

***Supporting Information:* Elucidating Structure–Spectral Properties Relationships of Negative Thermal Expansion $\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$: A First–Principles Study with Experimental Validation**

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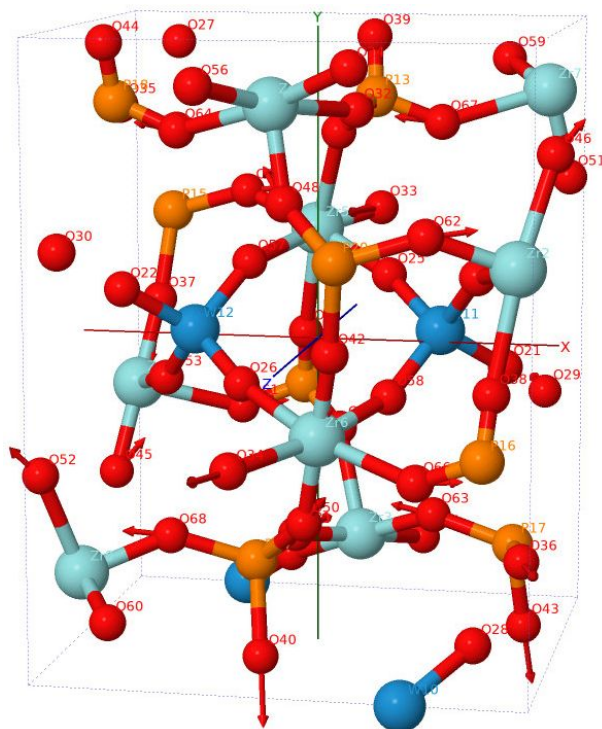
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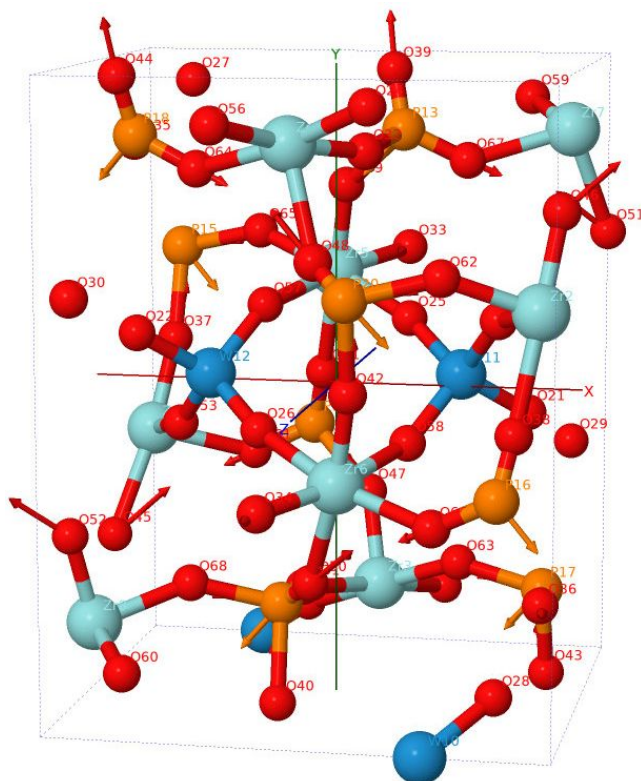
S1. IR- and Raman-Active Vibrational Modes

