Electronic Supplementary Material (ESI) for Dalton Transactions.

Atom	Wickoff position	x	y	z	Biso(Å^2)	Occ.
Sr	1*a*	0.00	0.00	0.00	0.63(4)	1
Co/Fe	1*b*	0.50	0.50	0.50	0.69(6)	1
O	3*c*	0.50	0.00	0.50	0.5	2.63

Table S1. Structural parameters obtained by the Rietveld's refinement of the x-ray powder diffraction data using the cubic *Pm-3m* space group. Occupation factors were fixed to the structural formula values. Fe and Co cations could not be distinguished because of their similar scattering factors.

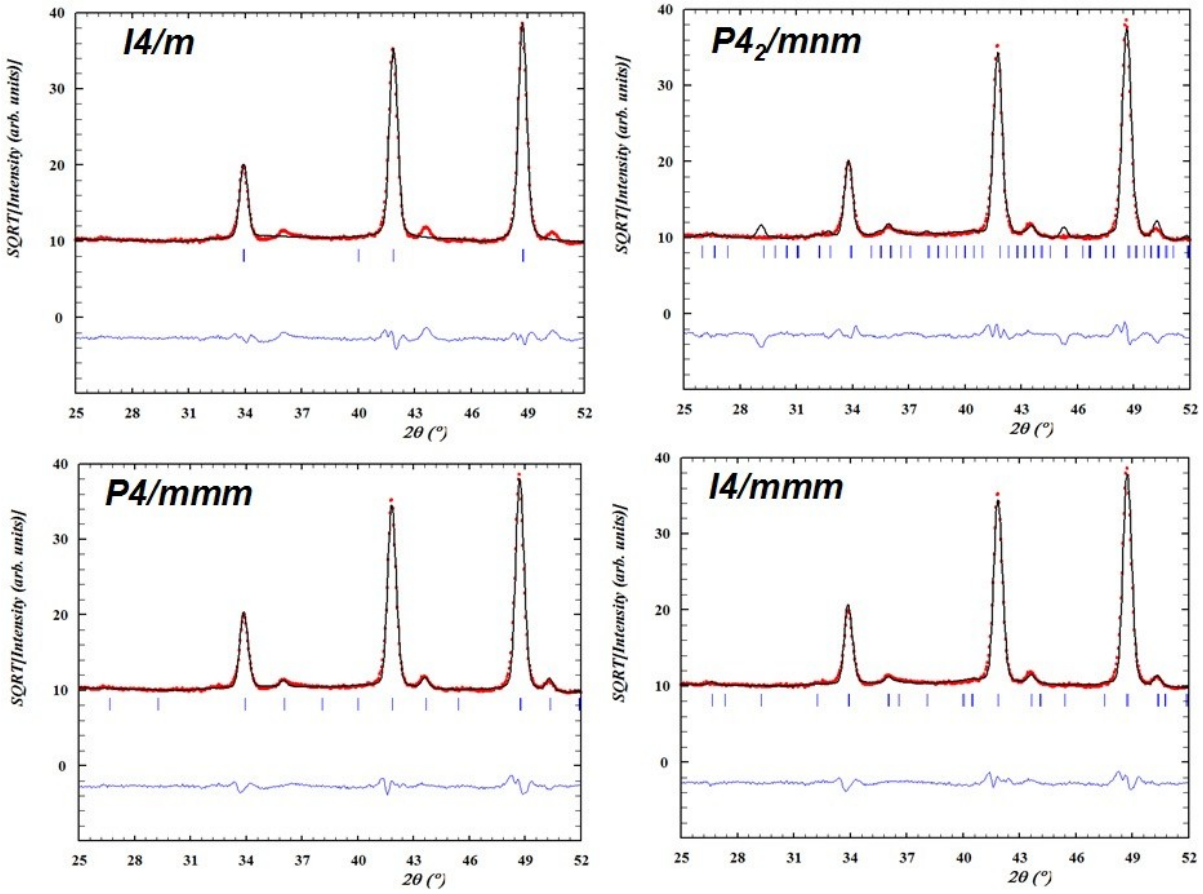

Figure S-1. Experimental (red dot) and calculated (thin solid line) neutron diffraction patterns at RT (D2B, ILL λ=1.594Å) for $SrFe_{0.25}Co_{0.75}O_{2.63}$ material on a particular angular window. The vertical bars indicate calculated Bragg peak positions for nuclear structures for

(a) Model based on *I4/m* , a = b = $a_p\sqrt{2}$ and c= 2 a_p

(b) Model based on *$P4_2$/mnm*, a = b = 2 $a_p\sqrt{2}$ and c = 4 a_p

(c) Model based on *P4/mmm*, a = b = a_p and c= 2 a_p

(d) Model based on *I4/mmm,* a = b = 2a_p and c= 4 a_p

Table S2. The *P4/mmm* tetragonal SG is characteristic of the "$Sr_2B_2O_{5.5}$" oxygen-vacancy ordering model.

Unit cell with lattice parameters a=3.86034(2) Å ≈ a_p, c=7.7318(1)Å ≈ $2a_p$ (a_p: lattice parameter of the cubic perovskite subcell). The agreement factors are χ^2=3.36, R_{wp}(%)=7.01, R_p(%)=5.43, R_{bragg}(%)=11.7 and R_f(%)=12.5. Atomic positions, thermal factors and occupancies obtained by Rietveld refinement of the neutron powder diffractogram using the tetragonal *P4/mmm* space group and referring to the $Sr_2B_2O_{5.5}$ model.

