Supplementary Information (SI) for Journal of Materials Chemistry C.

Rashba Asymmetric Topological Insulator BiTeCl under Compression: Equation of State, Vibrational Features and Electronic Properties

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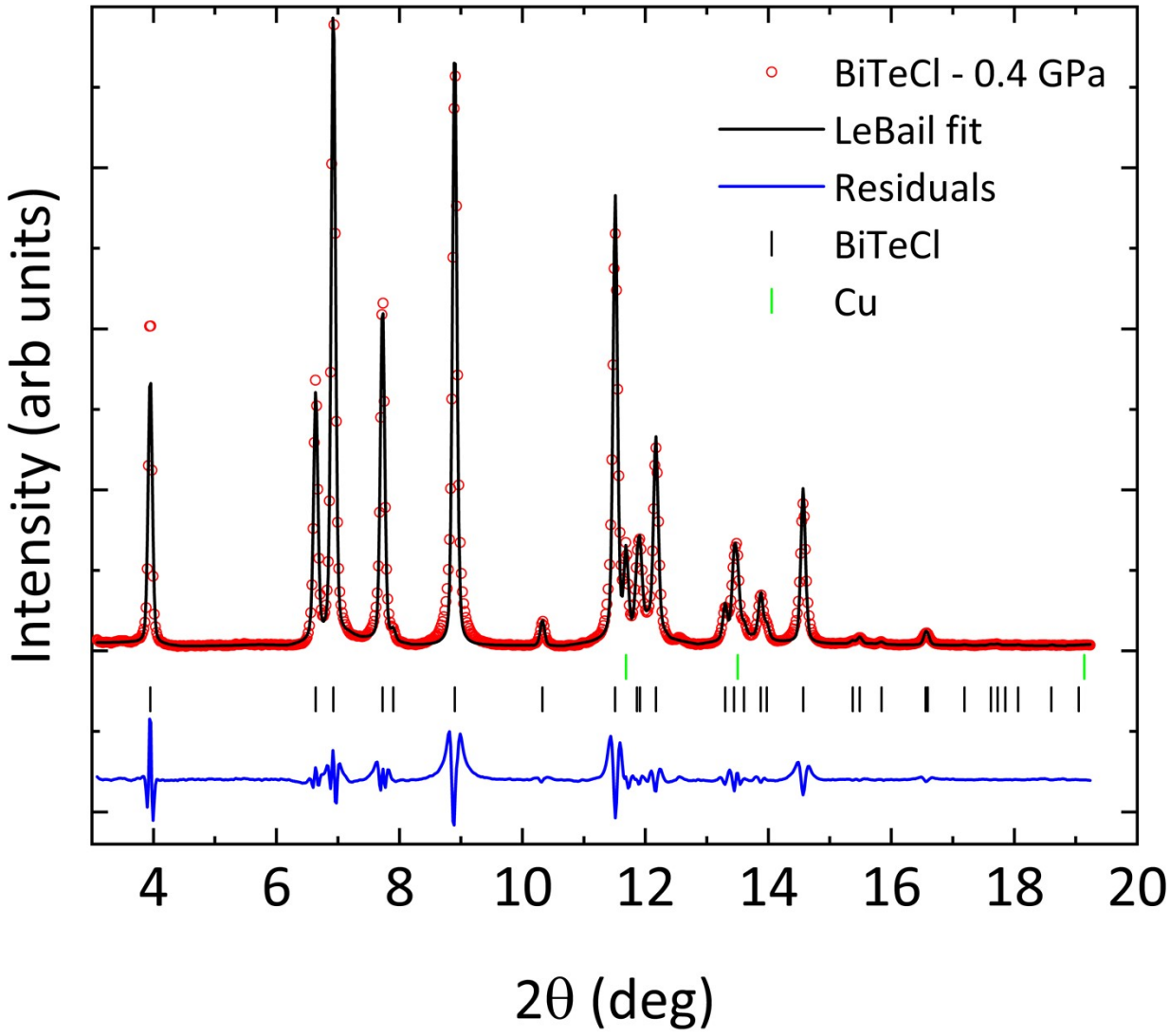

Figure S1. Powder x-ray diffraction pattern of BiTeCl in DAC at 0.4 GPa (red circles, λ=0.4246 Å) and LeBail fit using the $P6_3mc$ space group (black line). Residuals are represented by the blue line. Black ticks and green ticks mark the Bragg reflections for BiTeCl and Cu, respectively. Cell parameters as obtained by the Le Bail fit at 0.4 GPa are: a = 4.23491(25) Å, c = 12.3261(19) Å, V = 191.44(3) Å^3.