S1.1. Major IR-Active Vibrational Modes

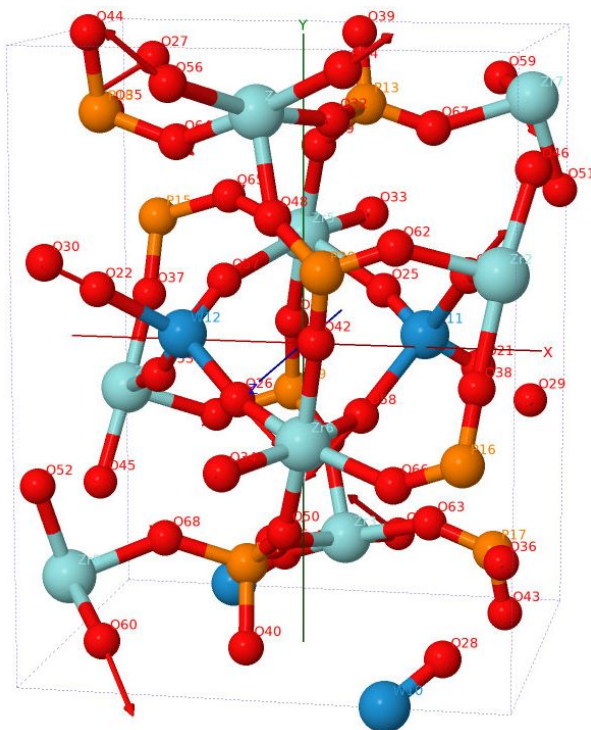
IR mode at 1065 cm^{-1} (m : medium) [B_{2u} ; $\nu_1(\text{PO}_4)$]:



IR mode at 1007 cm^{-1} (s: strong) [B_{2u} ; $\nu_3(\text{PO}_4)$]:



IR mode at 872 cm^{-1} (s) [B_{1u} ; $\nu_3(\text{WO}_4)$]:



IR mode at 837 cm^{-1} (s) [B_{3u} ; $\nu_3(\text{WO}_4)$]:

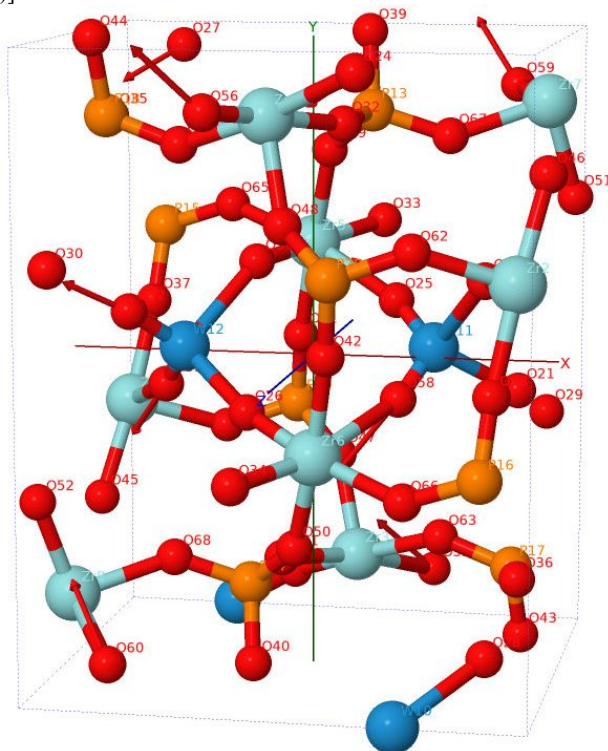
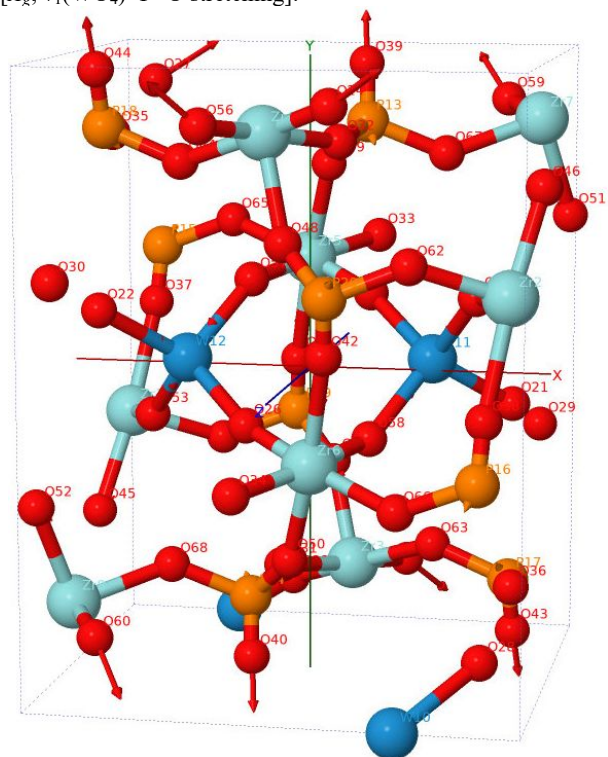
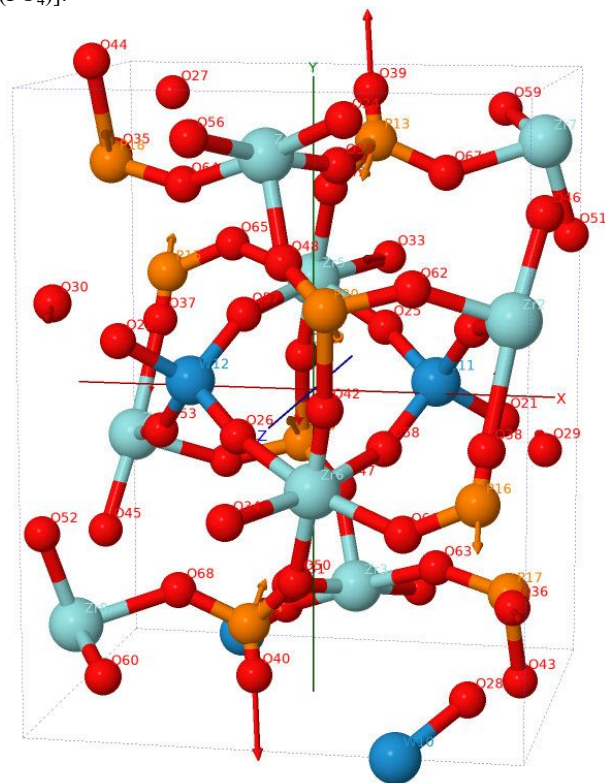


