

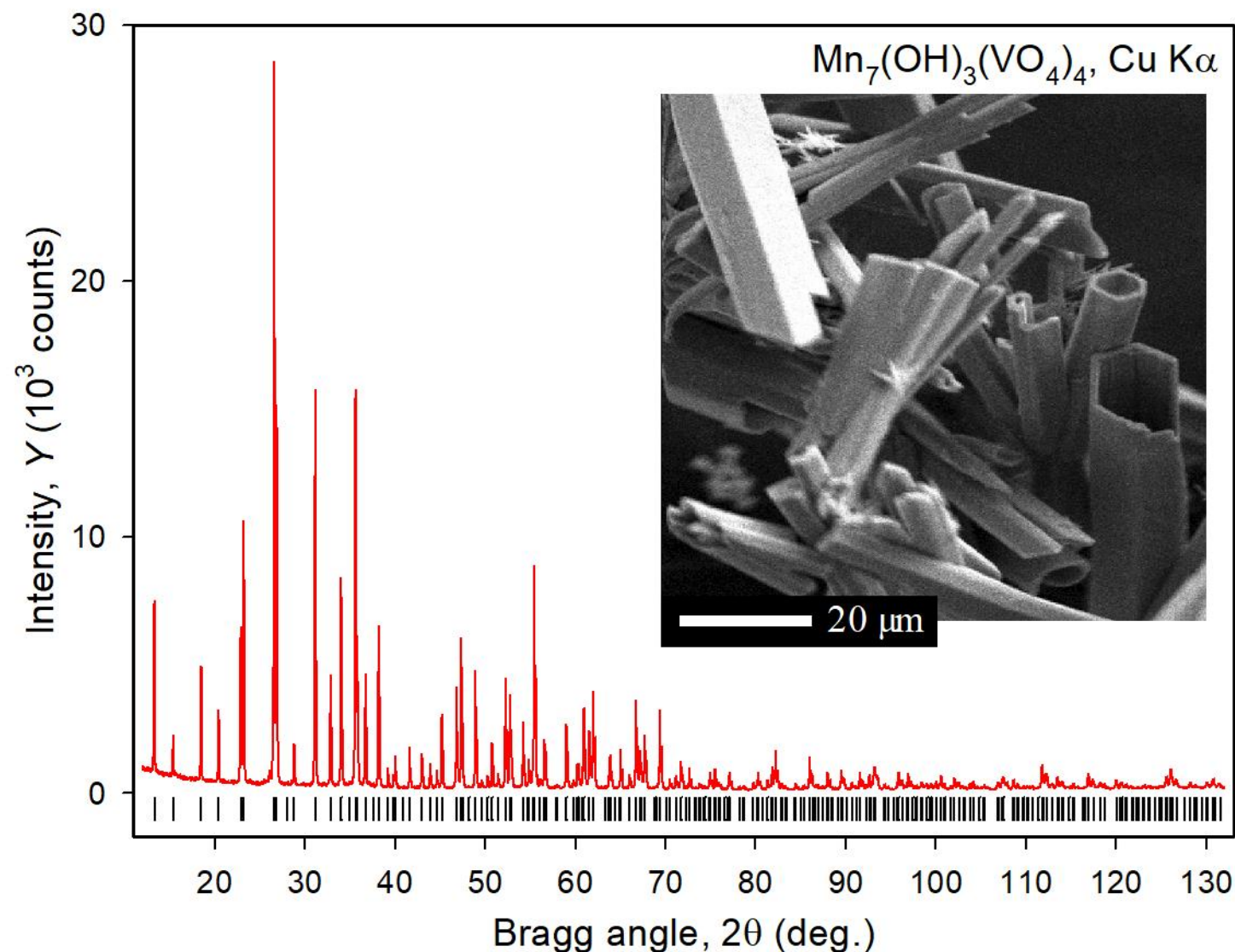
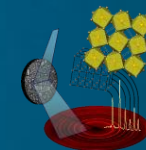


Figure 23.1. Powder diffraction pattern collected from ground $\text{Mn}_7(\text{OH})_3(\text{VO}_4)_4$ powder (screened through a $38 \mu\text{m}$ sieve) using $\text{Cu K}\alpha$ radiation. The *vertical bars* indicate calculated positions of the $\text{K}\alpha_1$ components of all possible Bragg reflections. *The inset* shows a scanning electron microscopy image of peculiar empty hexagonal-pipe particle morphology in its as-received state.