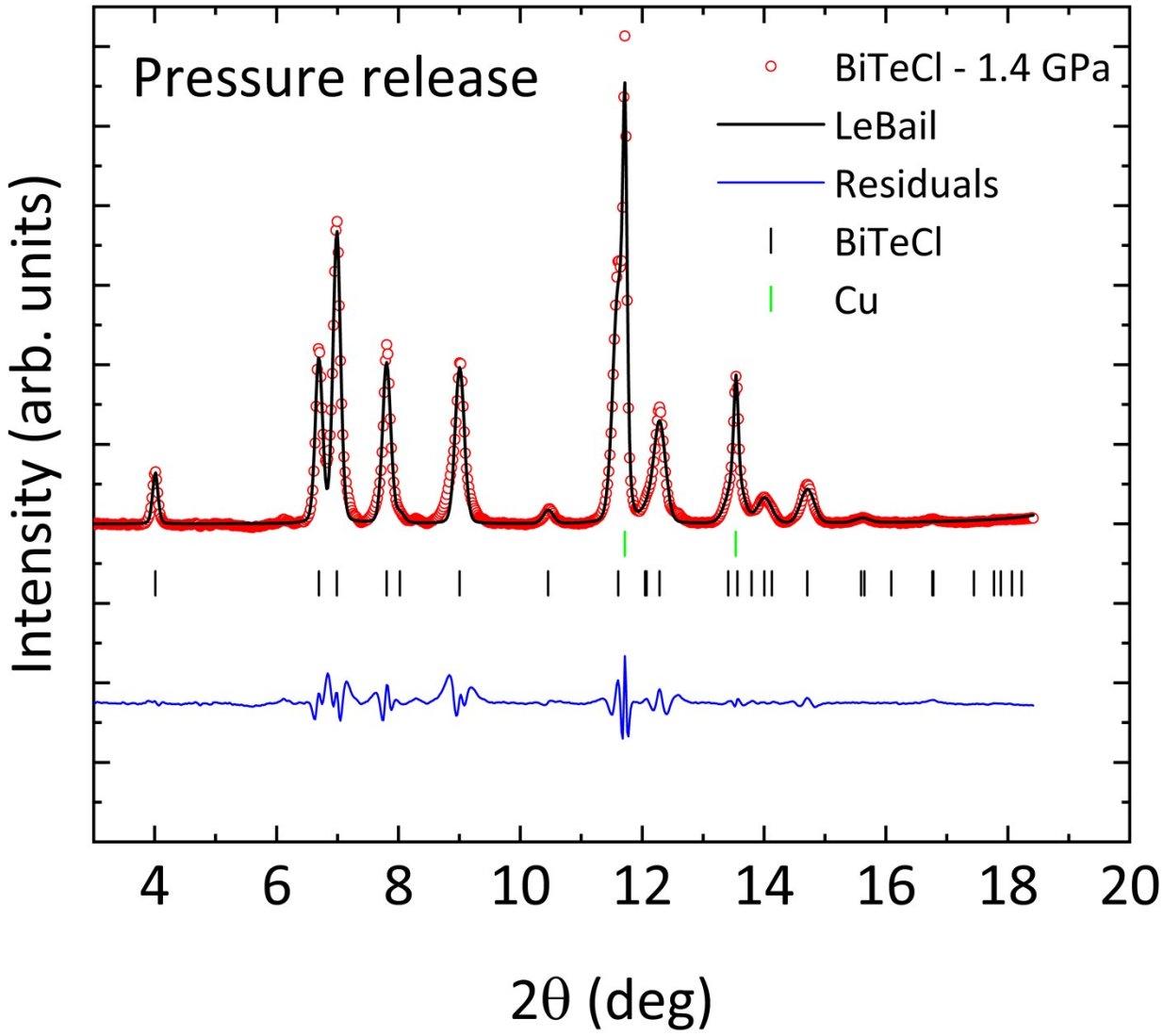

Figure S2. Powder x-ray diffraction pattern of BiTeCl in DAC at 1.4 GPa after pressure release (red circles, λ=0.4246 Å) and LeBail fit using the $P6_3mc$ space group (black line). Residuals are represented by the blue line. Black ticks and green ticks mark the Bragg reflections for BiTeCl and Cu, respectively. Cell parameters as obtained by the Le Bail fit at 0.4 GPa are: a = 4.1879(3) Å, c = 12.139(4) Å and V = 184.38(3) Å^3.

