

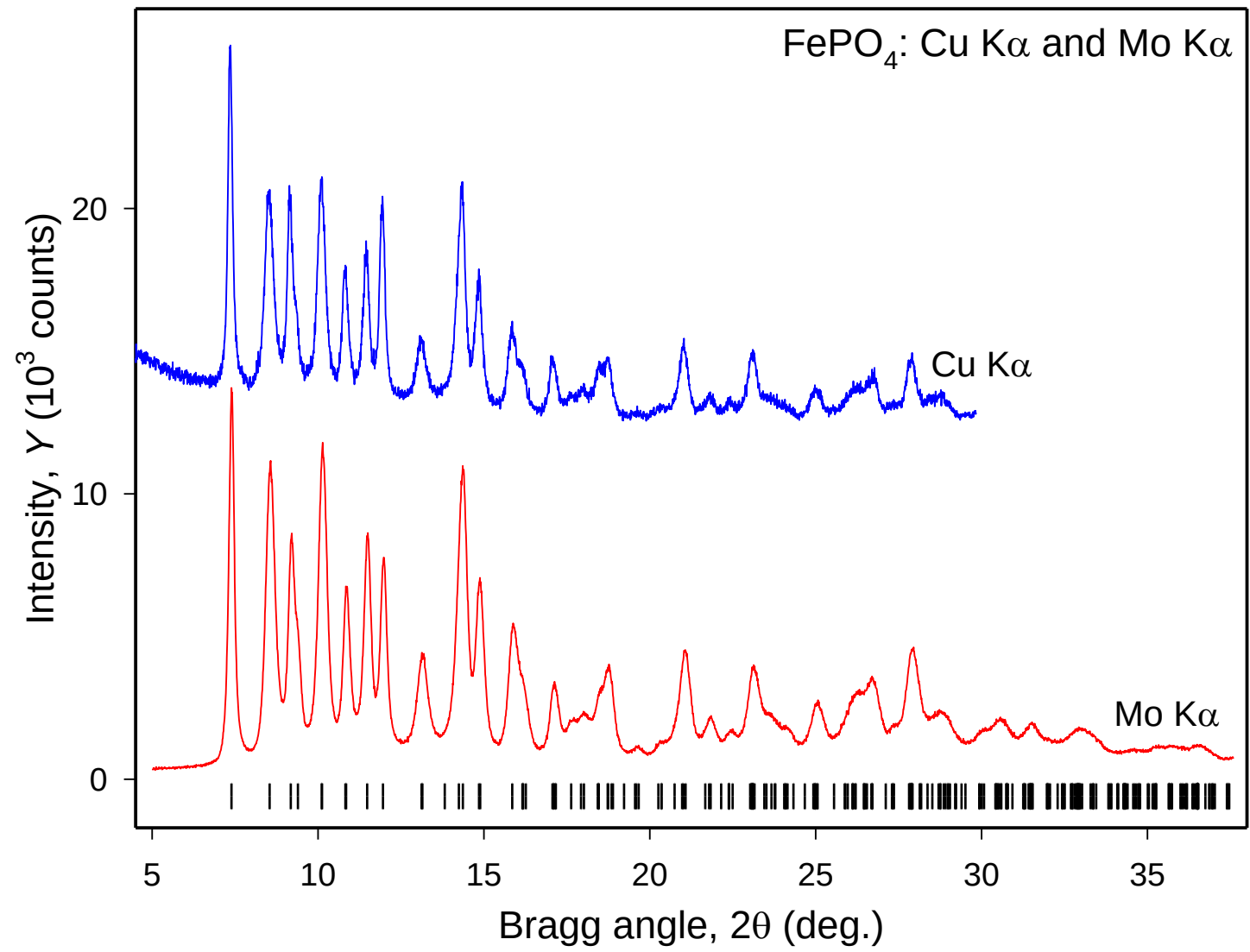
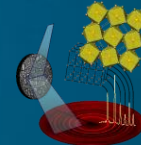


Figure 24.1. Powder diffraction patterns collected from monoclinic FePO₄ using Cu Kα radiation (*top*) and Mo Kα radiation on a rotating anode Rigaku TTRAX diffractometer (*bottom*). Bragg angles in the pattern collected using Cu Kα radiation have been converted to match Mo Kα radiation. The *vertical bars* indicate calculated positions of Bragg reflections for the locations of Kα₁ components.

