

# Precise Characterization of the Rich Structural Landscape Induced by Pressure in Multifunctional FeVO<sub>4</sub>

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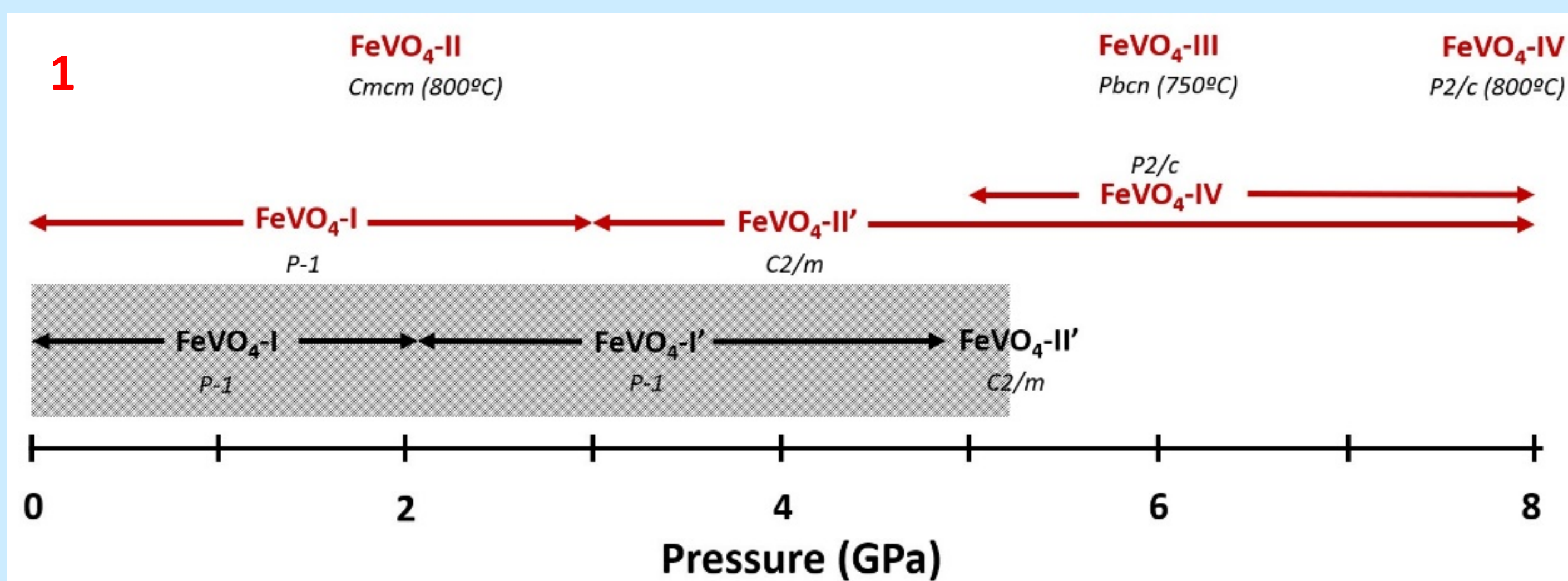
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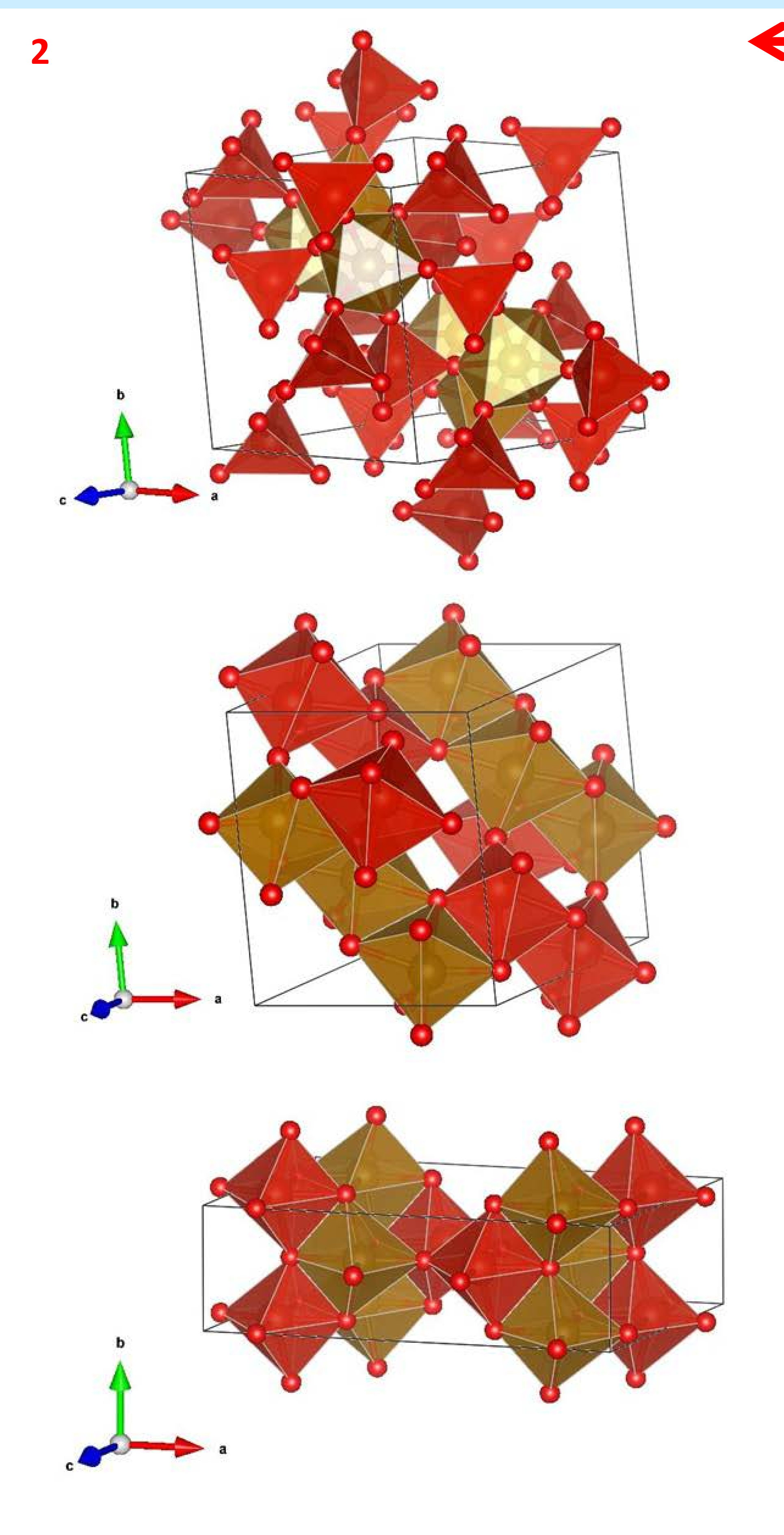
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We studied the HP behavior of FeVO<sub>4</sub> by means of single-crystal XRD and DFT calculations. We found that the structural sequence of FeVO<sub>4</sub> is different than previously assumed. In particular, we discovered a new HP phase at 2.11(4) GPa (FeVO<sub>4</sub>-I') which was not detected by previous studies. We determined that FeVO<sub>4</sub>, under compression (at RT) first transforms at 2.11(4) GPa from the ambient-pressure triclinic structure (FeVO<sub>4</sub>-I) to a second previously-unknown triclinic structure (FeVO<sub>4</sub>-I'), which experiences a subsequent phase transition at 4.80(4) GPa to a monoclinic structure (FeVO<sub>4</sub>-II'). Single-crystal XRD has enabled these novel findings and an accurate determination of the crystal structure of HP FeVO<sub>4</sub> polymorphs. The crystal structure of all polymorphs was accurately solved at all measured pressures. The pressure dependence of the unit-cell parameters, RT EOS, and polyhedral coordination were obtained. The structural phase transition detected at 2.11(4) GPa implies abrupt coordination modifications. DFT calculations support the conclusions extracted from experiments.

