FOUNDATIONS

ADVANCES

Volume 76 (2020)

Supporting information for article:

Borates or phosphates? That is the question

J. Contreras-García, F. Izquierdo-Ruiz, M. Marqués and F. J. Manjón

ABO$_4$ subfamilies

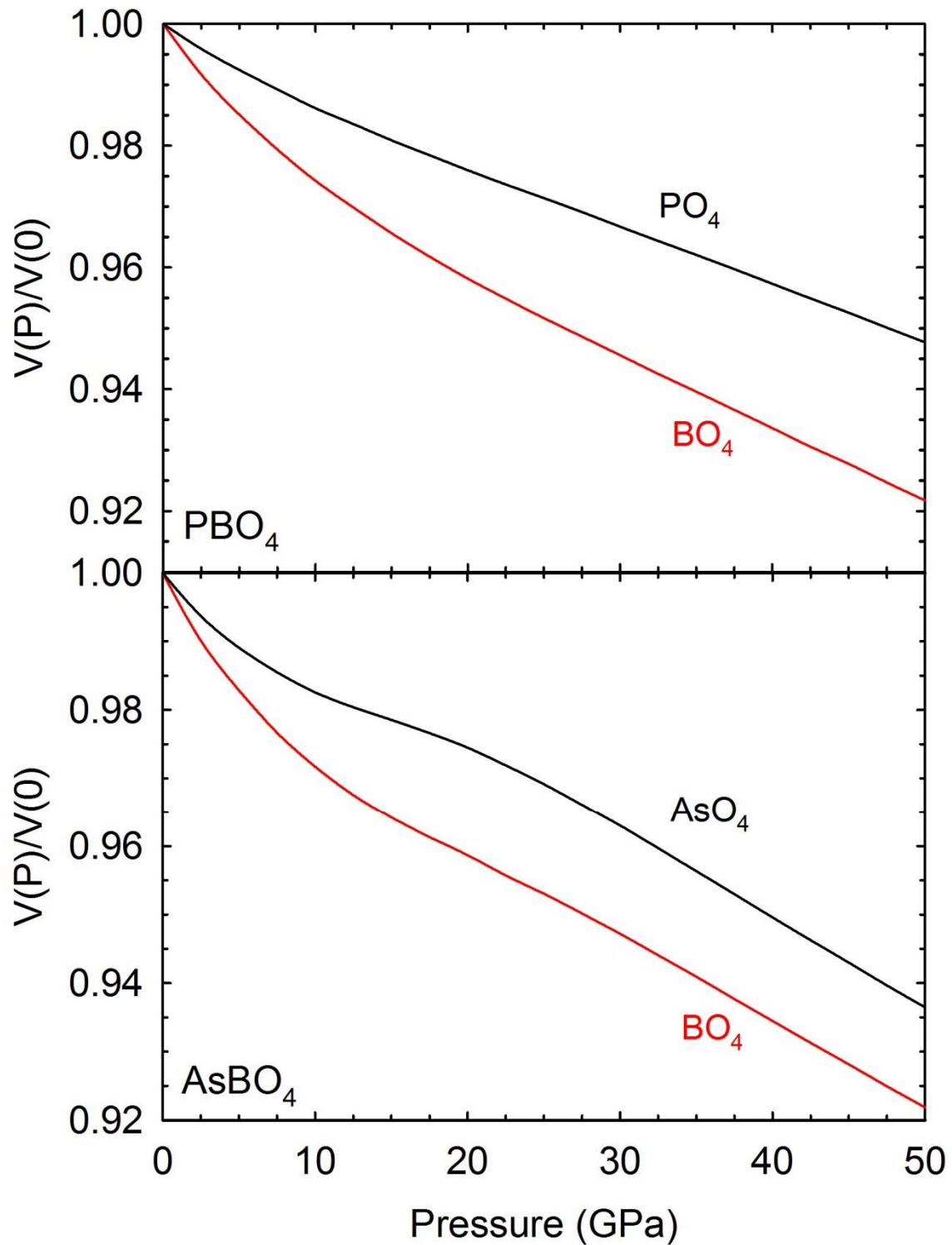$A^{1+}B^{7+}O_4$: chlorates, bromates, iodates, rhenates, manganates

$A^{2+}B^{6+}O_4$: sulphates, seleniates, telurates, chromates, molybdates, tungstates, uraniates