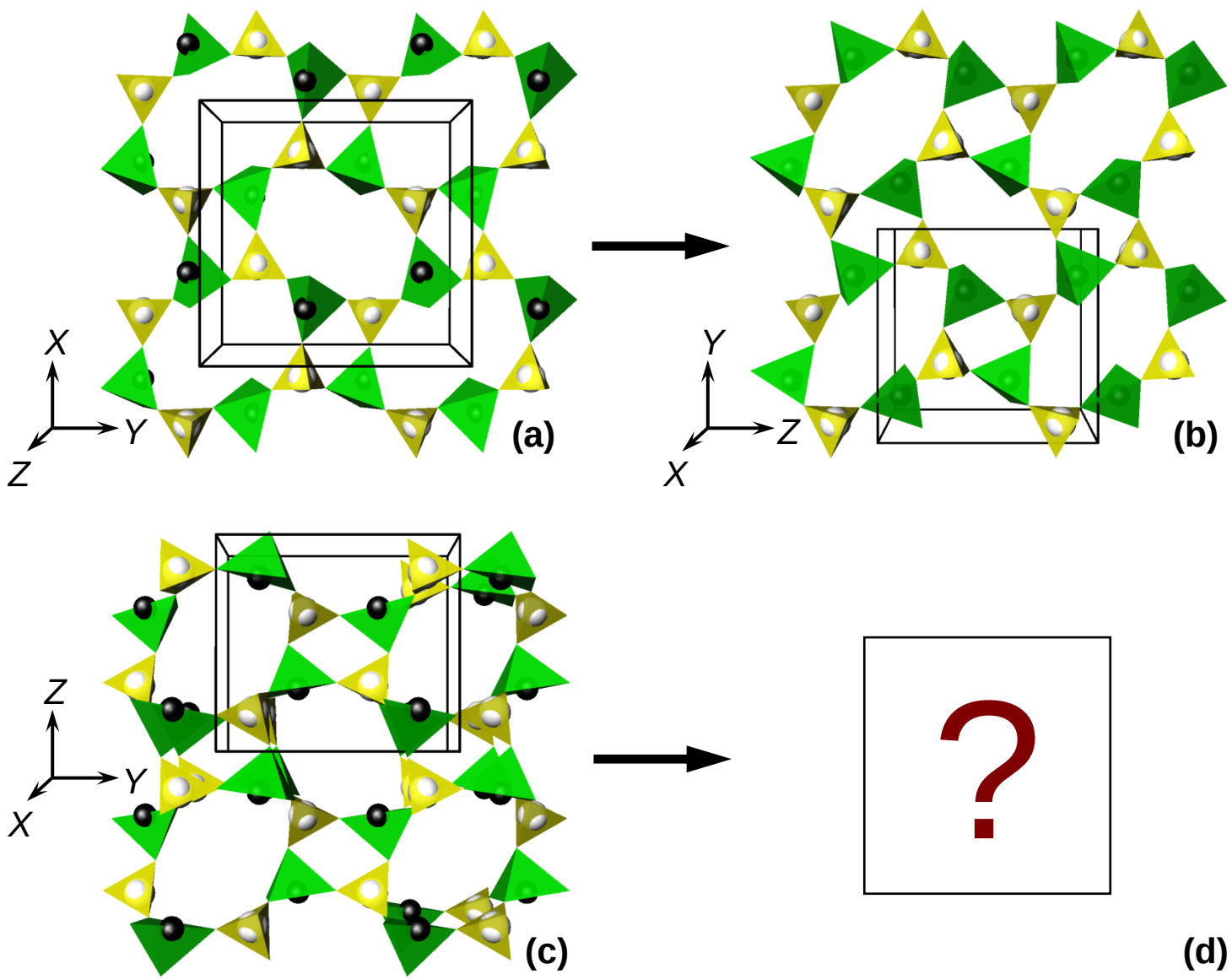
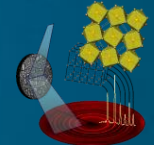


Figure 24.2. Analogy between the crystal structures of orthorhombic hydrate $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (a) and anhydrous orthorhombic FePO_4 (b) motivates the use of the monoclinic hydrate $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ structure (c) as the initial model for monoclinic anhydrous FePO_4 (d). The crystal structures are shown as packing of the corresponding $[\text{XO}_4]$ polyhedra of iron (*black spheres inside green tetrahedra*) and phosphorus (*white spheres inside yellow tetrahedra*) atoms without the oxygen atoms from water molecules that complete the coordination polyhedra of iron in the hydrates. Oxygen atoms are in the corners of the polyhedra.

