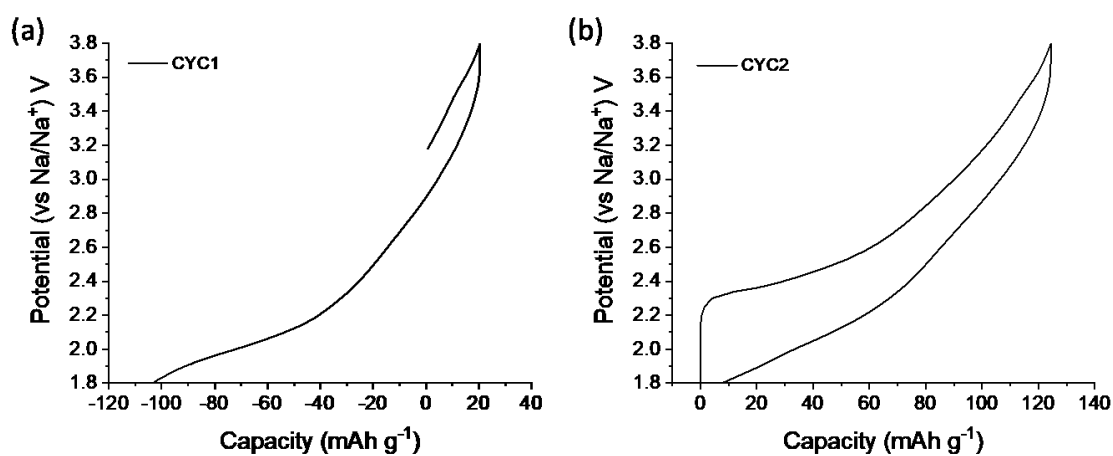


Figure S3. Charge/discharge curves for Oxy- $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$ on the (a) first cycle and (b) second cycle, cycled at 30°C at a rate of 200 mA g^{-1} between 1.8 and 3.8 V.

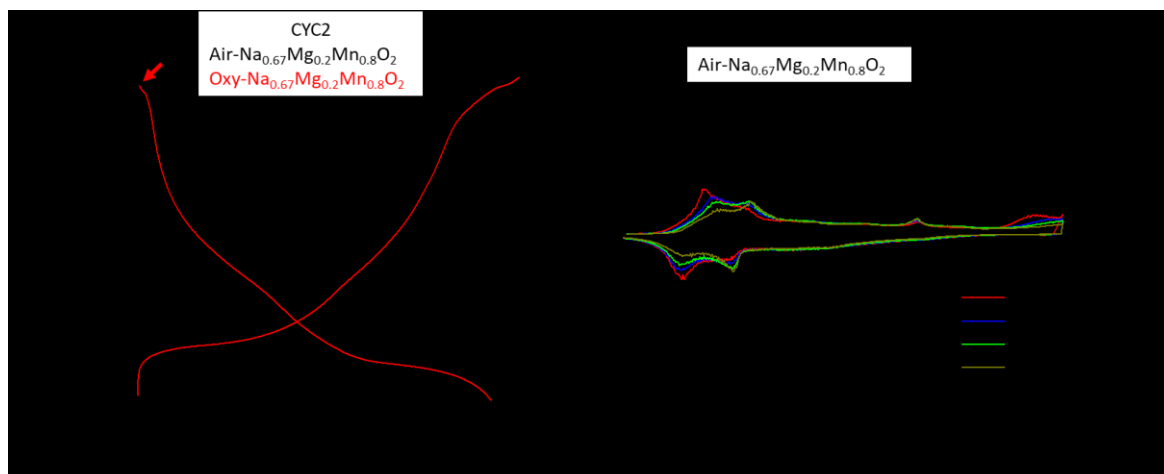


Figure S4. (a) Charge/discharge curves on the second cycle for Air-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ (black) and Oxy-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ (red) with an arrow indicating reversible oxygen redox and (b) dQ/dV plots corresponding to cycle 1 (black), cycle 2 (red), cycle 5 (blue), cycle 10 (green) and cycled 30 (dark yellow) for Air-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂.