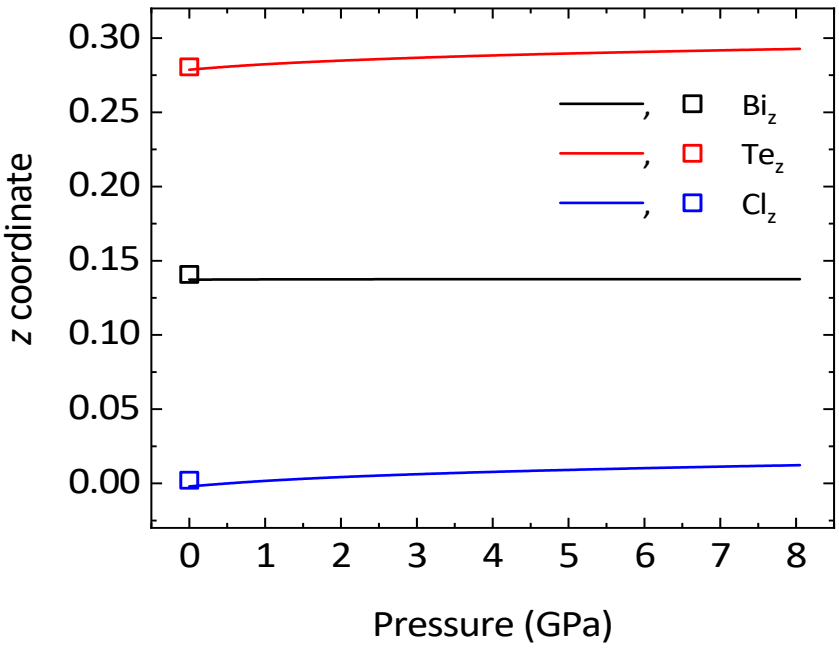

Figure S3. Pressure dependence of the experimental (symbols) and theoretical (lines) atomic *z* coordinate of the Bi, Te, and Cl atoms in the $P6_3mc$ phase of BiTeCl. Experimental data were obtained from single-crystal X-ray diffraction (SC-XRD) measurements.