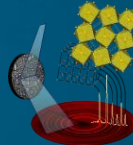


Table 24.1. The comparison of unit cell dimensions of the orthorhombic and monoclinic modifications of hydrated and anhydrous iron phosphates.

Compound	Space group	a, Å	b, Å	c, Å	β, deg.	V, Å ³
FePO ₄ ·2H ₂ O	Pbca	9.867	10.097	8.705	-	867.3
FePO ₄	Pbca	9.171	9.456	8.675	-	752.4
FePO ₄ ·2H ₂ O	P2 ₁ /n	5.307	9.755	8.675	90.16	449.1
FePO ₄	P2 ₁ /n	5.489	7.493	8.055	95.81	329.7

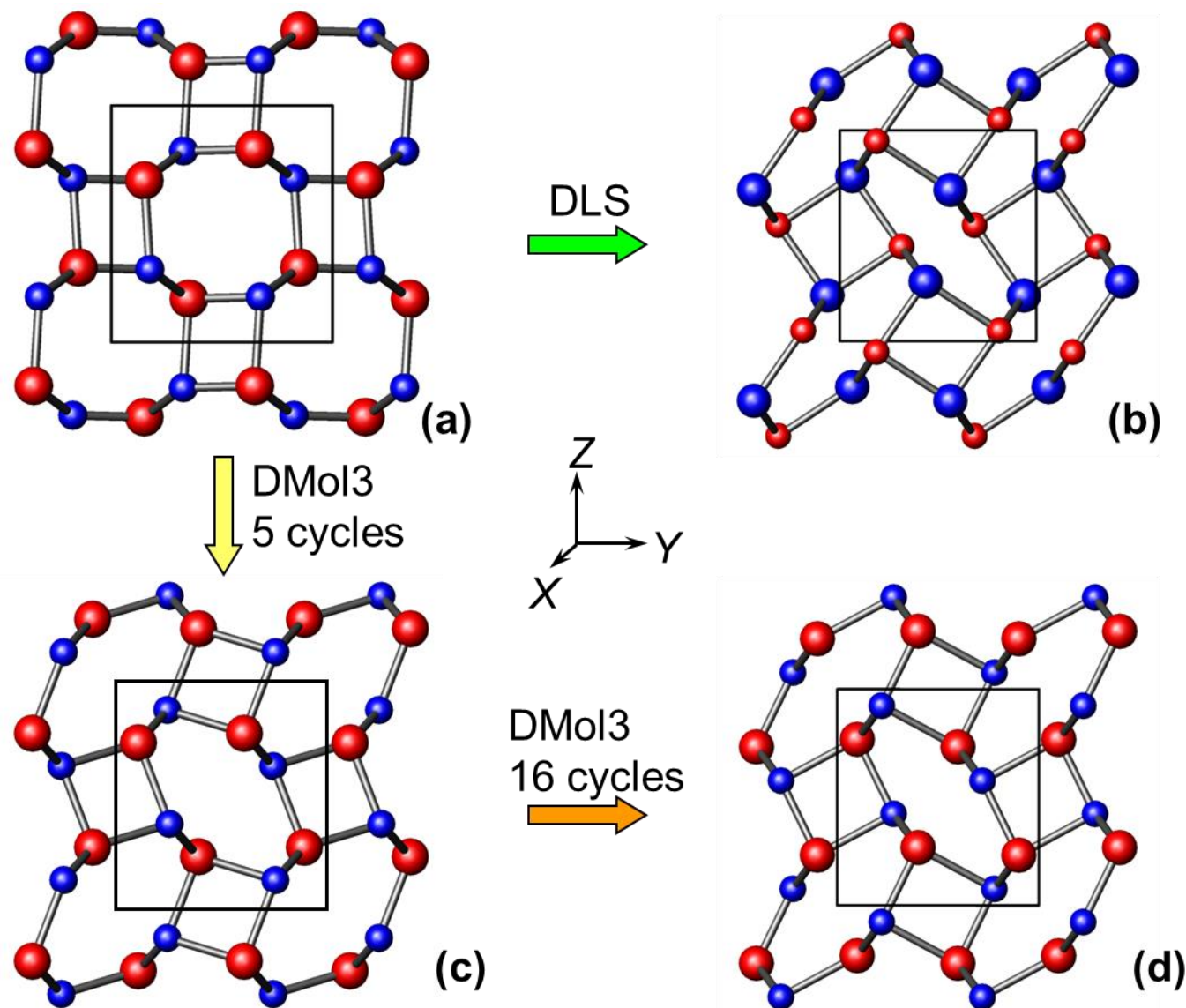
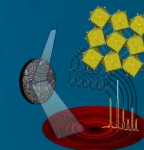


Figure 24.3. Back-bone models of the crystal structure of the anhydrous monoclinic FePO_4 projected along the X-axis: the initial Model A derived from the monoclinic hydrate $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (a); Model B1 after five optimization cycles as AlPO_4 using DMol3 (c); Model B after final optimization as AlPO_4 (16 cycles) using DMol3 (d); Model C optimized using DLS-76 (b).

