

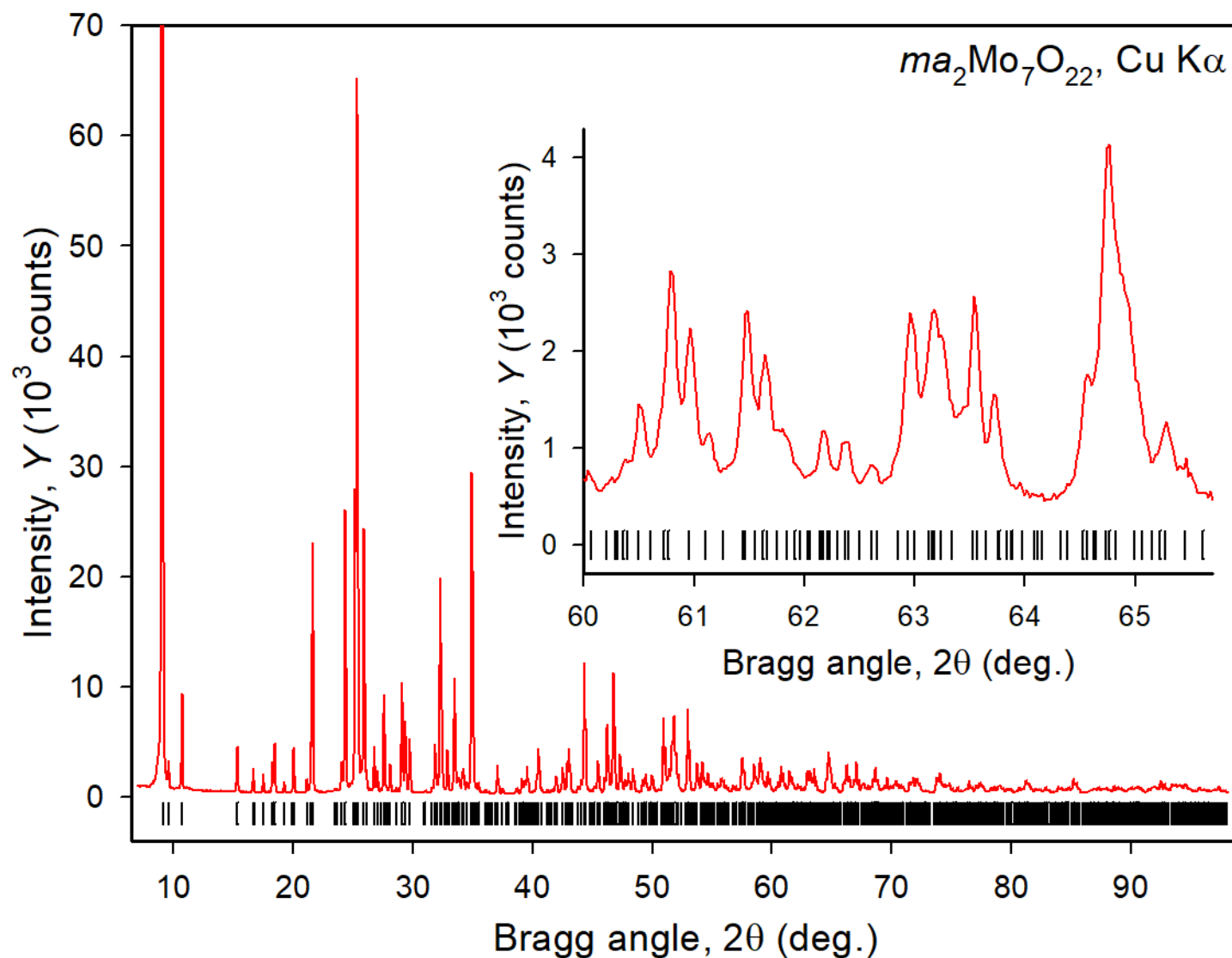
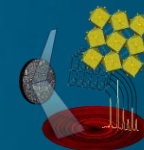


Figure 22.1. Powder diffraction pattern collected from a ground $ma_2Mo_7O_{22}$ powder using Cu K α radiation in step scan mode with a step size of 0.02° . The counting time was 30 sec/step in the range $7^\circ \leq 2\theta \leq 67^\circ$, and 60 sec/step for $67^\circ \leq 2\theta \leq 98^\circ$. The counting time was increased at higher Bragg angles to improve the counting statistics for a large number of weak Bragg peaks possible in this range.