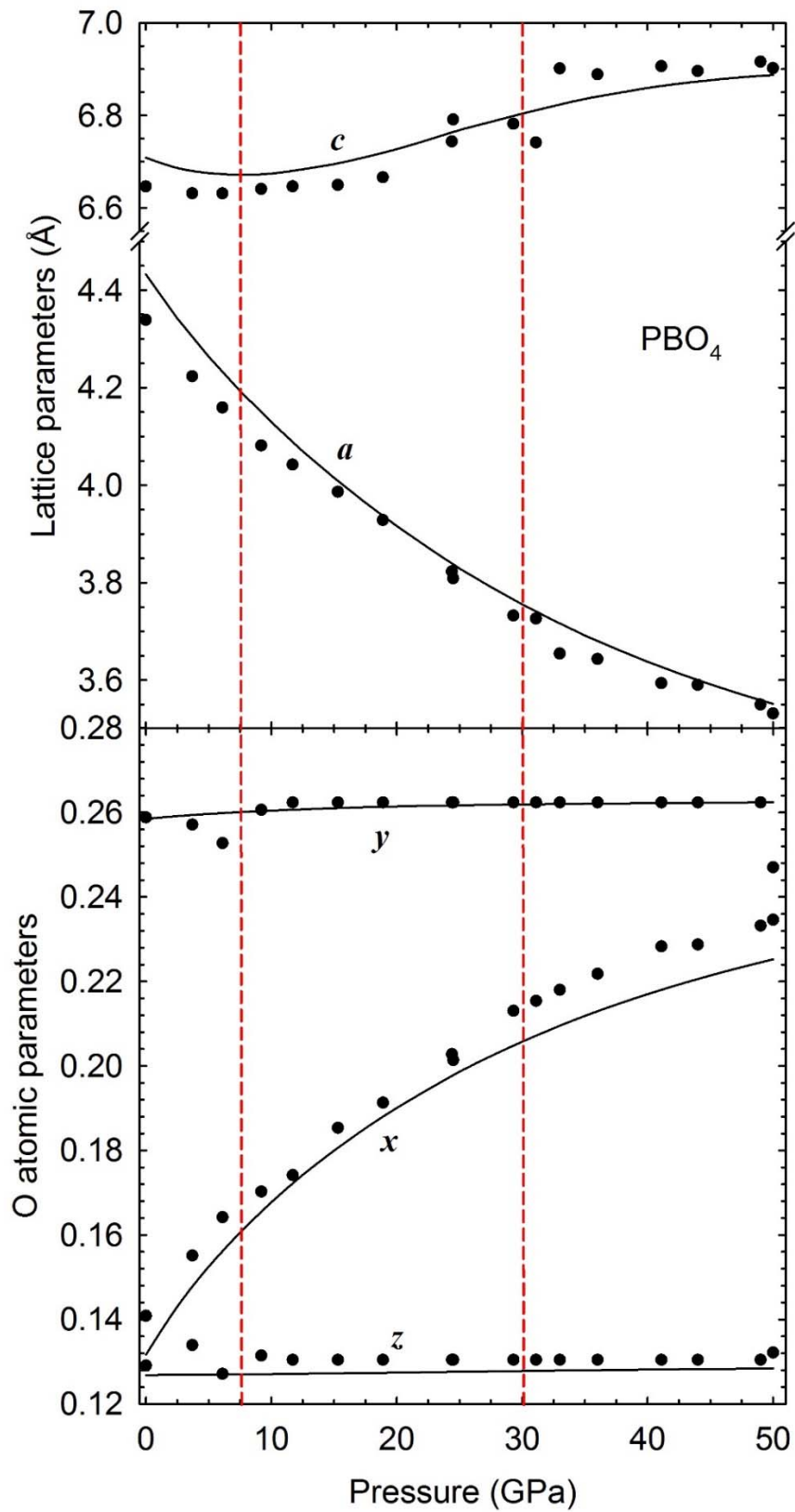$A^{3+}B^{5+}O_4$: phosphates, arsenates, antimoniates, vanadates, niobates, tantalates