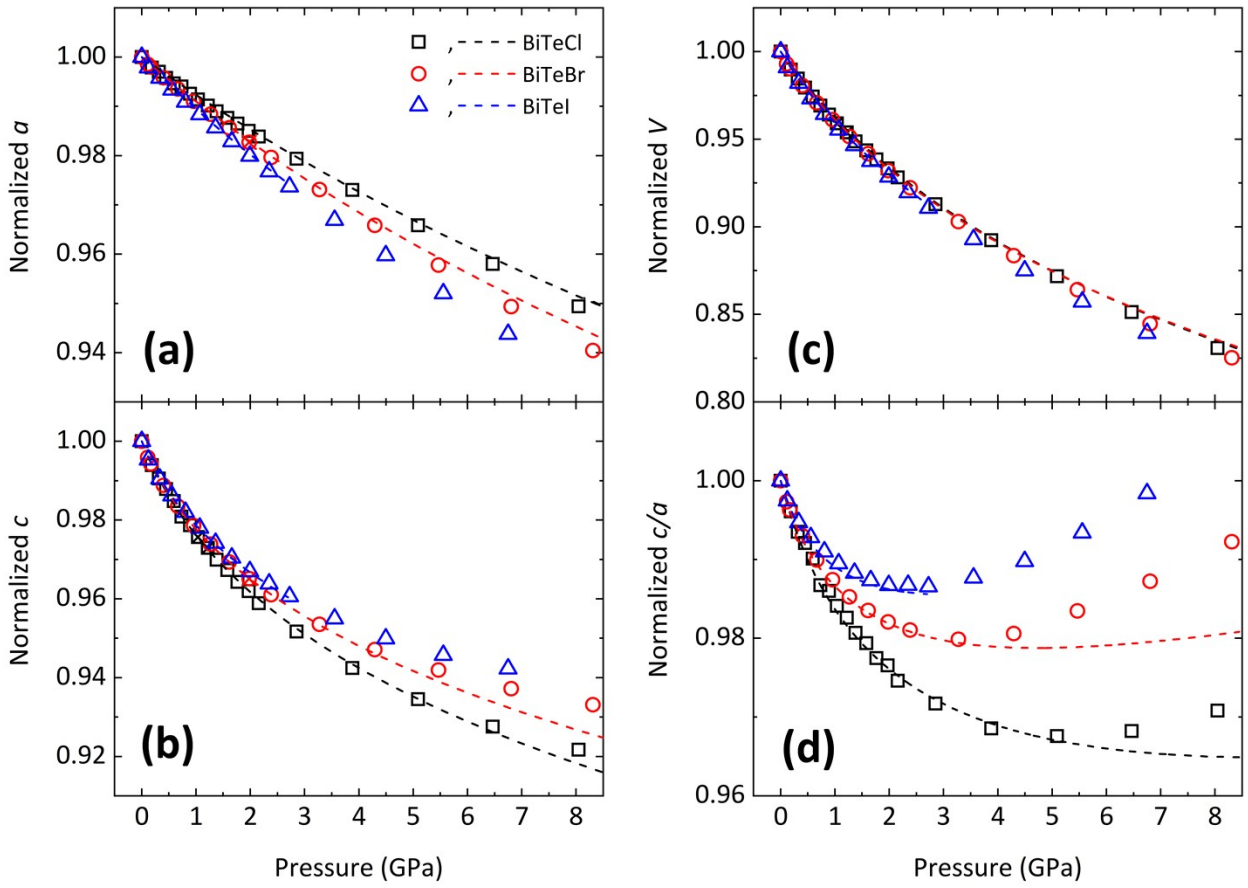

Figure S4. Pressure dependence of the theoretical normalized values of (a) *a* and (b) *c* lattice parameters, (c) unit-cell volume, and (d) *c/a* ratio for the LP phase of BiTeCl, BiTeBr, and BiTeBr, respectively. Dashed lines correspond to BM3-EOS fits, calculated up to ~5.3, ~2.7, and ~3.3 GPa for BiTeCl, BiTeI, and BiTeBr, respectively (see main manuscript). The legend shown in (a) is common for all plots.

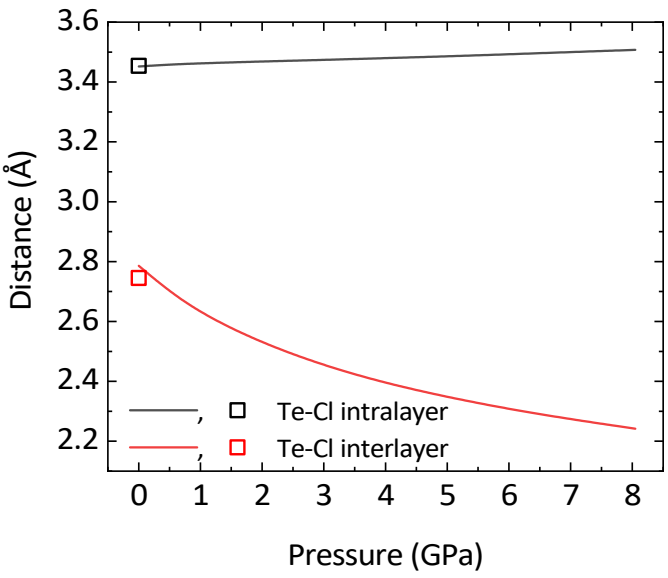

Figure S5. Pressure dependence of the intralayer (black line) and interlayer (red line) interplanar distance for the Te and Cl planes in the $P6_3mc$ phase of BiTeCl. Open squares represent experimental values at RP as obtained from SC-XRD measurements.