The *vertical bars* indicate calculated positions of the $K\alpha_1$ components of all possible Bragg reflections. The inset shows an expanded view from 60° to 65.7° , which contains 76 possible reflections.

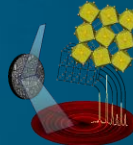


Table 22.1. Unit cell dimensions for Mo_7O_{22} – containing compounds found in the ICSD database.

Compound	a, Å	b, Å	c, Å	β , °	V, Å ³	ICSD	Ref.
Cs ₂ Mo ₇ O ₂₂	21.54(1)	5.537(3)	18.91(1)	122.71(3)	1897.7	1887	1
Tl ₂ Mo ₇ O ₂₂	20.512(6)	5.526(2)	19.460(6)	125.20(3)	1802.4	343	2
ma ₂ Mo ₇ O ₂₂	23.0648(6)	5.5134(2)	19.5609(5)	122.931(1)	2087.8		

[1] B.M. Gatehouse and B.K. Miskin, The crystal structures of cesium pentamolybdate, Cs₂Mo₅O₁₆, and cesium heptamolybdate, Cs₂Mo₇O₂₂, Acta Cryst. **31**, 1293 (1975). <https://doi.org/10.1107/S0567740875005080>

[2] P. Tolédano, M. Touboul, and P. Herpin, Structure cristalline de l’heptamolybdate de thallium(I), Tl₂Mo₇O₂₂, Acta Cryst. **B32**, 1859 (1976). <https://doi.org/10.1107/S0567740876006535>

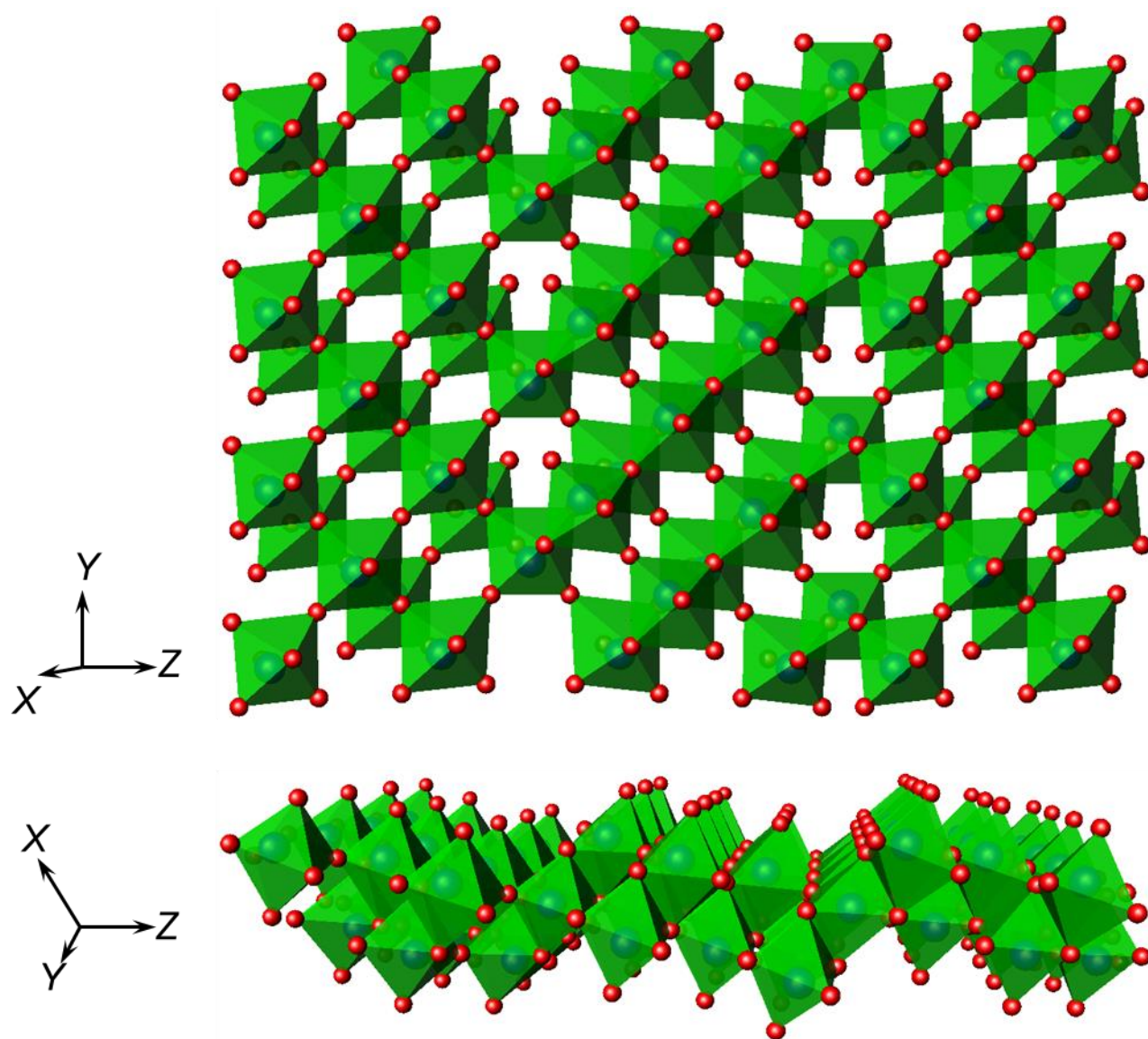
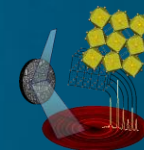