$A^{4+}B^{4+}O_4$: silicates, germanates, titanates, zirconates

$A^{5+}B^{3+}O_4$: borates

Figures

Figure S1: Evolution of BO_4 (in red) and AO_4 (A=P,As) (in black) polyhedral volumes with pressure in both PBO_4 (top) and $AsBO_4$ (down).
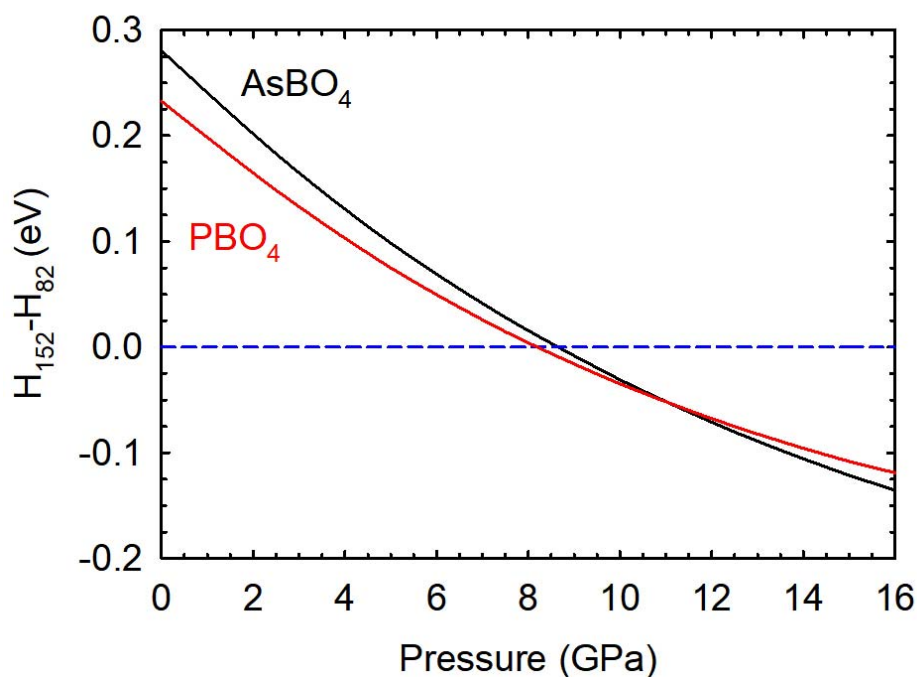
Figure S2. Pressure dependence of the lattice parameters (top) and O atomic parameters (down) in PBO4. Experimental and theoretical data are represented by symbols and lines, respectively. Experimental data are taken from Haines *et al.* (2003).