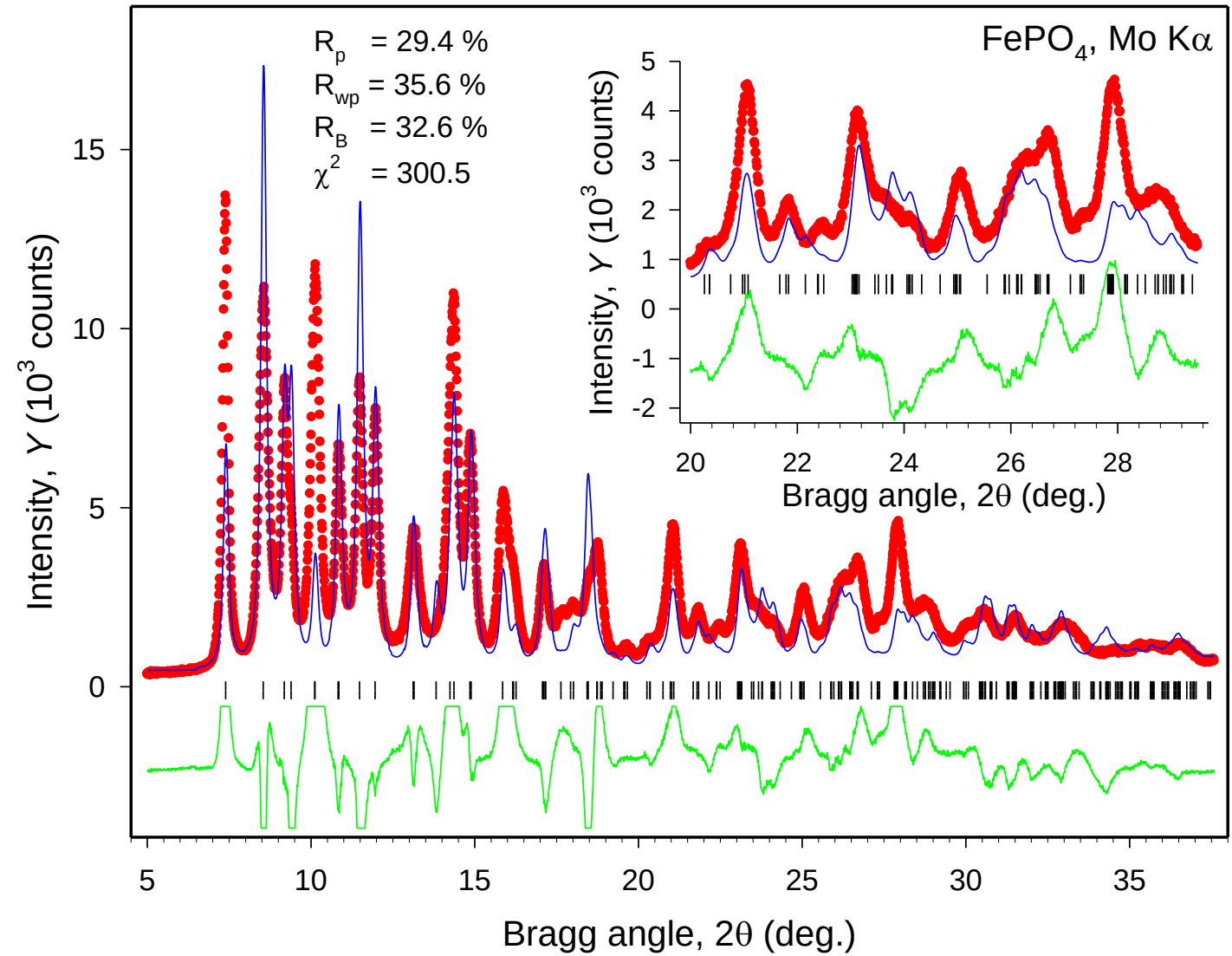
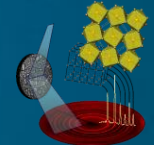


Figure 24.4. The observed and calculated powder diffraction patterns of anhydrous FePO₄ after the initial Rietveld least-squares minimization with only the scale factor and linear background refined.