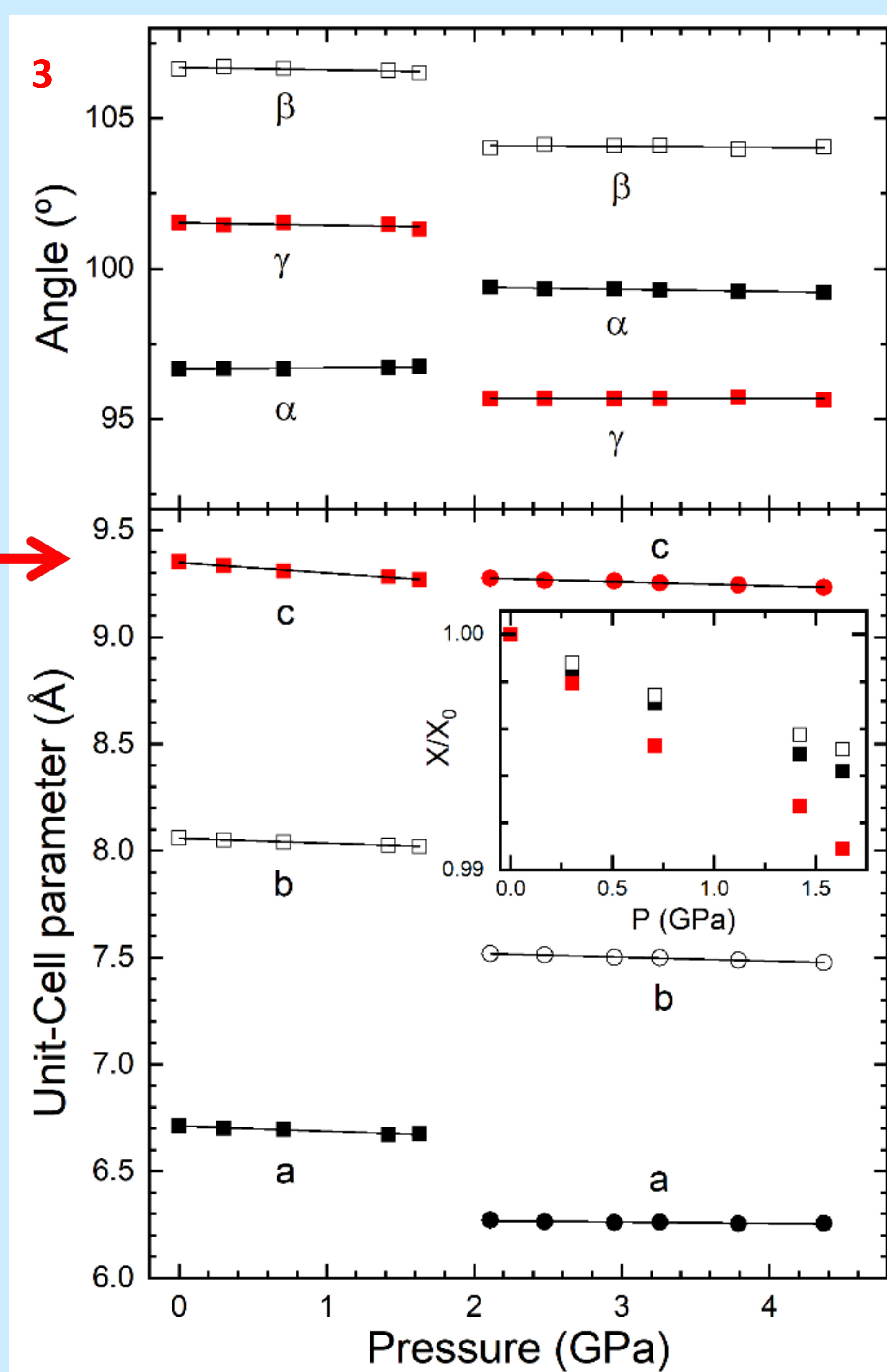
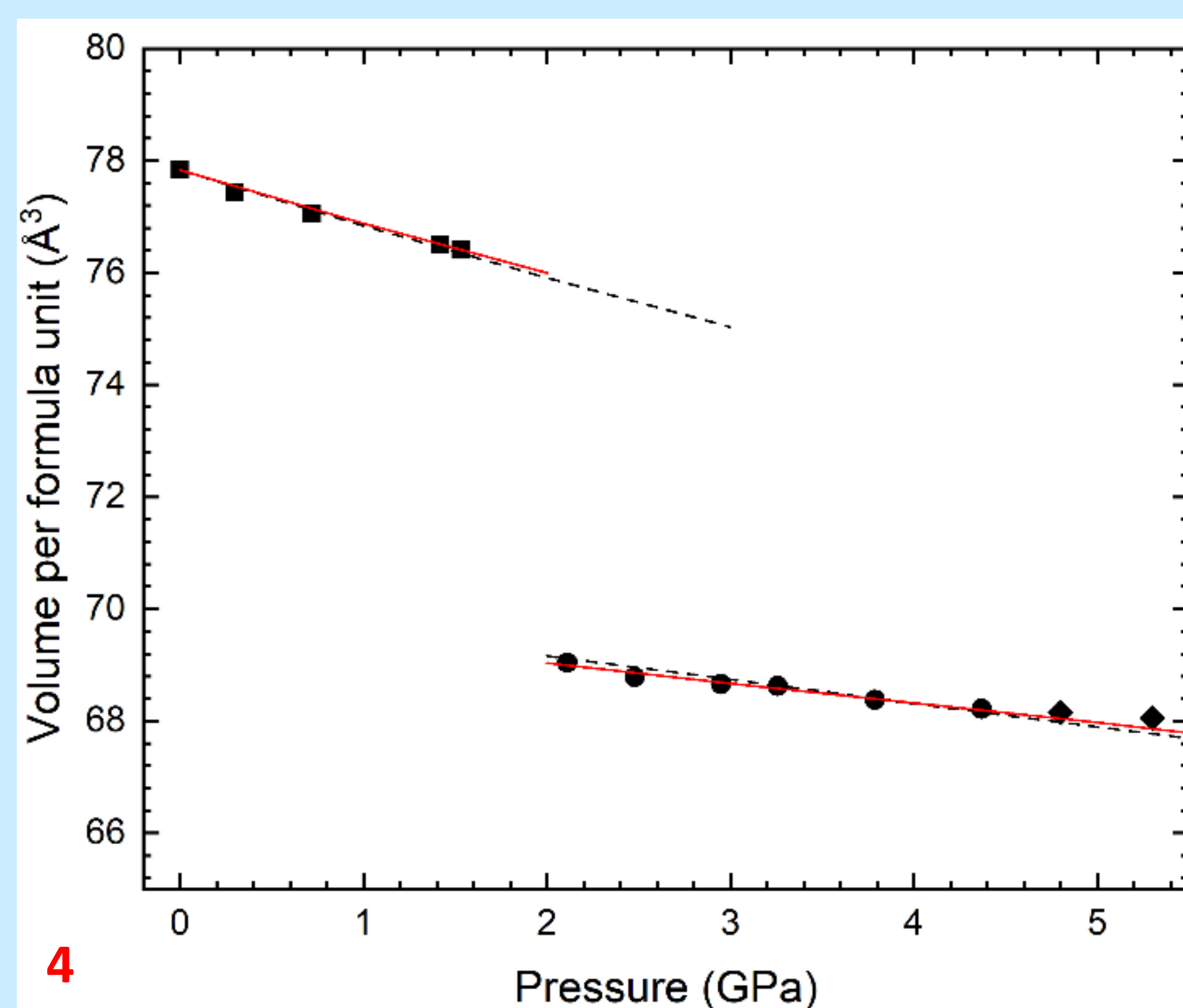