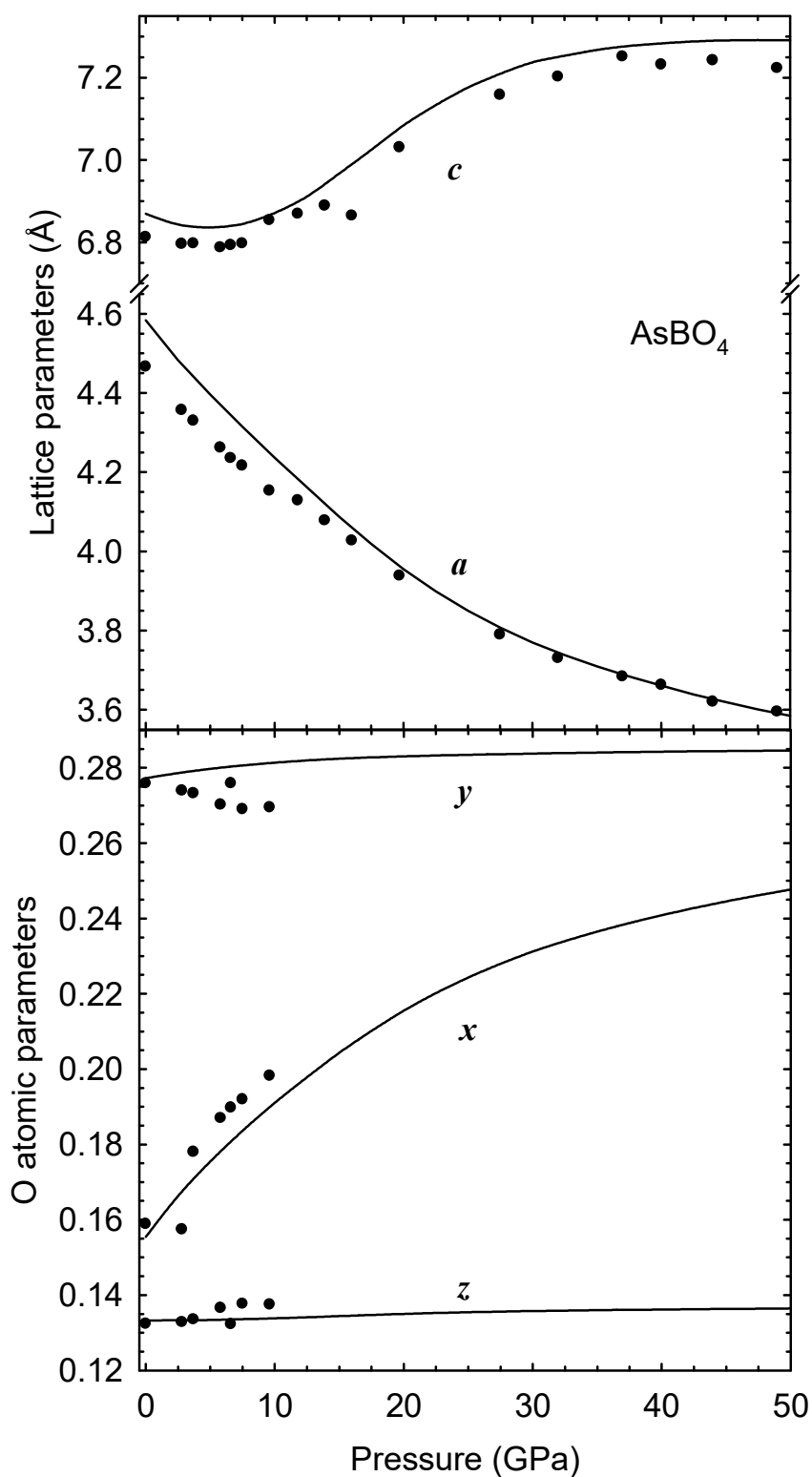
Figure S3. Pressure dependence of the lattice parameters (top) and O atomic parameters (down) in AsBO4. Experimental and theoretical data are represented by symbols and lines, respectively. Experimental data are taken from Haines *et al.* (2003). Rietveld refinements were only performed up to 10 GPa.
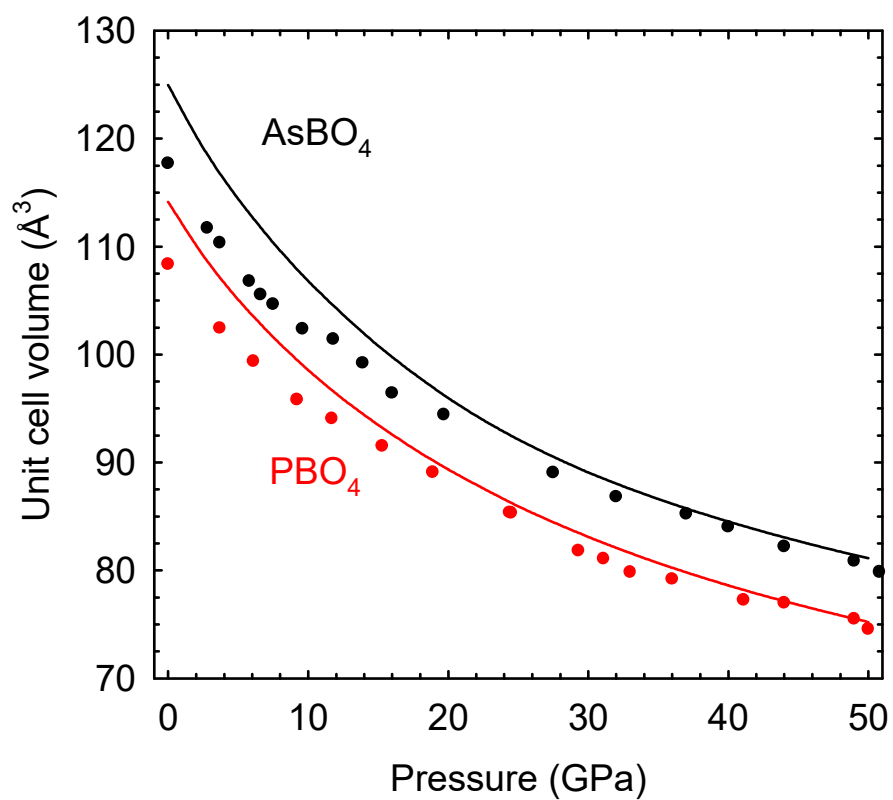