Figure 22.2. Metal oxide layer in the crystal structure of $ma\text{Mo}_7\text{O}_{22}$, shown in two different orientations. The Mo atoms are represented as *large dark spheres* inside the octahedra, and the O atoms are shown as *small red spheres*.

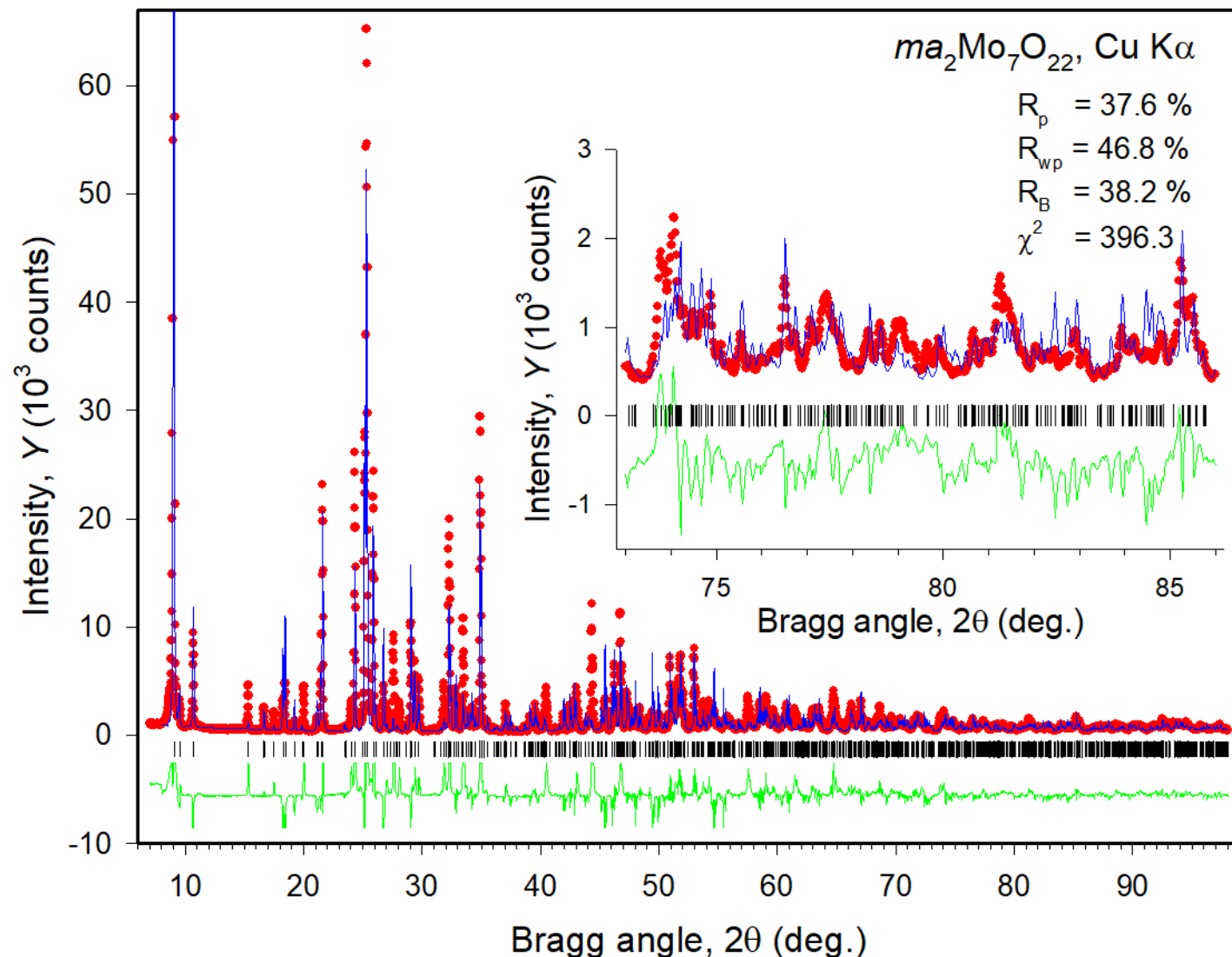
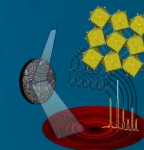


Figure 22.3. The observed and calculated powder diffraction patterns of $ma_2Mo_7O_{22}$ after the initial Rietveld least squares minimization with only the scale factor and the background refined.

The ordinate is reduced to $\sim 1/4$ of the maximum intensity to better illustrate low intensity Bragg peaks. The inset highlights the range between 73 and 86° 2θ .