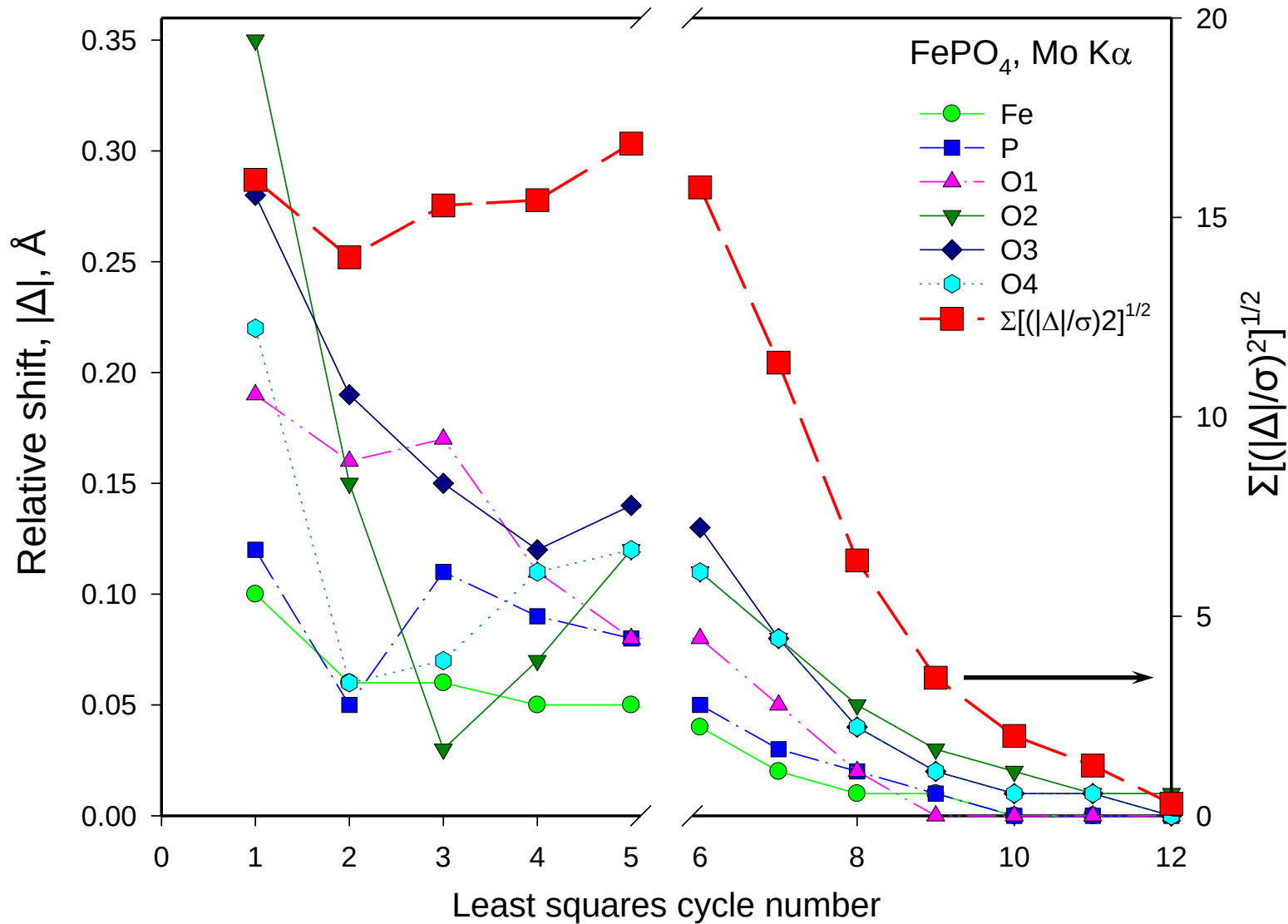
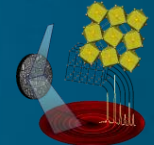


Figure 24.5. Relative shifts of individual atoms (left-hand scale) and the average shift-to-standard deviation (Δ/σ) ratio during the first 12 cycles of least-squares refinement of atomic coordinates in the crystal structure model of anhydrous monoclinic FePO₄. Both the P–O distances and O–P–O angles were restrained with a weight of four during the initial five cycles. The weight was increased to 10 starting from cycle 6. The initial five cycles show erratic shifts for the P and O atoms. From the sixth cycle onward, the shifts of all atoms steadily decrease and approach zero after cycle 12.