Figure S4. Pressure dependence of experimental (symbols) and theoretical (lines) unit cell volume in PBO_4 (in red) and $AsBO_4$ (in black). Experimental data are taken from Haines *et al.* (2003).
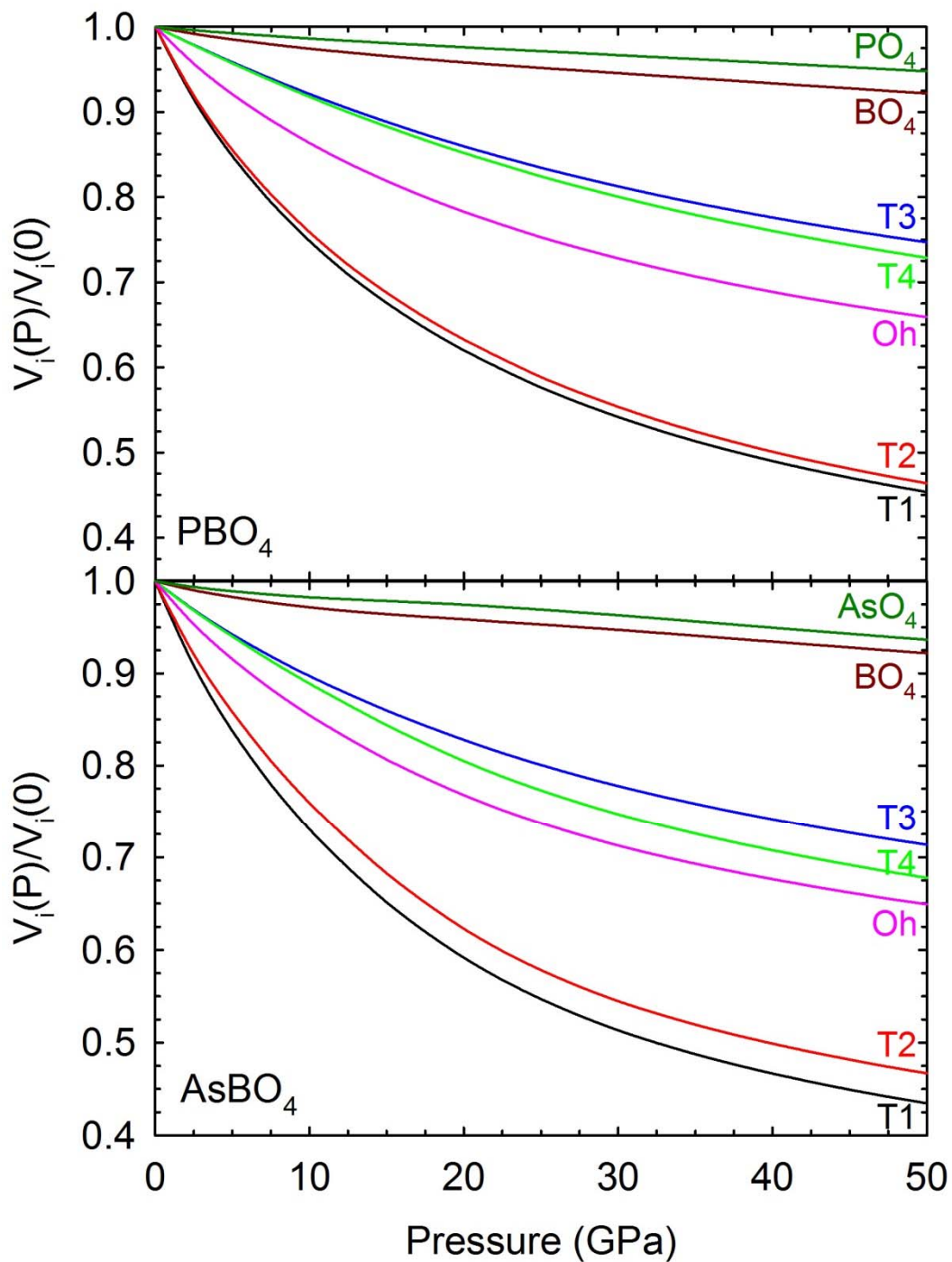
Figure S5. Pressure dependence of the theoretical enthalpy difference (per formula unit) of the berlinite structure (solid line) with respect to the high cristobalite structure (blue dashed horizontal line) for PBO_4 (in red) and $AsBO_4$ (in black).

