Supplementary Information for

Zr₄O₅N₂ - intergrowth of fluorite and bixbyite anion layers formed by coupled site-selective anion and vacancy ordering

C.W. Michie^(a), J.B. Claridge^(a), S.J. Clarke^(b), M.J. Rosseinsky^(a)

^aDepartment of Chemistry, The University of Liverpool, Liverpool L69 7ZD, UK.

^bInorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QR, UK

Figure S1 PXRD patterns of $\gamma\text{-Zr}_2\text{ON}_2$ (top) and $\text{Zr}_4\text{O}_5\text{N}_2$ (bottom). The tick markers below each pattern correspond to the positions of the Bragg reflections for each phase.

Table S2: Bond angles (°) at the zirconium sites from the refinement of $\text{Zr}_4\text{O}_5\text{N}_2$ against HPRD PND data.

O/N(4)–Zr1–O/N(4)	74.5(1) × 4	O/N(1)–Zr2–O/N(1)	93.7(3) × 1
O/N(4)–Zr1–O/N(4)	117.7(3) × 2	O/N(1)–Zr2–O/N(2)	104.7(1) × 4
O/N(4)–Zr1–O/N(5)	166.8(2) × 4	O/N(1)–Zr2–O/N(3)	83.8(2) × 2
O/N(4)–Zr1–O/N(5)	118.7(1) × 4	O/N(1)–Zr2–O/N(3)	177.5(3) × 1
O/N(4)–Zr1–O/N(5)	69.6(2) × 4	O/N(2)–Zr2–O/N(2)	136.5(4) × 1
O/N(4)–Zr1–O/N(5)	98.4(1) × 4	O/N(2)–Zr2–O/N(3)	76.0(2) × 4
O/N(5)–Zr1–O/N(5)	68.5(2) × 4	O/N(3)–Zr2–O/N(3)	98.7(4) × 1
O/N(5)–Zr1–O/N(5)	105.6(3) × 2		
O/N(1)–Zr3–O/N(2)	168.2(3) × 1	O/N(1)–Zr4–O/N(2)	79.6(2) × 1
O/N(1)–Zr3–O/N(3)	81.7(3) × 1	O/N(1)–Zr4–O/N(3)	91.5(2) × 1
O/N(1)–Zr3–O/N(4)	78.7(2) × 2	O/N(1)–Zr4–O/N(4)	78.6(2) × 1
O/N(1)–Zr3–O/N(5)	109.6(2) × 2	O/N(1)–Zr4–O/N(4)	100.3(2) × 1
O/N(2)–Zr3–O/N(3)	110.1(3) × 1	O/N(1)–Zr4–O/N(5)	126.4(2) × 1
O/N(2)–Zr3–O/N(4)	93.4(2) × 2	O/N(1)–Zr4–O/N(5)	163.1(2) × 1
O/N(2)–Zr3–O/N(5)	75.5(2) × 2	O/N(2)–Zr4–O/N(3)	74.6(2) × 1
O/N(3)–Zr3–O/N(4)	127.7(2) × 2	O/N(2)–Zr4–O/N(4)	113.8(2) × 1
O/N(3)–Zr3–O/N(5)	70.9(2) × 2	O/N(2)–Zr4–O/N(4)	167.2(2) × 1
O/N(4)–Zr3–O/N(4)	95.1(3) × 1	O/N(2)–Zr4–O/N(5)	73.8(2) × 1
O/N(4)–Zr3–O/N(5)	161.2(3) × 2	O/N(2)–Zr4–O/N(5)	102.7(2) × 1
O/N(4)–Zr3–O/N(5)	70.9(1) × 2	O/N(3)–Zr4–O/N(4)	92.6(2) × 1
O/N(5)–Zr3–O/N(5)	119.3(3) × 1	O/N(3)–Zr4–O/N(4)	165.2(3) × 1
		O/N(3)–Zr4–O/N(5)	73.4(2) × 1

		O/N(3)-Zr4-O/N(5)	123.6(3) × 1
O/N(4)-Zr4-O/N(4)	78.5(2) × 1	O/N(4)-Zr4-O/N(5)	114.7(2) × 1
O/N(4)-Zr4-O/N(5)	71.2(2) × 1	O/N(4)-Zr4-O/N(5)	115.2(2) × 1
O/N(4)-Zr4-O/N(5)	73.6(2) × 1	O/N(5)-Zr4-O/N(5)	69.8(2) × 1