1. Schematic representation of the rich polymorphism of FeVO<sub>4</sub> indicating the pressure-temperature conditions where each polymorph has been found. In the top, we show the results of ex-situ HP-HT studies. The red lines in the center are from previous RT-HP experiments and the black lines in the bottom are from the present study. Pressure is indicated at the bottom of the figure.



2. Crystal structure of FeVO<sub>4</sub>-I (top), HP FeVO<sub>4</sub>-I' (center), and HP FeVO<sub>4</sub>-II' (bottom). Fe (V) coordination polyhedra are shown in brown (red). Red spheres are oxygen atoms.

3. Pressure dependence of unit-cell parameters of FeVO<sub>4</sub>-I and FeVO<sub>4</sub>-I'. Symbols are from experiments and lines are linear fits. The inset shows the relative change of unit-cell parameters with pressure in FeVO<sub>4</sub>-I. We used red color for c/c<sub>0</sub>, white color for b/b<sub>0</sub>, and black color for a/a<sub>0</sub>.



4. Pressure dependence of the unit-cell volume of the three polymorphs of FeVO<sub>4</sub>. FeVO<sub>4</sub>-I is represented by squares; FeVO<sub>4</sub>-I' by circles, and FeVO<sub>4</sub>-II' by diamonds. The red solid lines are the EOSs here determined for FeVO<sub>4</sub>-I and FeVO<sub>4</sub>-I'. The dashed black lines are the EOSs determined from powder XRD for FeVO<sub>4</sub>-II'.

| EOS Parameters (2nd order) |  |                              |
|----------------------------|--|------------------------------|
| FeVO <sub>4</sub> -I       | V <sub>0</sub> = 77.82(4) Å <sup>3</sup> | K <sub>0</sub> = 80(4) GPa   |
| FeVO <sub>4</sub> -I'      | V <sub>0</sub> = 66.6(2) Å <sup>3</sup>  | K <sub>0</sub> = 180(20) GPa |
| FeVO <sub>4</sub> -II'     | V <sub>0</sub> = 66.7(1) Å <sup>3</sup>  | K <sub>0</sub> = 145(5) GPa  |

## Conclusions

- Using single-crystal XRD and DFT calculations we have shown that the HP structural behavior of multifunctional FeVO<sub>4</sub> is more complex than believed before.
- We found evidence of the existence of a new triclinic polymorph (FeVO<sub>4</sub>-I') which is stable from 2.11(4) GPa to 4.37(4) GPa. Its crystal structure has been solved as well as the structure of FeVO<sub>4</sub>-II', a monoclinic polymorph found beyond 4.80(4).
- Room-temperature equations of state have been determined for the different polymorphs (see Table).
- The HP phases are considerably less compressible than the low-pressure phase (see Table).
- The transition from FeVO<sub>4</sub>-I to the new HP FeVO<sub>4</sub>-I' phase causes a large volume collapse and a change in the cationic coordination.
- The structural changes associated with the phase transition at 2.11(4) GPa cause a color change of FeVO<sub>4</sub>, which suggests a collapse of the band gap.

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