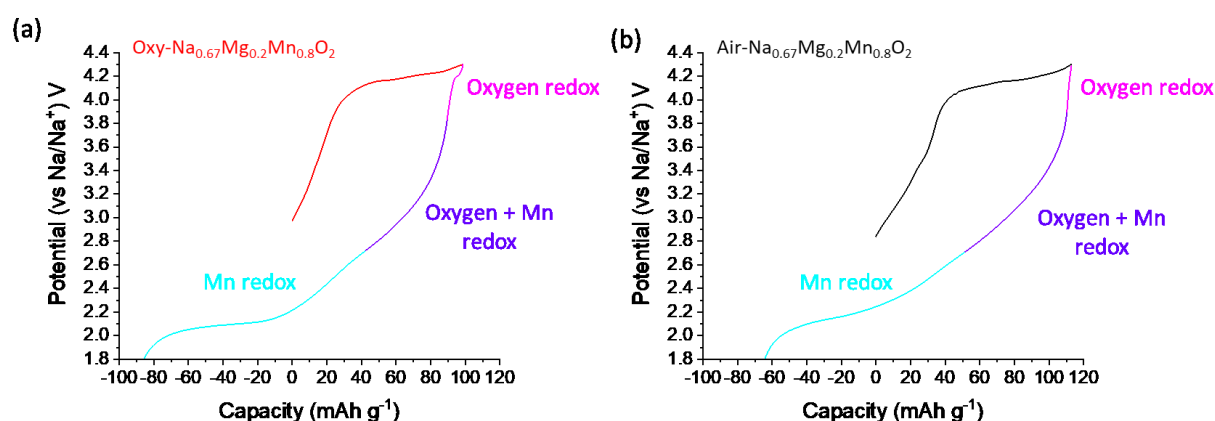


Figure S5. Charge/discharge curves on the first cycle (a) Oxy-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ and (b) Air-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ where the contribution of discharge capacity is color coded for oxygen redox in magenta, combination of oxygen and Mn redox in violet and Mn redox in cyan.

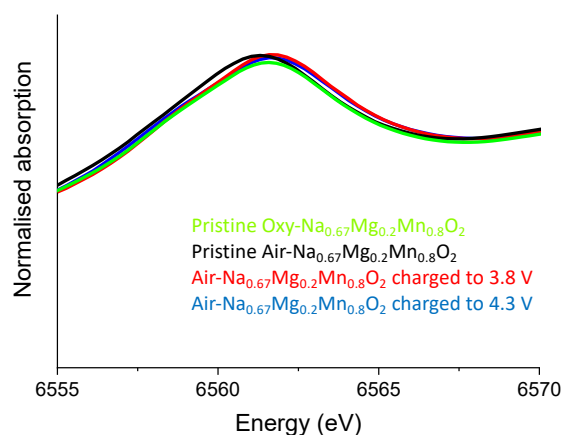


Figure S6. Zoom of the inflection point for Mn K-edge XANES spectra of the pristine and charged Air- $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$ compared with pristine Oxy- $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$.

Table S2. Rietveld refinement results of (a) Air- $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$ charged to 4.3 V, (b) Air- $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$ cycled between 1.8-3.8 V and (c) Air- $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$ cycled between 1.8-4.3 V.

| (a) Air-$\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$ charged to 4.3 V | | | | | | |
|---|----------------|-----|-----|-----------|-----------|------|
| R _{exp} : 2.47 % R _{wp} : 3.03 % 98% P3 2% O3 | | | | | | |
| Lattice parameters P3 Space group $R3m$ $a = 2.8601(6)$ $c = 16.900(4)$ Å | | | | | | |
| atom | Wyckoff symbol | x/a | y/b | z/c | Occupancy | Biso |
| Mn1/Mg1 | 3a | 0 | 0 | 0 | 0.81/0.19 | 0.5 |
| Na1 | 3a | 0 | 0 | 0.1718(6) | 0.35(1) | 1.2 |
| O1 | 3a | 0 | 0 | 0.3828(8) | 1 | 0.6 |
| O2 | 3a | 0 | 0 | 0.6045(8) | 1 | 0.6 |