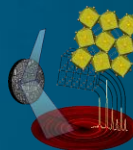


Table 23.1. Comparing the unit cell dimensions of potentially closely related compounds identified through searches of the ICSD and PDF databases, with the title compound listed in the 3rd row.

Compound	a, Å	c, Å	V, Å ³	ICSD	PDF	Ref.
$\text{Zn}_7(\text{OH})_3(\text{VO}_4)_3\text{SO}_4$	12.8130(6)	5.1425(2)	731.15	402888	88-1317	1
$\text{Mn}_{6-x}(\text{OH})_3(\text{HPO}_3)_4$	13.1957(6)	5.1770(3)	780.68	75269	47-0868	2
$\text{Mn}_7(\text{OH})_3(\text{VO}_4)_4$	13.2294(1)	5.25529(7)	796.54	88468	50-1796	3

- [1] K. Kato, Y. Kanke, Y. Oka, and T. Yao, Crystal structure of zinc hydroxide vanadate(V) $\text{Zn}_7(\text{OH})_3(\text{SO}_4)(\text{VO}_4)_3$, *Z. Kristallogr.* **213**, 26 (1998). <https://doi.org/10.1524/ncrs.1998.213.14.26>
- [2] M.P. Attfield, R.E. Morris, and A.K. Cheetham, Synthesis and structures of two isostructural phosphites, $\text{Fe}_{11}(\text{HPO}_3)_8(\text{OH})_6$ and $\text{Mn}_{11}(\text{HPO}_3)_8(\text{OH})_6$, *Acta Cryst.* **C50**, 981 (1994). <https://doi.org/10.1107/S0108270194001368>
- [3] Unit cell dimensions as refined from full profile fitting.

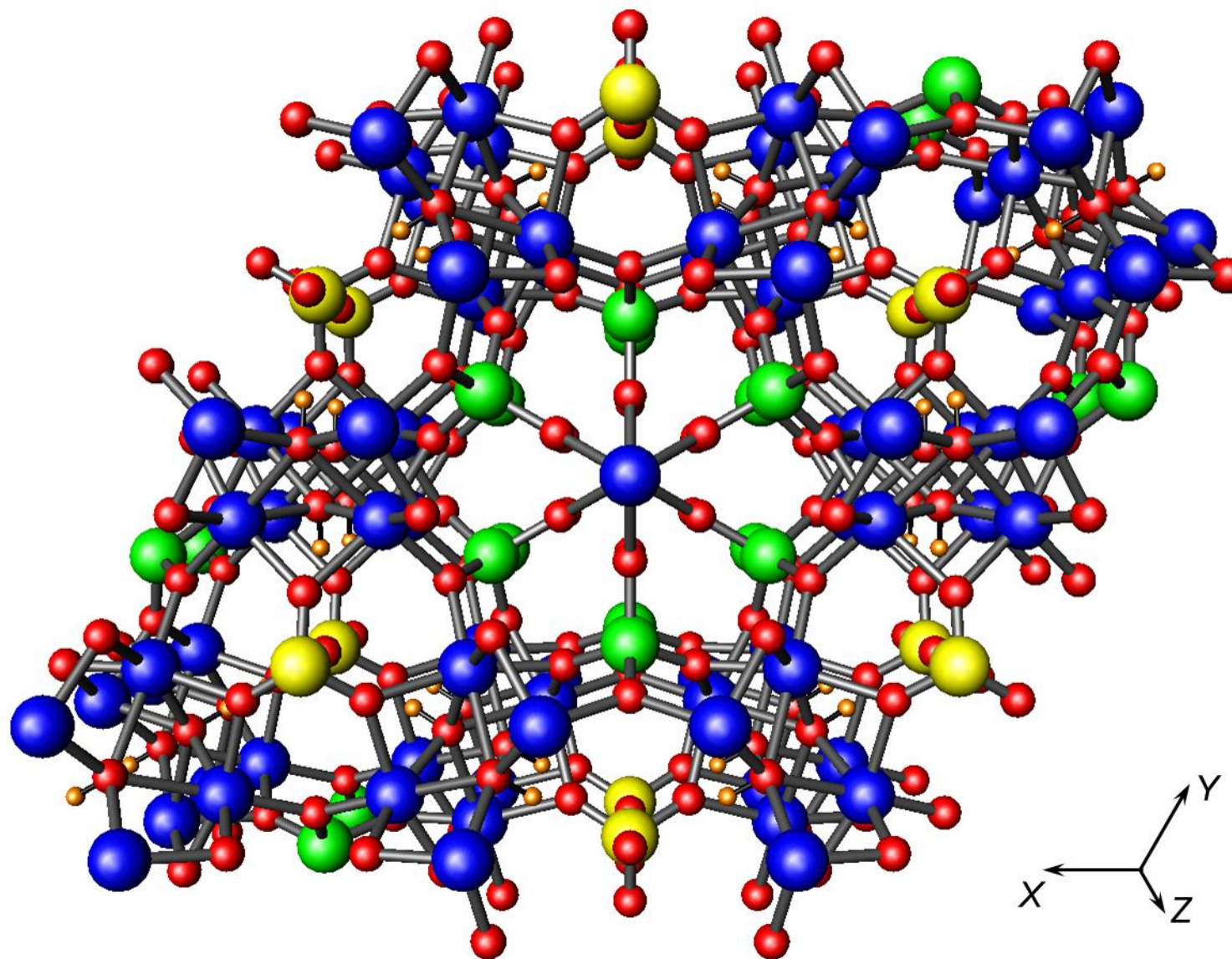
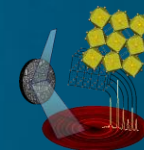