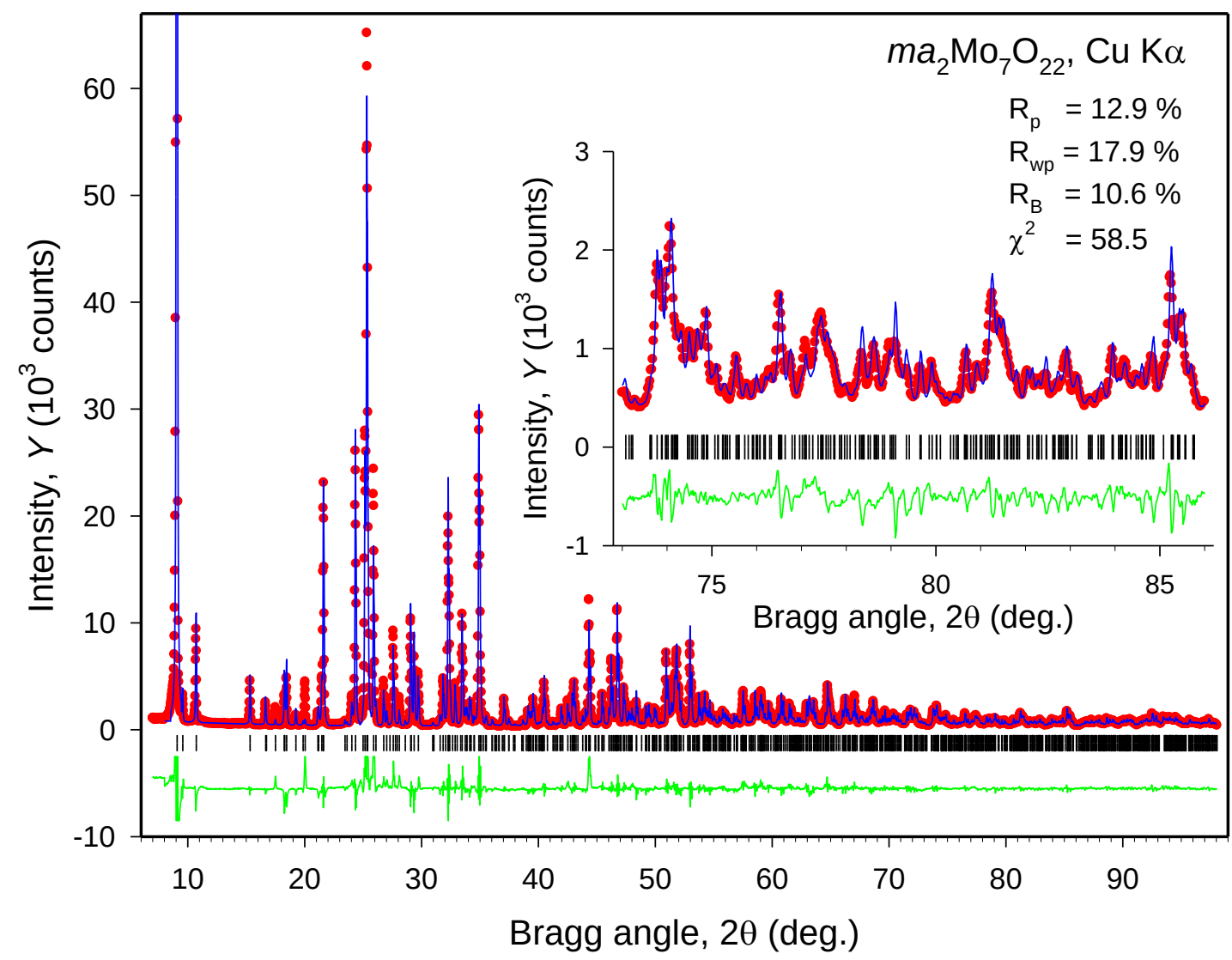
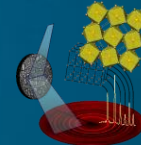


Figure 22.4. The observed and calculated powder diffraction patterns of $ma_2Mo_7O_{22}$ after accounting for preferred orientation. The individual atomic parameters of the Mo and O atoms were refined along with several profile parameters and correction for porosity effect.