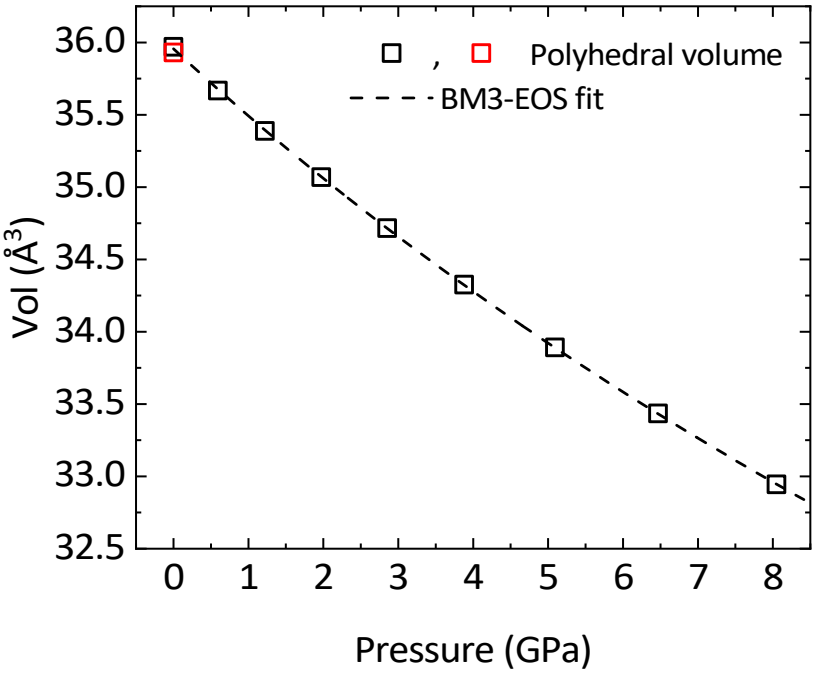

Figure S6. Pressure dependence of the experimental (red symbol) and calculated (black symbols) polyhedral volume of the Bi octahedron. The experimental data point was obtained from SC-XRD measurements. The dashed line represents the BM3-EOS fit of the theoretical data, whose parameters are V_0=35.956(6) Å^3, B_0=74.6(7) GPa, and $B_0^{'}$=4.80(20).

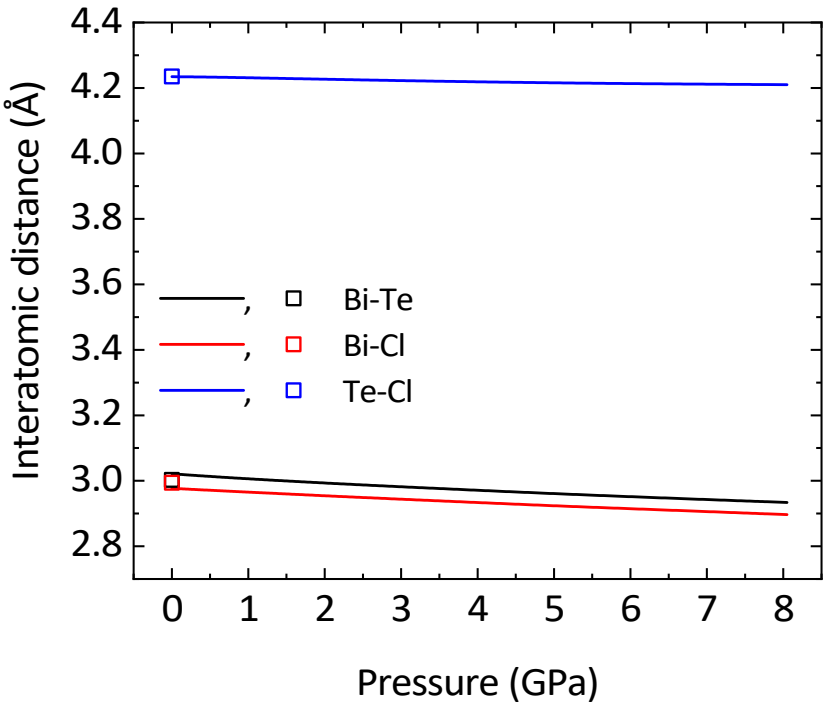

Figure S7. Pressure dependence of the experimental (symbols) and calculated (lines) interatomic distances Bi-Te, Bi-Cl, and Te-Cl (along the polyhedral edges) in BiTeCl. Experimental data were obtained from SC-XRD measurements. The relative compressibility for the Bi-Te, Bi-Cl and Te-Cl distances are $4.67(10) \times 10^{-3}$ GPa^{-1}, $3.980(22) \times 10^{-3}$ GPa^{-1}, and $1.21(8) \times 10^{-3}$ GPa^{-1}, respectively.