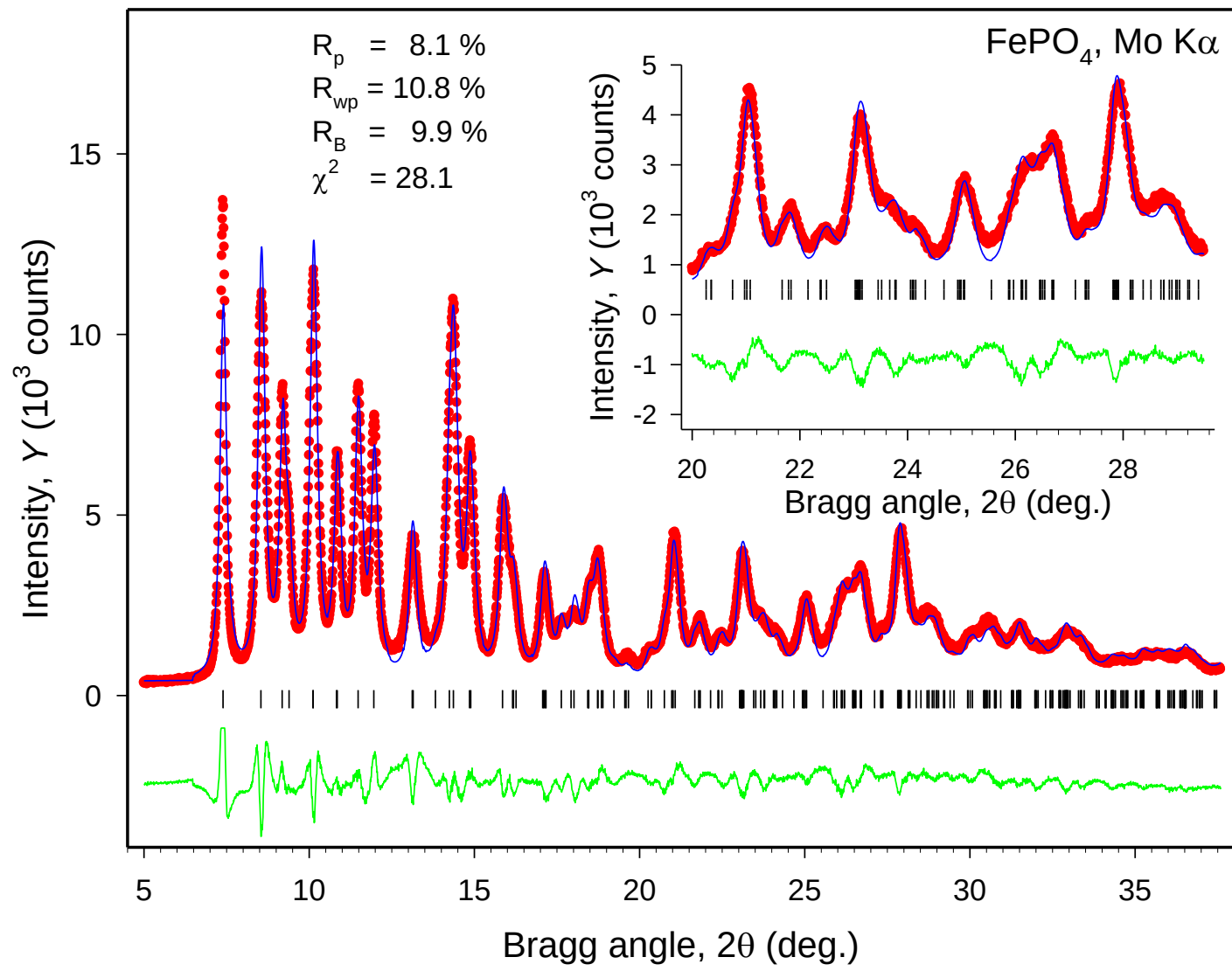
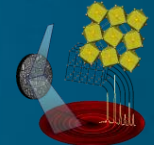


Figure 24.6. The observed and calculated powder diffraction patterns of anhydrous FePO₄ after the refinement of atomic coordinates, restrained to match the ideal geometry of the PO₄ group with a weight of 10, along with linear background, preferred orientation, grain-size peak broadening parameter, and unit cell dimensions.