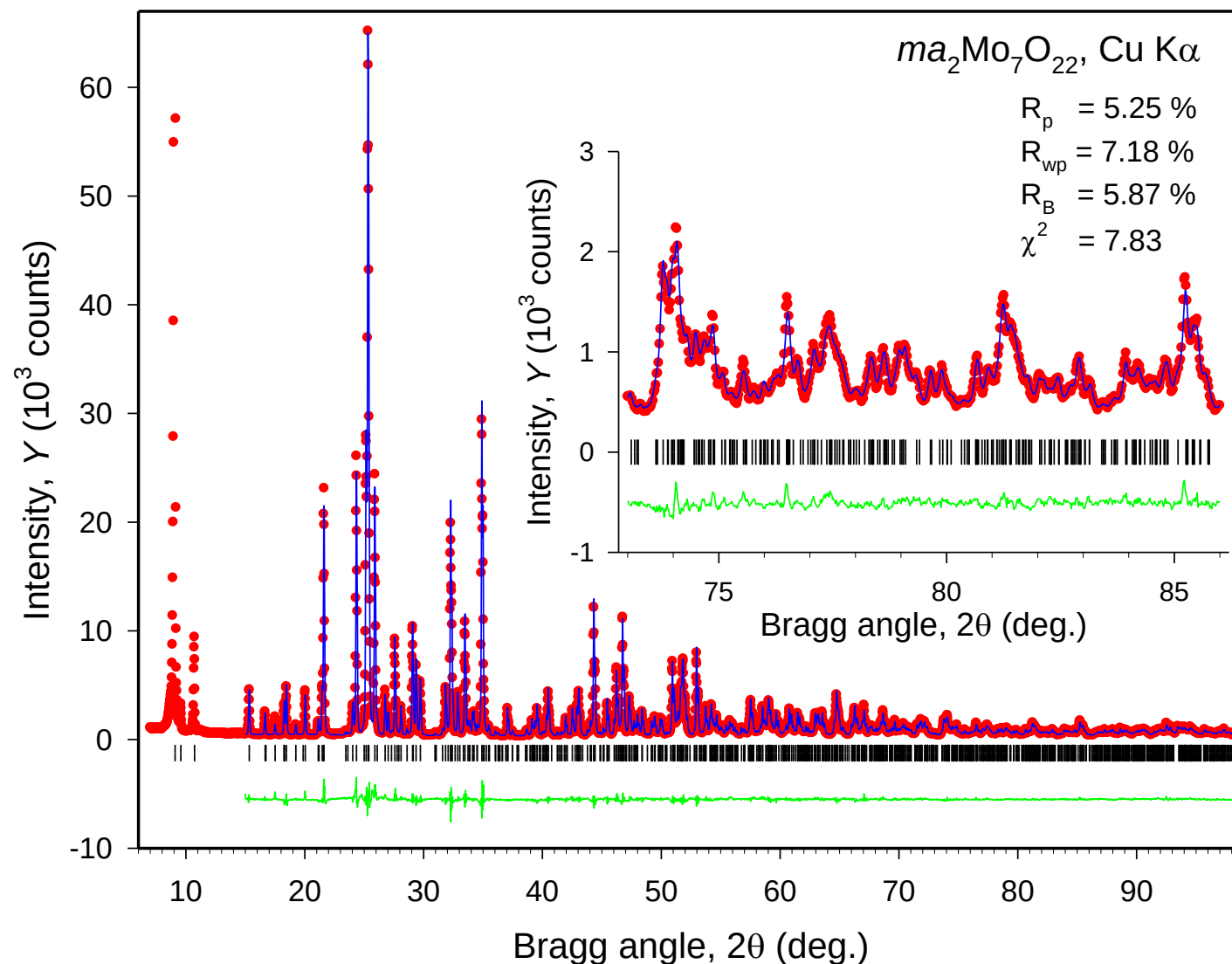
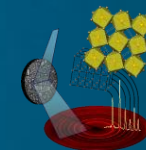


Figure 22.5. The final Rietveld plot of $ma_2Mo_7O_{22}$ refinement. The range below $15^\circ 2\theta$ was excluded from the final refinement due to the presence of an extremely strong peak – nearly an order of magnitude stronger than all other peaks. This peak is highly susceptible to various experimental errors and could significantly distort the least-squares minimization.