Figure 23.2. The model of the crystal structure of $\text{Mn}_7(\text{OH})_3(\text{VO}_4)_4$, derived from $\text{Zn}_7(\text{OH})_3(\text{VO}_4)_3\text{SO}_4$, assuming that Mn atoms substitute for Zn (*large blue spheres*), and V atoms occupy positions of both V (*large green spheres*) and S (*large yellow spheres*). Oxygen atoms are shown as medium-sized *red spheres* and hydrogen atoms are depicted using *small orange spheres*.

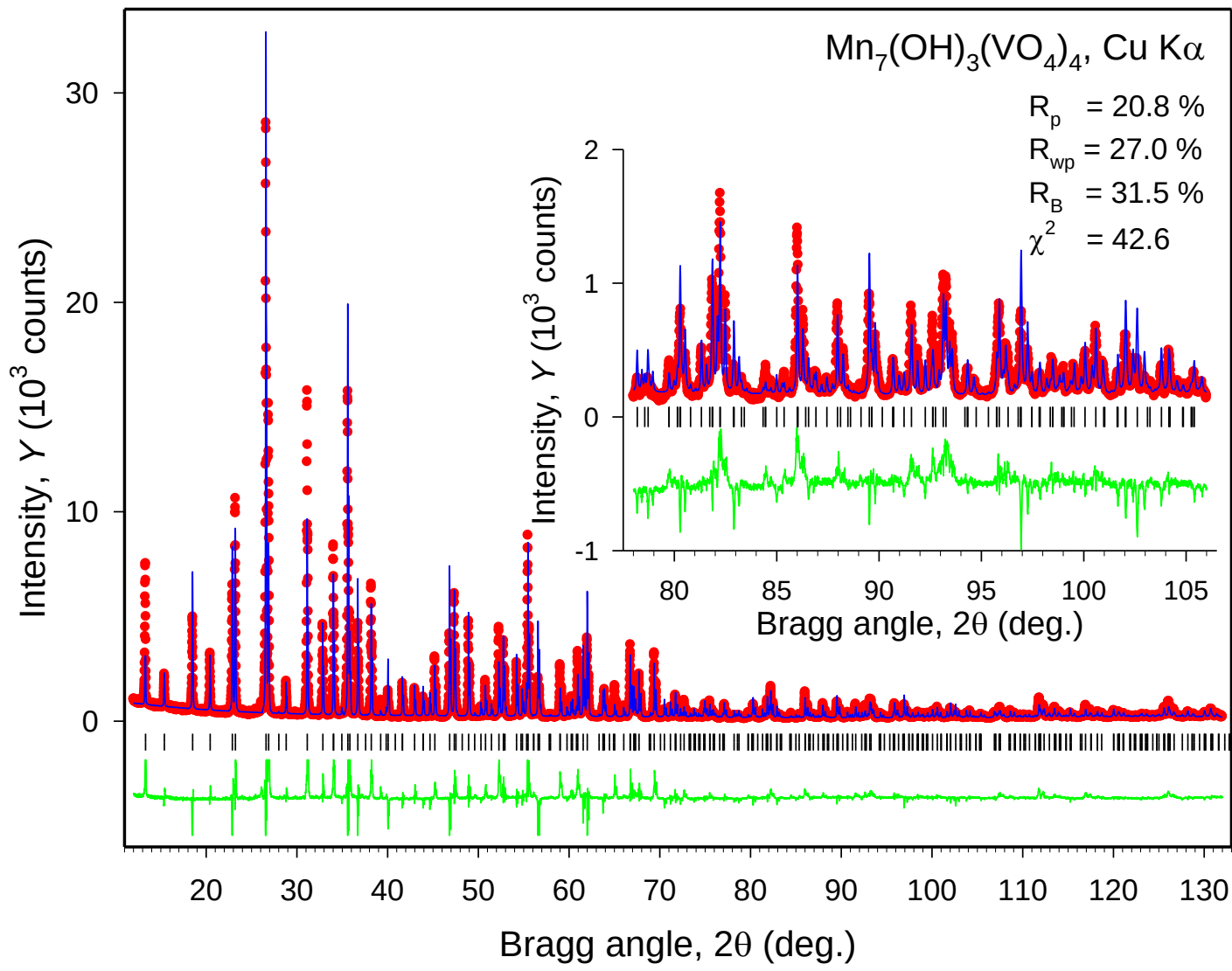
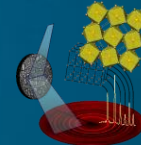


Figure 23.3. The observed and calculated diffraction patterns of $\text{Mn}_7(\text{OH})_3(\text{VO}_4)_4$ after the initial Rietveld minimization, where only the scale factor and the background were refined.