As expected, the transformation from the high cristobalite structure towards the low quartz or berlinite structure is found in our calculations performed at 0K around 8.2 GPa (8.7 GPa) for PBO_4 ($AsBO_4$). These values compare reasonably well with the phase transition experimentally reported at 5 GPa and 500ºC for PBO_4 (Dachille & Dent Glasser, 1959) and suggest that the high stability (up to 50 GPa) of the high cristobalite structure of both compounds at room temperature is due to the frustration of the first-order phase transition around 5 to 10 GPa by kinetic considerations.
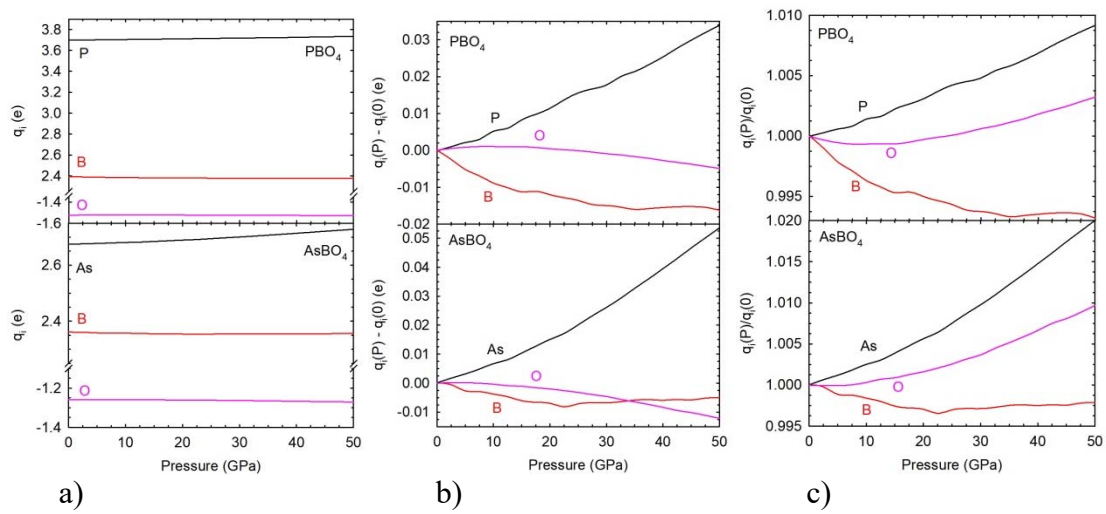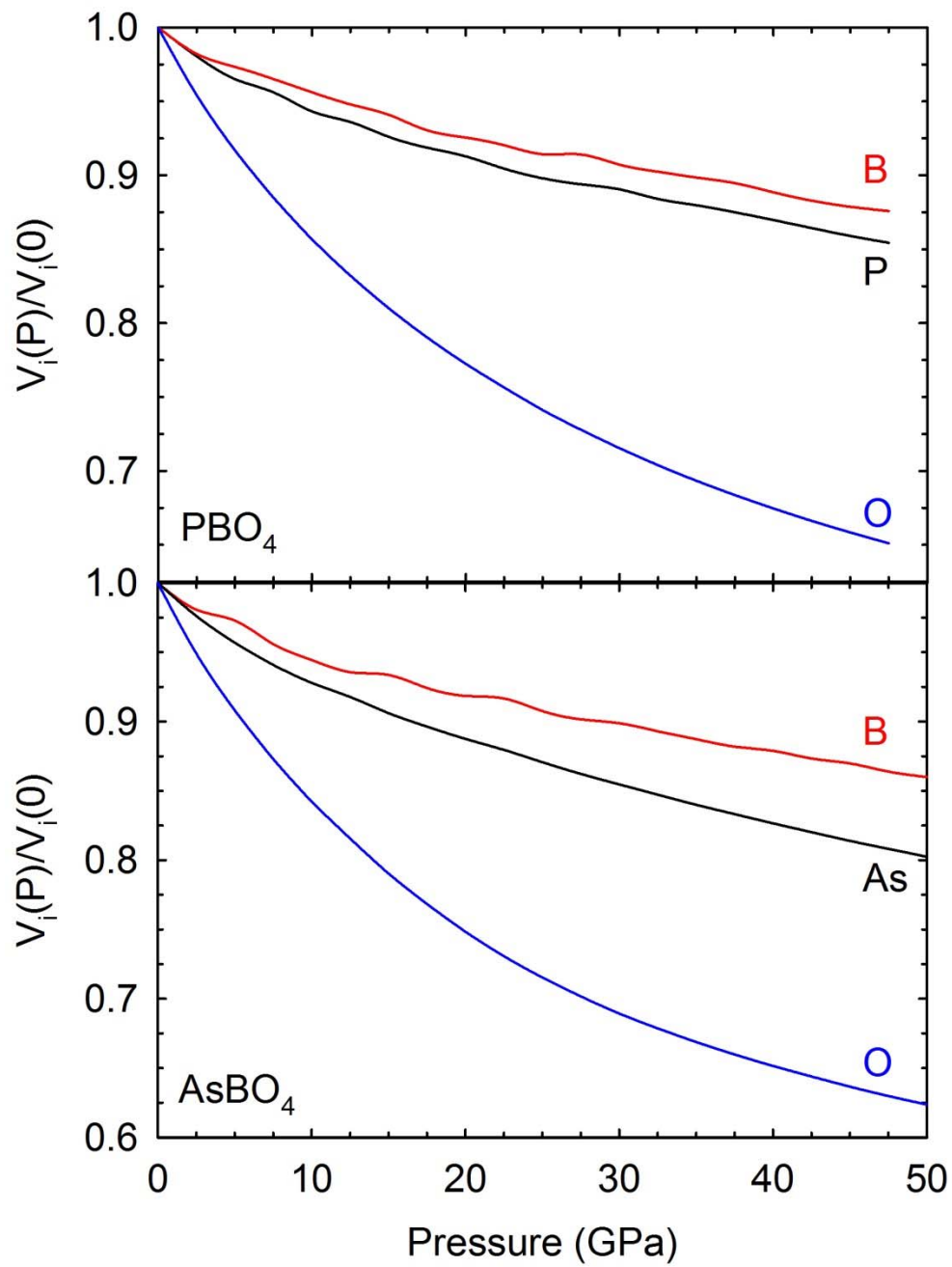
Figure S6. Pressure dependence of QTAIM charges in PBO_4 and $AsBO_4$: a) Total atomic charges, b) Absolute change of the atomic charges with respect to 0 GPa, and c) Relative change of the atomic charges with respect to 0 GPa.
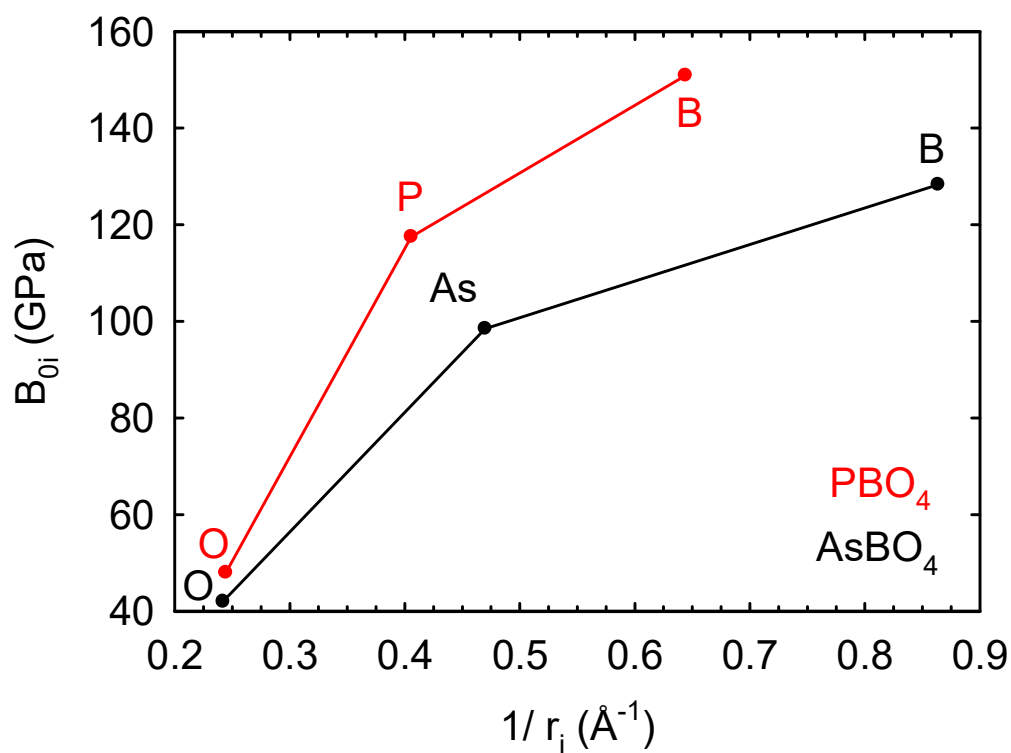
Figure S7. Pressure dependence of polyhedral volumes at tetrahedral (T) and octahedral (Oh) voids in PBO_4 (top) and $AsBO_4$ (bottom). The pressure dependence of the polyhedral volumes of PO_4, BO_4 and AsO_4 are also shown.