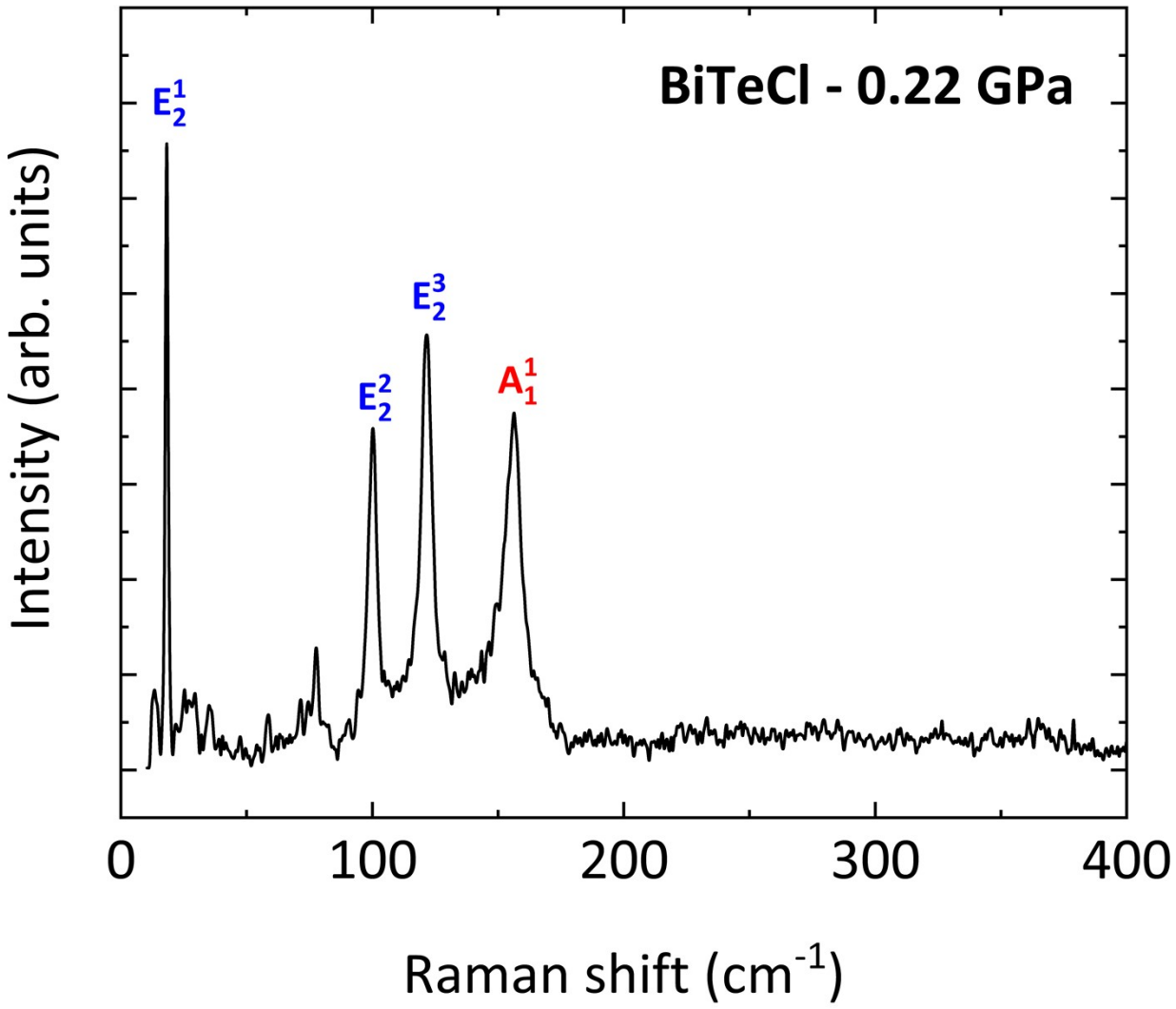

Figure S8. Raman spectrum of BiTeCl in DAC at nearly-RP (0.22 GPa) as obtained using a red laser (λ=632.8 nm). Experimentally detectable modes are indicated.