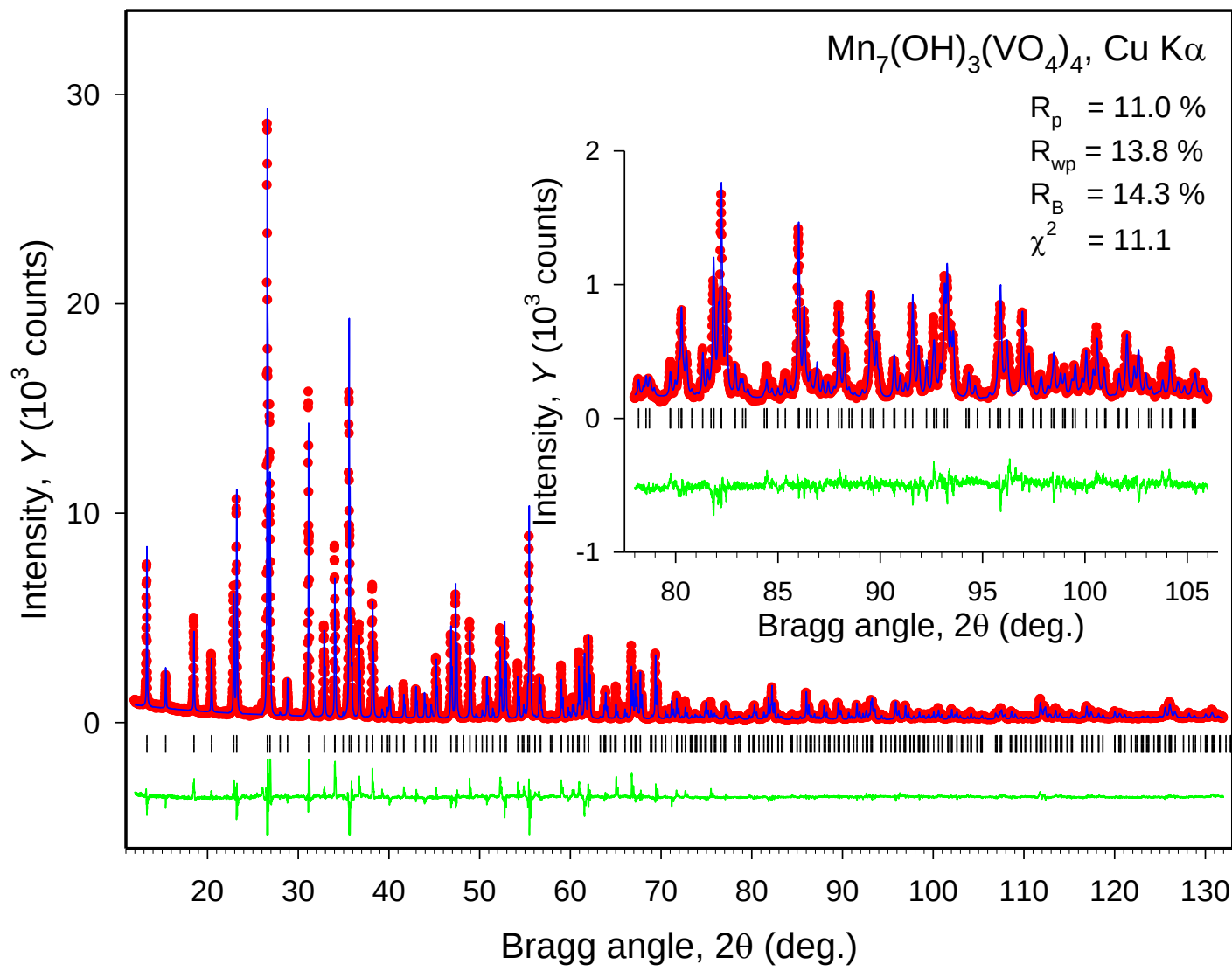
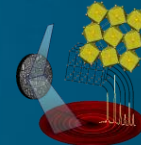


Figure 23.4. The observed and calculated diffraction patterns of $\text{Mn}_7(\text{OH})_3(\text{VO}_4)_4$ after refining preferred orientation, individual atomic parameters, and occupancies of Mn2, V2, and O6.