| (b) Air-$\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$ cycled between 1.8-3.8 V | | | | | | |
|--|----------------|------------|-----|-----------|-----------|------|
| R _{exp} : 2.03 % R _{wp} : 2.52 % 89% O'3 11% P3 | | | | | | |
| Lattice parameters O'3 Space group $C2/m$ $a = 5.435(13)$ Å $b = 2.9070(6)$ Å $c = 5.7240(12)$ Å $\beta = 110.48(1)^\circ$ | | | | | | |
| atom | Wyckoff symbol | x/a | y/b | z/c | Occupancy | Biso |
| Mn1/Mg1 | 2a | 0 | 0 | 0 | 0.81/0.19 | 0.5 |
| Na1 | 2d | 0 | 0.5 | 0.5 | 1 | 1.2 |
| O1 | 4i | 0.2812(10) | 0 | 0.8047(5) | 1 | 0.6 |
| Lattice parameters P3 Space group $R3m$ $a = 2.9032(11)$ $c = 16.623(5)$ Å | | | | | | |
| Mn1/Mg1 | 3a | 0 | 0 | 0 | 0.81/0.19 | 0.5 |
| Na1 | 3a | 0 | 0 | 0.172(2) | 0.63(2) | 1.5 |
| O1 | 3a | 0 | 0 | 0.390(8) | 1 | 0.6 |
| O2 | 3a | 0 | 0 | 0.609(7) | 1 | 0.6 |

| (c) Air-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ cycled between 1.8-4.3 V | | | | | | |
|---|----------------|------------|-----|-----------|-----------|------|
| $R_{\text{exp}} : 2.35 \% R_{\text{wp}} : 2.80 \% 86\% \text{ O}'3 \ 14\% \text{ P3}$ | | | | | | |
| Lattice parameters O'3 Space group $C2/m$ $a = 5.415(2) \text{ \AA}$ $b = 2.9054(7) \text{ \AA}$ $c = 5.748(2) \text{ \AA}$ $\beta = 110.70(1)^\circ$ | | | | | | |
| atom | Wyckoff symbol | x/a | y/b | z/c | Occupancy | Biso |
| Mn1/Mg1 | 2a | 0 | 0 | 0 | 0.81/0.19 | 0.5 |
| Na1 | 2d | 0 | 0.5 | 0.5 | 1 | 1.2 |
| O1 | 4i | 0.2833(14) | 0 | 0.8130(9) | 1 | 0.6 |
| Lattice parameters P3 Space group $R3m$ $a = 2.893(2) \text{ \AA}$ $c = 16.720(7) \text{ \AA}$ | | | | | | |
| Mn1/Mg1 | 3a | 0 | 0 | 0 | 0.81/0.19 | 0.5 |
| Na1 | 3a | 0 | 0 | 0.166(2) | 0.71(4) | 1.5 |
| O1 | 3a | 0 | 0 | 0.386(7) | 1 | 0.6 |
| O2 | 3a | 0 | 0 | 0.607(8) | 1 | 0.6 |

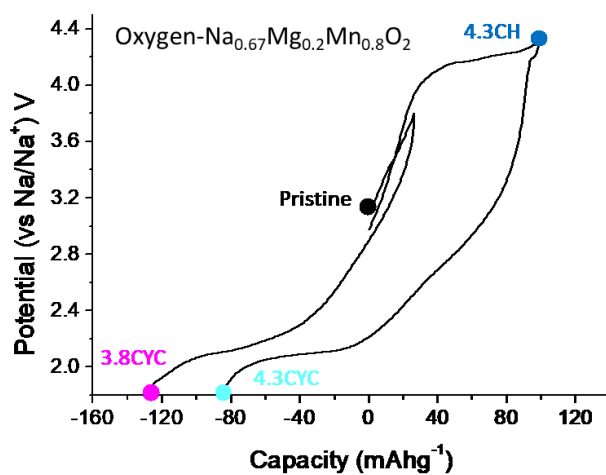


Figure S7. Galvanostatic cycling curves recorded at 10 mA g^{-1} for Oxy-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ cycled at 30°C in the two voltage windows: 1.8-3.8 V and 1.8-4.3 V with the points where PXRD were conducted.