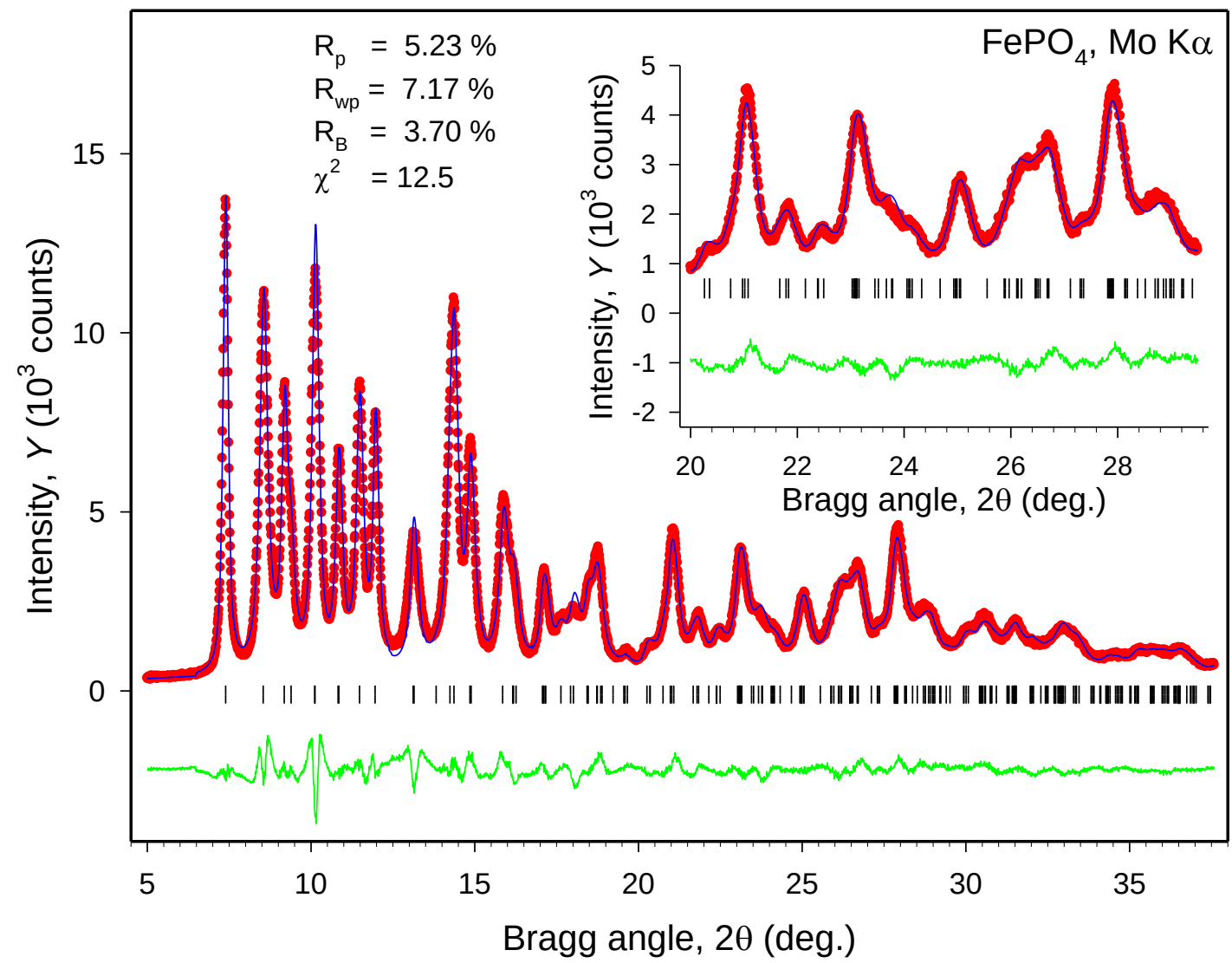
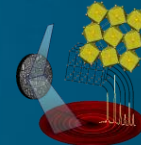


Figure 24.7. The final Rietveld plot of FePO₄ data. The inset highlights the details between 20° and ~29° 2θ. The true background is quite difficult to determine due to heavily overlapped Bragg peaks, especially at 2θ > 20°.