Figure S8. Pressure dependence of QTAIM atomic basin relative volumes in PBO$_4$ (top) and AsBO$_4$ (down).

Figure S9. Pressure dependence of the QTAIM atomic bulk modulus, B_{0i}, as a function of $1/r_i$ in PBO_4 and $AsBO_4$. Atomic radii have been estimated from a spherical approximation of the topological volume.
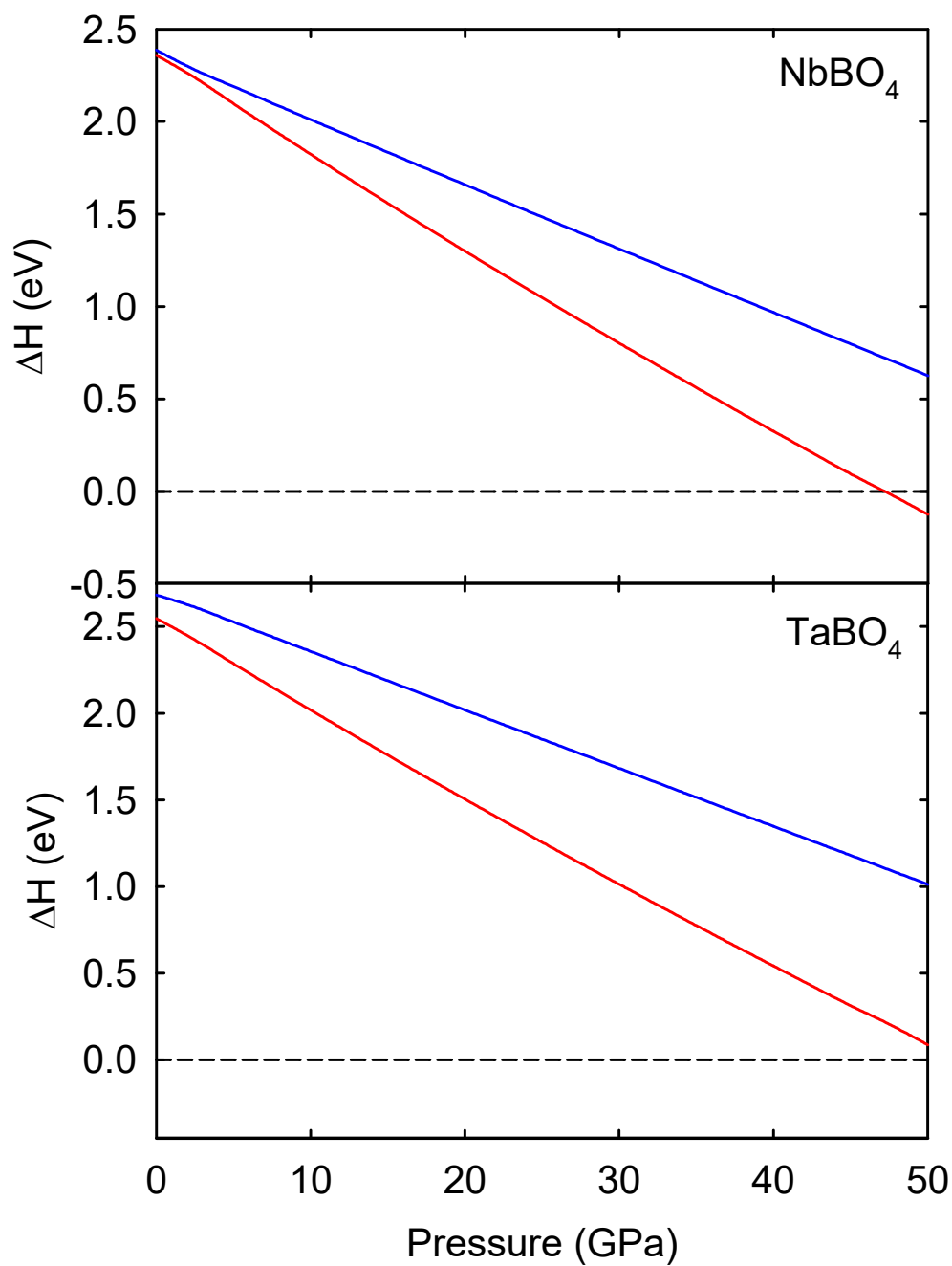
Figure S10. Pressure dependence of the theoretical enthalpy difference (per formula unit) of the scheelite (red) and monazite (blue) structures with respect to the zircon structure (dashed horizontal line) in NbBO4 (top) and TaBO4 (bottom).