Table S3. Rietveld refinement results of (a) Oxy-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ charged to 4.3 V, (b) Oxy-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ cycled between 1.8-3.8 V and (c) Oxy-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ cycled between 1.8-4.3 V.

| (a) Oxy-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ charged to 4.3 V | | | | | | |
|--|----------------|-----|-----|------------|-----------|------|
| R _{exp} : 2.40 % R _{wp} : 3.02 % 100% P3 | | | | | | |
| Space group <i>R3m</i> <i>a</i> = 2.8561(10) <i>c</i> = 16.9210(12) Å | | | | | | |
| atom | Wyckoff symbol | x/a | y/b | z/c | Occupancy | Biso |
| Mn1/Mg1 | 3a | 0 | 0 | 0 | 0.76/0.20 | 0.5 |
| Na1 | 3a | 0 | 0 | 0.1750(7) | 0.42(1) | 1.2 |
| O1 | 3a | 0 | 0 | 0.3806(11) | 1 | 0.6 |
| O2 | 3a | 0 | 0 | 0.6066(11) | 1 | 0.6 |

| (b) Oxy-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ cycled between 1.8-3.8 V | | | | | | |
|---|----------------|-----------|-----|-----------|-----------|------|
| R _{exp} : 2.03 % R _{wp} : 2.28 % 82% O'3 18% P3 | | | | | | |
| Lattice parameters O'3 Space group <i>C2/m</i> <i>a</i> = 5.457(2) Å <i>b</i> = 2.8948(11) Å <i>c</i> = 5.694(2) Å β = 110.06(1)° | | | | | | |
| atom | Wyckoff symbol | x/a | y/b | z/c | Occupancy | Biso |
| Mn1/Mg1 | 2a | 0 | 0 | 0 | 0.76/0.20 | 0.5 |
| Na1 | 2d | 0 | 0.5 | 0.5 | 1 | 1.2 |
| O1 | 4i | 0.2527(7) | 0 | 0.8241(6) | 1 | 0.6 |
| Lattice parameters P3 Space group <i>R3m</i> <i>a</i> = 2.893 (3) <i>c</i> = 16.70(3) Å | | | | | | |
| Mn1/Mg1 | 3a | 0 | 0 | 0 | 0.76/0.20 | 0.5 |
| Na1 | 3a | 0 | 0 | 0.185(2) | 0.76(2) | 1.2 |
| O1 | 3a | 0 | 0 | 0.386(3) | 1 | 0.6 |
| O2 | 3a | 0 | 0 | 0.606(5) | 1 | 0.6 |

| (c) Oxy-Na_{0.67}Mg_{0.2}Mn_{0.8}O₂ cycled between 1.8-4.3 V | | | | | | |
|--|----------------|------------|-----|-----------|-----------|------|
| R _{exp} : 1.99 % R _{wp} : 2.38 % 57% O'3 43% P3 | | | | | | |
| Lattice parameters O'3 Space group <i>C2/m</i> <i>a</i> = 5.384(8) Å <i>b</i> = 2.893(2) Å <i>c</i> = 5.721(11) Å β = 110.48(5)° | | | | | | |
| atom | Wyckoff symbol | x/a | y/b | z/c | Occupancy | Biso |
| Mn1/Mg1 | 2a | 0 | 0 | 0 | 0.76/0.20 | 0.5 |
| Na1 | 2d | 0 | 0.5 | 0.5 | 1 | 1.2 |
| O1 | 4i | 0.2348(11) | 0 | 0.8141(9) | 1 | 0.6 |
| Lattice parameters P3 Space group <i>R3m</i> <i>a</i> = 2.886(2) <i>c</i> = 16.692(12) Å | | | | | | |
| Mn1/Mg1 | 3a | 0 | 0 | 0 | 0.76/0.20 | 0.5 |
| Na1 | 3a | 0 | 0 | 0.1759(8) | 0.71(2) | 1.2 |
| O1 | 3a | 0 | 0 | 0.392(2) | 1 | 0.6 |
| O2 | 3a | 0 | 0 | 0.600(3) | 1 | 0.6 |