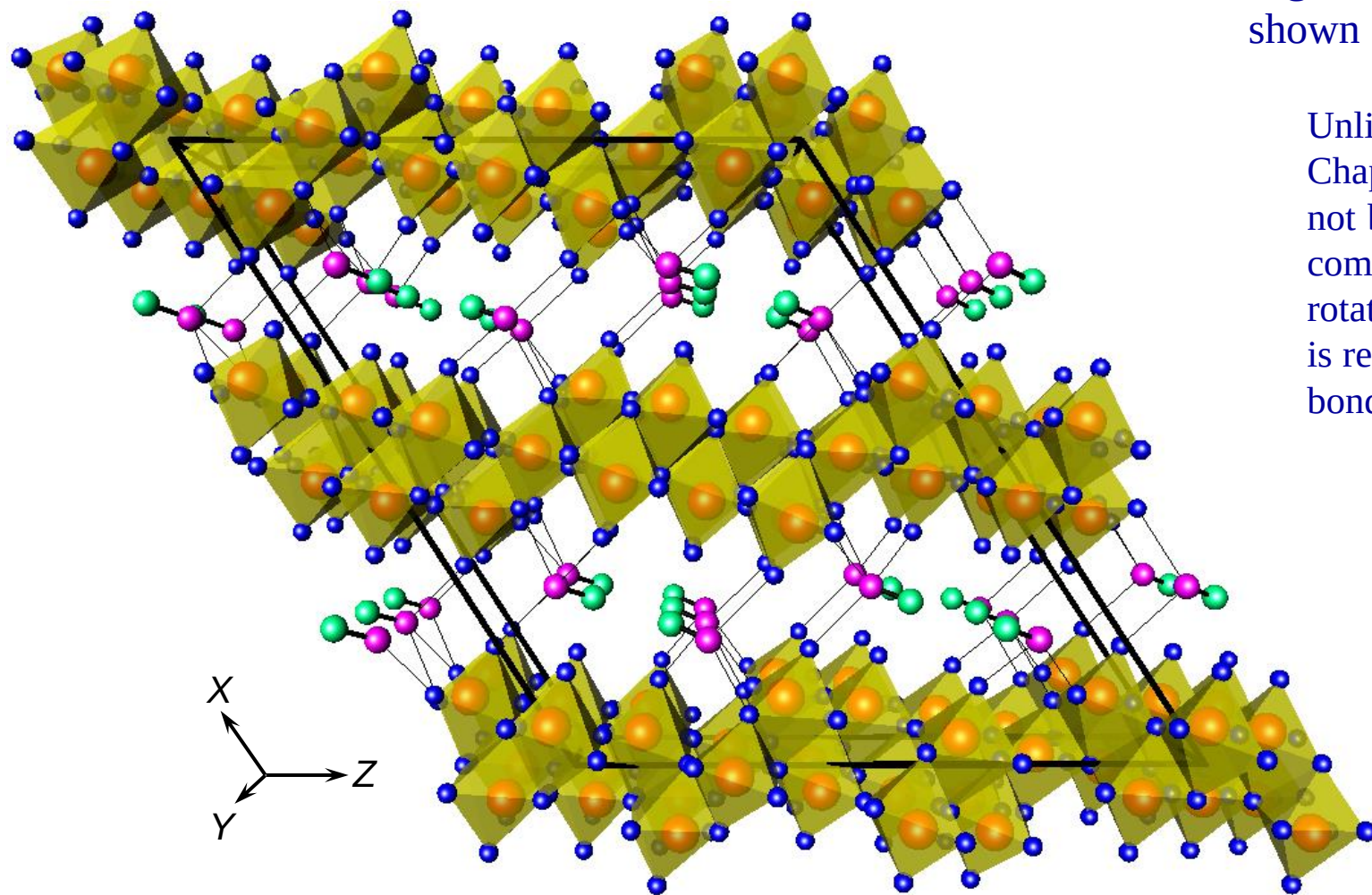
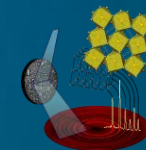


Figure 22.6. The crystal structure of $ma_2Mo_7O_{22}$ shown along the Y-axis in a perspective view.

Unlike in the crystal structure of the $tmaV_3O_7$ (see Chap. 21), the coordinates of hydrogen atoms could not be located from Fourier maps nor can be easily computed because the methylammonium ion can rotate around the C–N bond, although this rotation is restrained by the formation of N–H $\cdots$ O hydrogen bonds, which can be used to predict their location.

The Mo atoms are depicted as *large orange spheres* inside translucent octahedra formed by oxygen atoms (*small blue spheres*). The N atoms are shown as *magenta spheres*, and the C atoms as *green spheres*. The N–[H] $\cdots$ O hydrogen bonds are shown using *thin lines*, without depicting the hydrogen atoms.