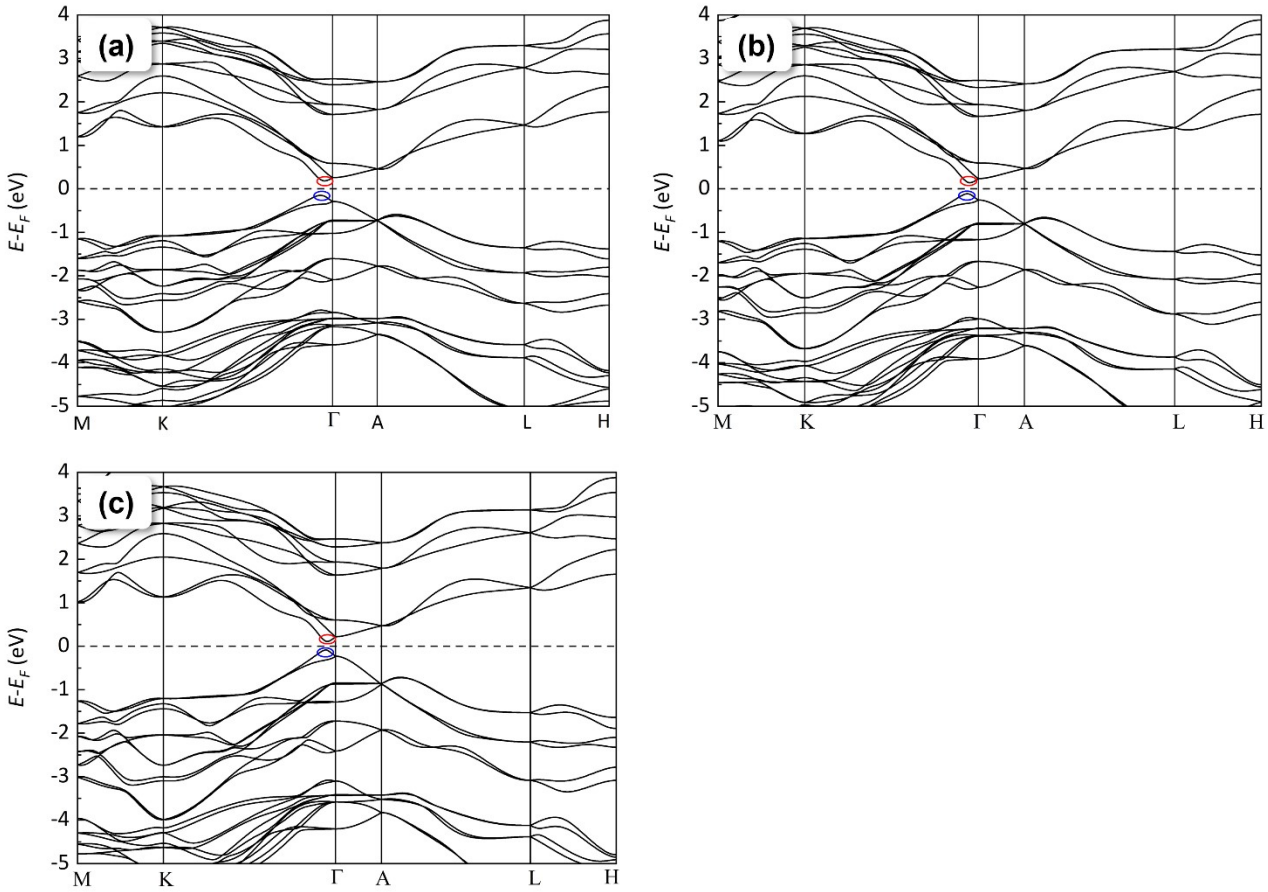

Figure S9. Calculated electronic band structure of BiTeCl at a pressure of (a) 2 GPa, (b) 4 GPa, (c) 6 GPa. Red (blue) ovals indicate the conduction band minimum (valence band maximum).