Atom	Wickoff position	x	y	z	Biso (Å^2)	Occ.
Sr1	2g	0.0000	0.0000	0.2610(3)	1.00(3)	1.00
Co1/Fe1	1c	0.5	0.5	0.0000	0.6(1)	0.740(5)/0.260(5)
Co2/Fe2	1d	0.5	0.5	0.5	0.7(1)	0.760(5)/0.240(5)
O1	2h	0.5	0.5	0.2352(6)	2.6(1)	0.90(1)
O2	2f	0.0000	0.5	0.0000	2.3(3)	0.72(1)
O3	2e	0.5	0.0000	0.5	0.81(4)	1.0

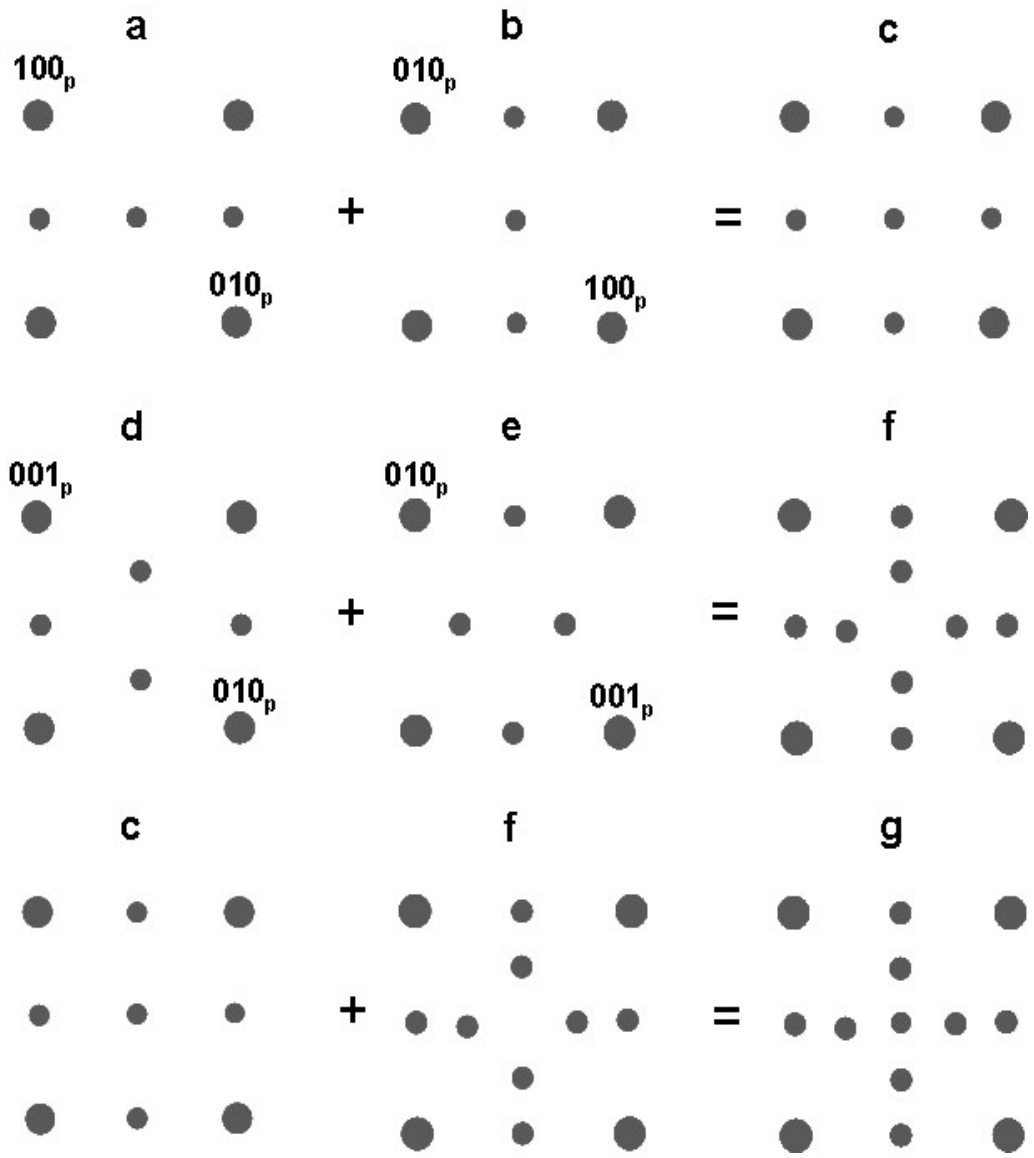

Figure S-2. displays squematic representations of planes of the reciprocal lattice along different zone axis and different orientations of a crystal with a $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ unit cell.

The pattern represented in Fig. S2c (similar to the SAED pattern in Fig. 3a) is a combination of the patterns represented in Fig. S2a and S2b.The pattern in Fig. S2f is a combination of the patterns in Fig. S2d and S2e. The pattern represented in Fig. S2g (similar to the SAED pattern in Fig. 3b) is a combination of the patterns represented in Fig. 2c and f. According to these representations, the FFT in Fig. 3 (similar to the SAED pattern in Fig. 2b) corresponds to Fig. S2g, which indicates that the crystal is formed by four different domains with $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ unit cell perpendicularly oriented. Fig. 4 shows a single domain of a crystal along the $[100]_p$ zone axis and the FFT corresponds to Fig. S2d and the FFT in Fig. 5 (similar to the SAED pattern in Fig. 2a) correspond to the representation in Fig. S2c.