Figure S1. Graphical representations of the vibration vectors superimposed on the structure of $\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$ for strong- and medium-intensity IR-active bands.

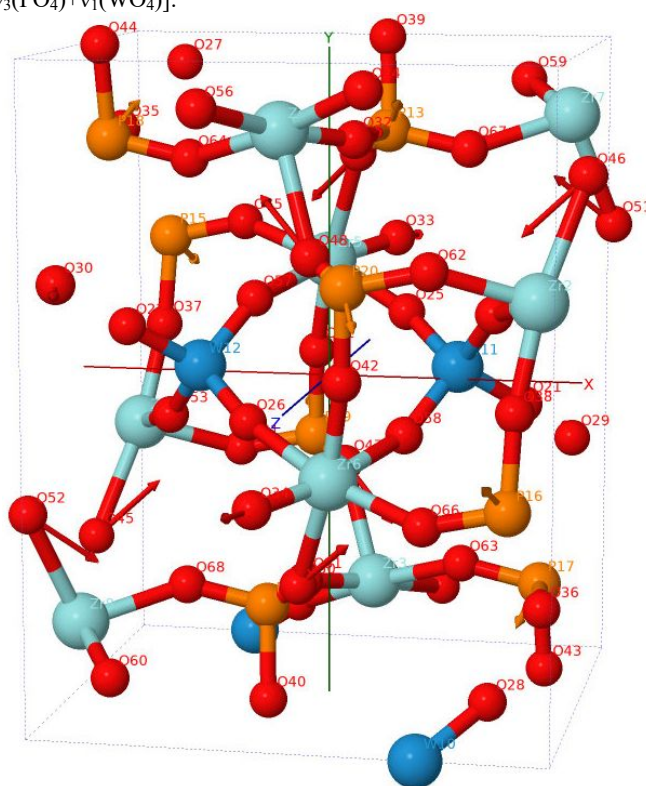
S1.2. Major Raman-Active Vibrational Modes

Raman mode at 1034 cm^{-1} (s: strong) [A_g ; $\nu_1(\text{WO}_4)+\text{P-O}$ stretching]:

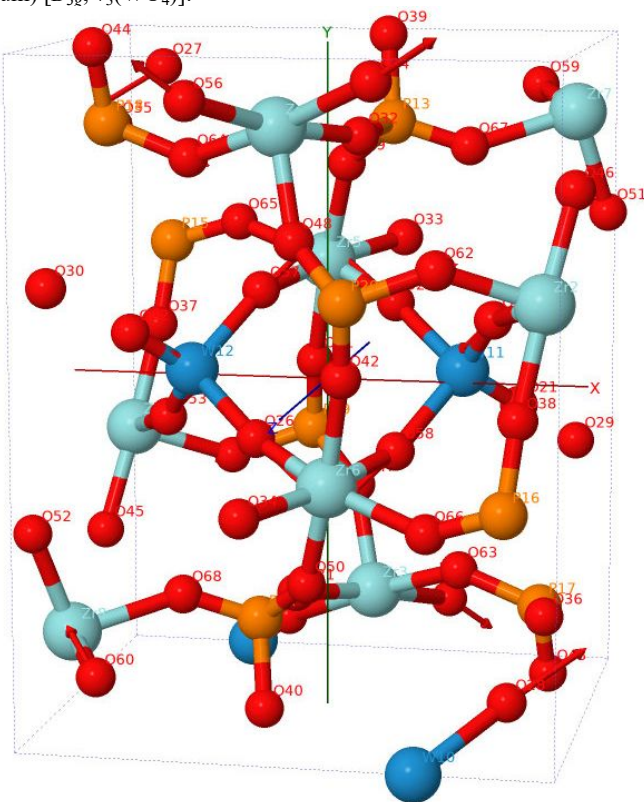


Raman mode at 1022 cm^{-1} (*s*) [B_{3g} ; $\nu_3(\text{PO}_4)$]:

Raman mode at 1002 cm^{-1} (s) [A_g ; $\nu_3(\text{PO}_4)+\nu_1(\text{WO}_4)$]:



Raman mode at 874 cm^{-1} (m : medium) [B_{3g} ; $\nu_3(\text{WO}_4)$]:



Raman mode at 831 cm^{-1} (s) [B_{2g} ; $\nu_3(\text{WO}_4)$]:

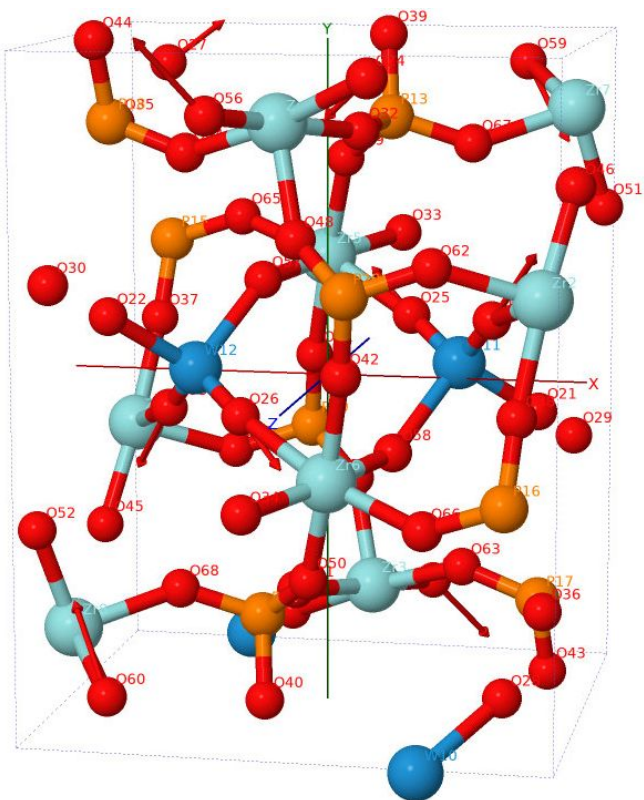


Figure S2. Graphical representations of the vibration vectors superimposed on the structure of $\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$ for strong- and medium-intensity Raman-active bands.