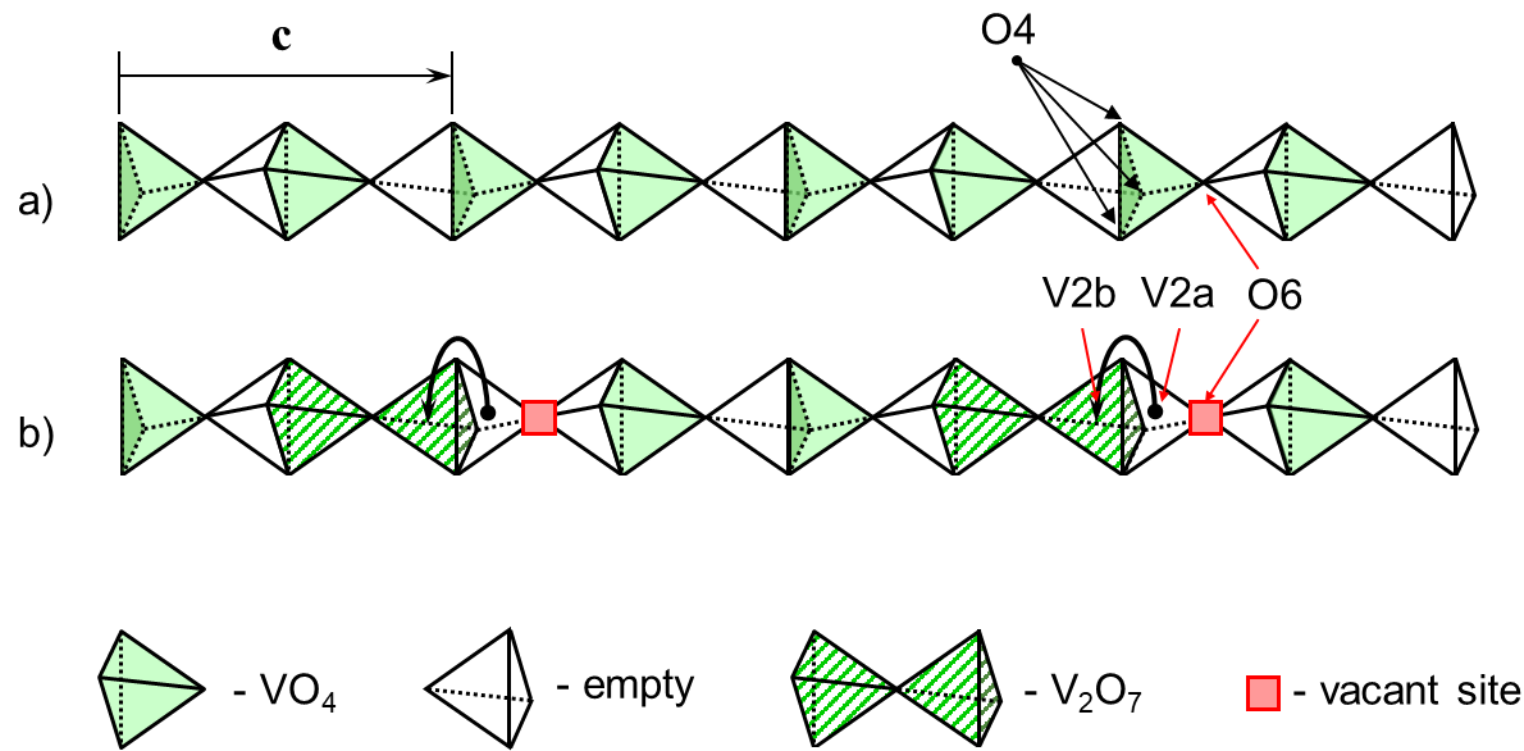
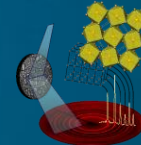


Figure 23.5. Chains of tetrahedra in the $\text{Mn}_7(\text{OH})_3(\text{VO}_4)_4$ structure. The fully ordered chain (a) with the composition VO_4 , where vanadium occupies every other tetrahedron (green), with the remaining are vacant (white). The disordered chain (b) shows some vanadium atoms occupy pairs of neighboring tetrahedra, forming V_2O_7 groups (hatched), thus creating vacancies on the O6 site (pink square) and resulting in the chemical composition $(\text{VO}_4)_{1-x}(\text{V}_2\text{O}_7)_{x/2}$.

$g_{\text{V2a}} + g_{\text{V2b}} = 1$, and in general, $g_{\text{V2a}} + g_{\text{V2b}} \leq 1$ **Eq. 23.1**

$g_{\text{V2a}} = g_{\text{O6}}$ **Eq. 23.2**

Example of computed shift for g_{V2a} of 0.02 affecting other parameters:

$g_{\text{V2a}} = g_{\text{V2a}} + 0.02,$
 $g_{\text{V2b}} = g_{\text{V2b}} - 0.02,$
 $g_{\text{O6}} = g_{\text{O6}} + 0.02$ **Eq. 23.3**