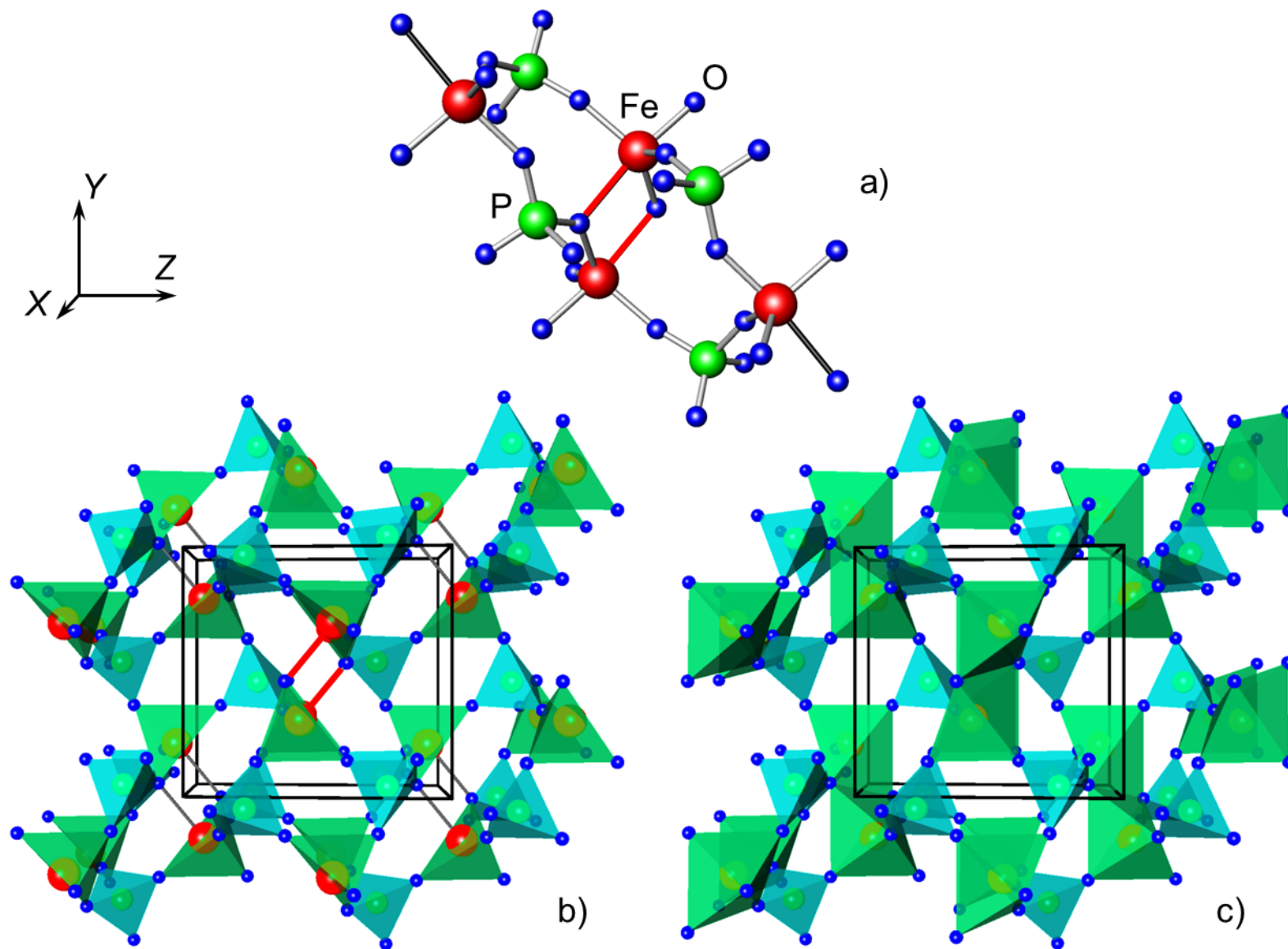
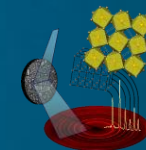


Figure 24.8. The crystal structure of monoclinic anhydrous FePO_4 shown along the X -axis in various representations.

- a) The bipyramid of alternating Fe (red spheres) and P (green spheres) atoms with weak Fe–O bonds (thick red lines).
- b) The packing of the distorted $[\text{FeO}_4]$ (green) and nearly ideal $[\text{PO}_4]$ (blue-gray) tetrahedra.
- c) The packing of the stretched $[\text{FeO}_5]$ trigonal bipyramids (green) and $[\text{PO}_4]$ (blue) tetrahedra.