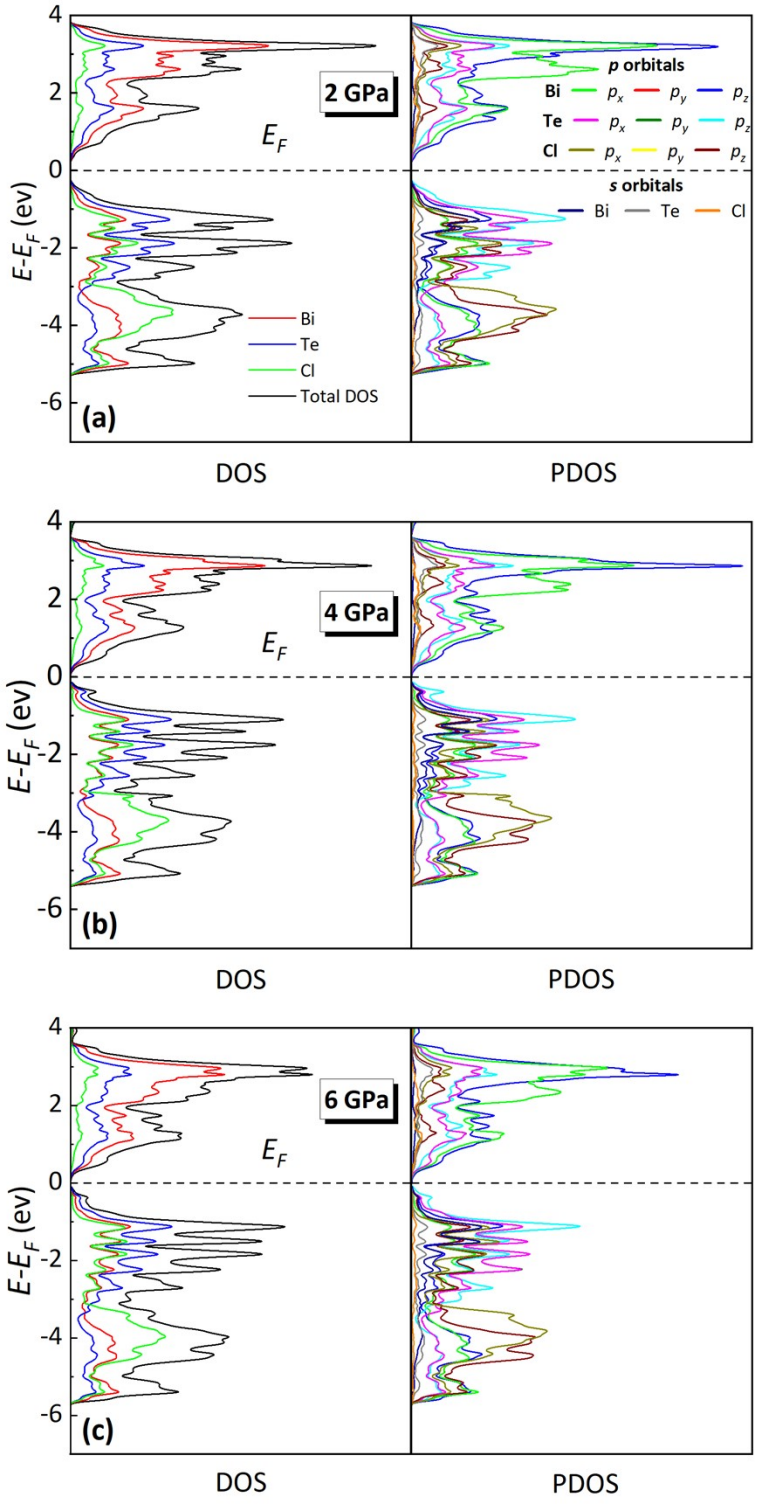

Figure S10. Calculated total DOS and PDOS (projected on orbitals) for BiTeCl at 2 GPa (a), 4 GPa (b), and 6 GPa (c). Contributions from each atom/orbital are shown in different colors (see common legend in (a)).

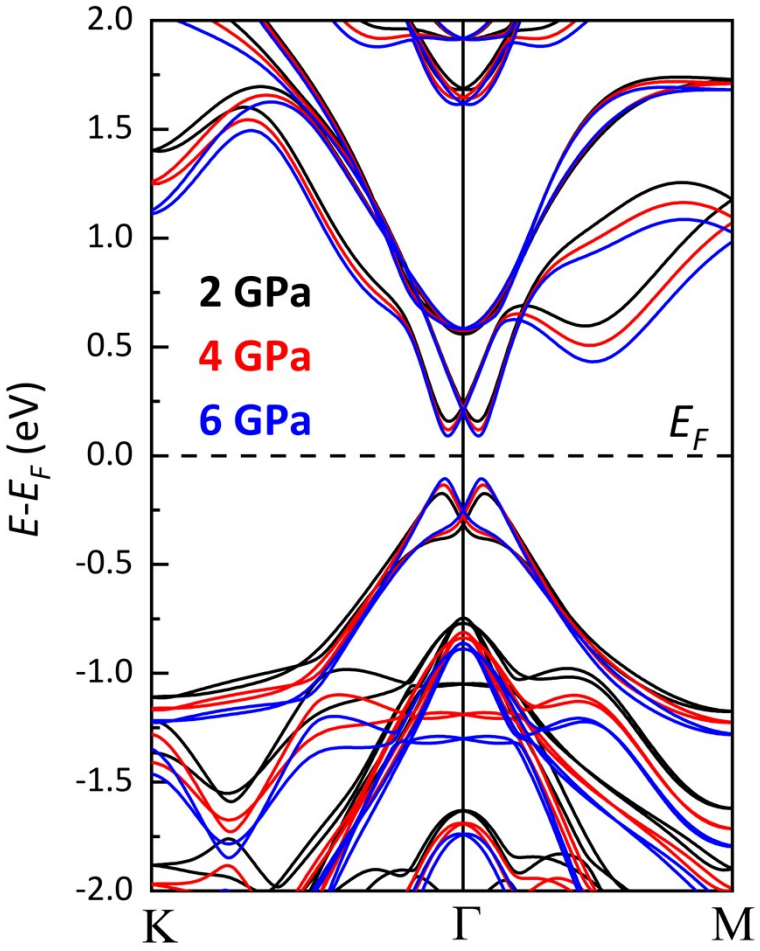

Figure S11. Detail of the theoretical band structure of BiTeCl along the K-Γ-M path of the BZ, at 2, 4, and 6 GPa (black, red, and blue lines, respectively) showing the effect of pressure on the Rashba splitting at Γ (see also main manuscript).