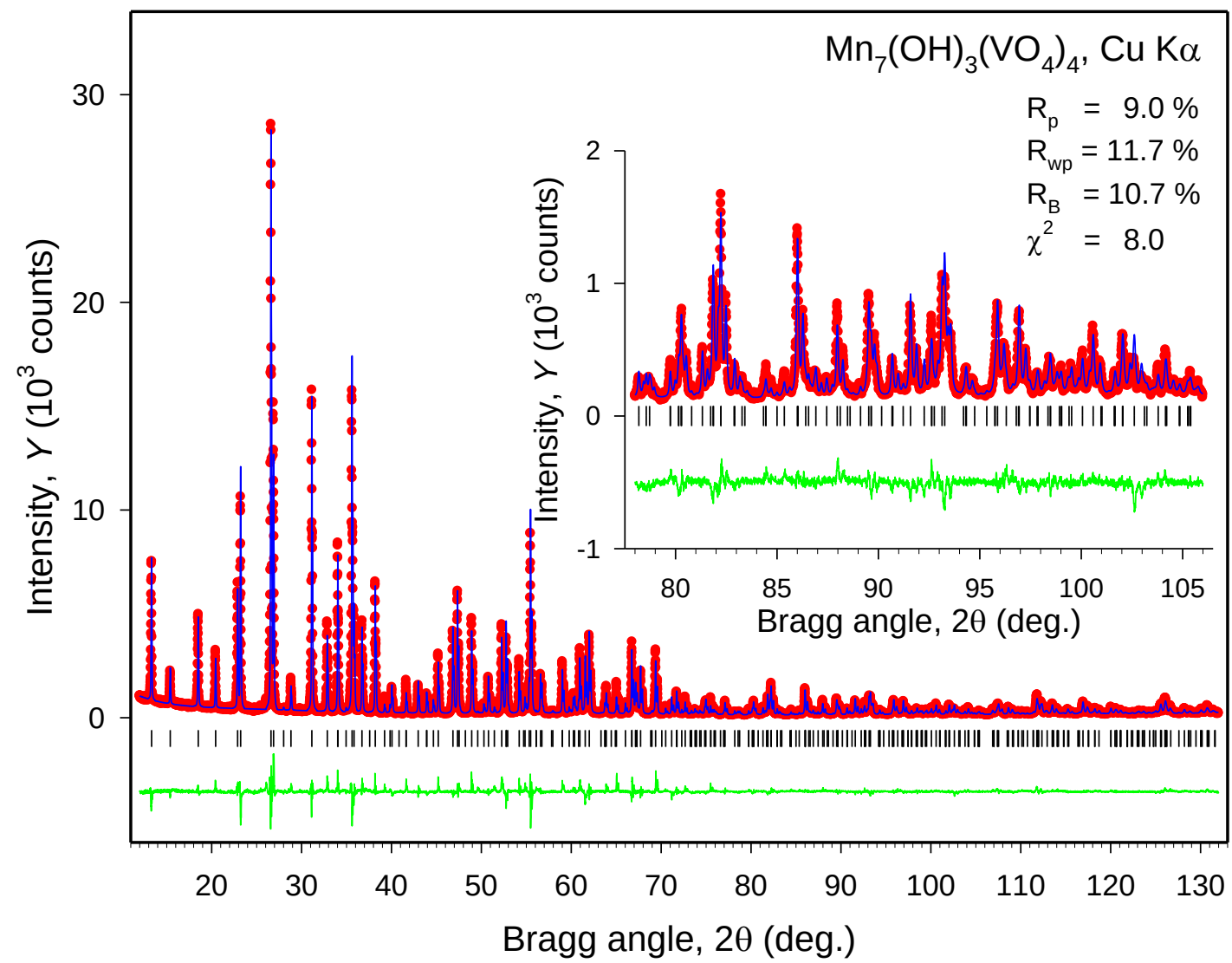
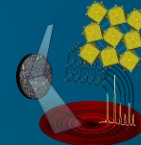
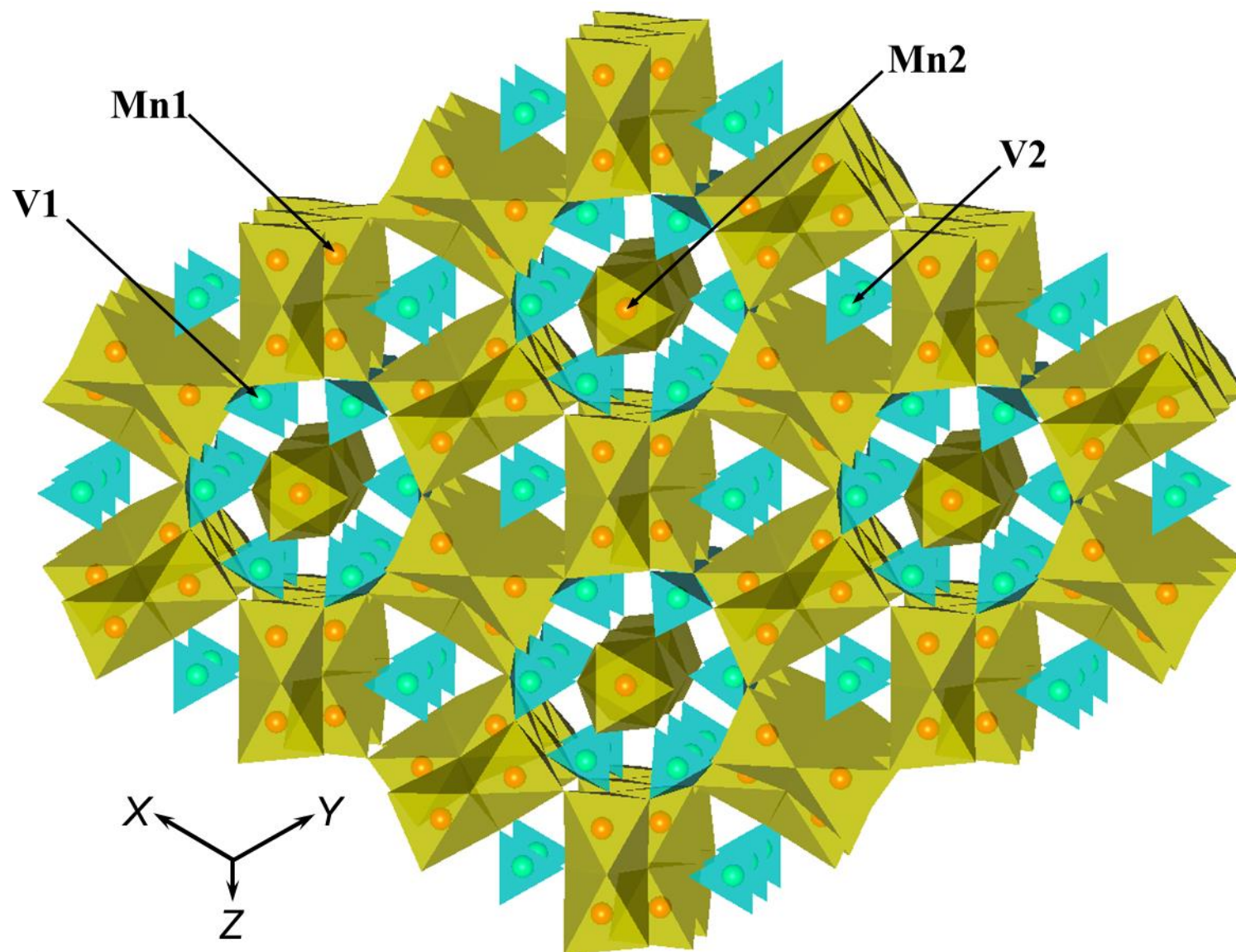
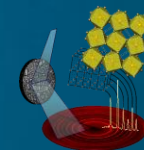
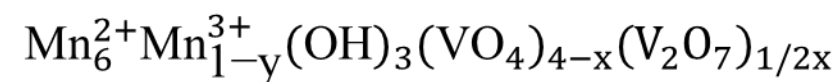


Figure 23.6. The final Rietveld plot of $\text{Mn}_7(\text{OH})_3(\text{VO}_4)_4$ data.



Final composition:



$$x = 0.181(4), y = 2/3 x$$

Figure 23.7. The model of the crystal structure of $\text{Mn}_{7-y}(\text{OH})_3(\text{VO}_4)_{4-x}(\text{V}_2\text{O}_7)_{x/2}$ shown along the Z-axis. The Mn1 sites (Mn^{2+}) and partially occupied Mn2 sites (Mn^{3+}) are shown as *orange spheres* inside the *golden* $[\text{MnO}_6]$ octahedra, while the V1 and V2 sites are shown as *green spheres* inside the *blue* $[\text{VO}_4]$ tetrahedra. Hydrogen atoms from the hydroxyl groups are not shown in this figure.