Supplementary Information

Structural, vibrational and electrical study of compressed BiTeBr

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Structural properties under pressure

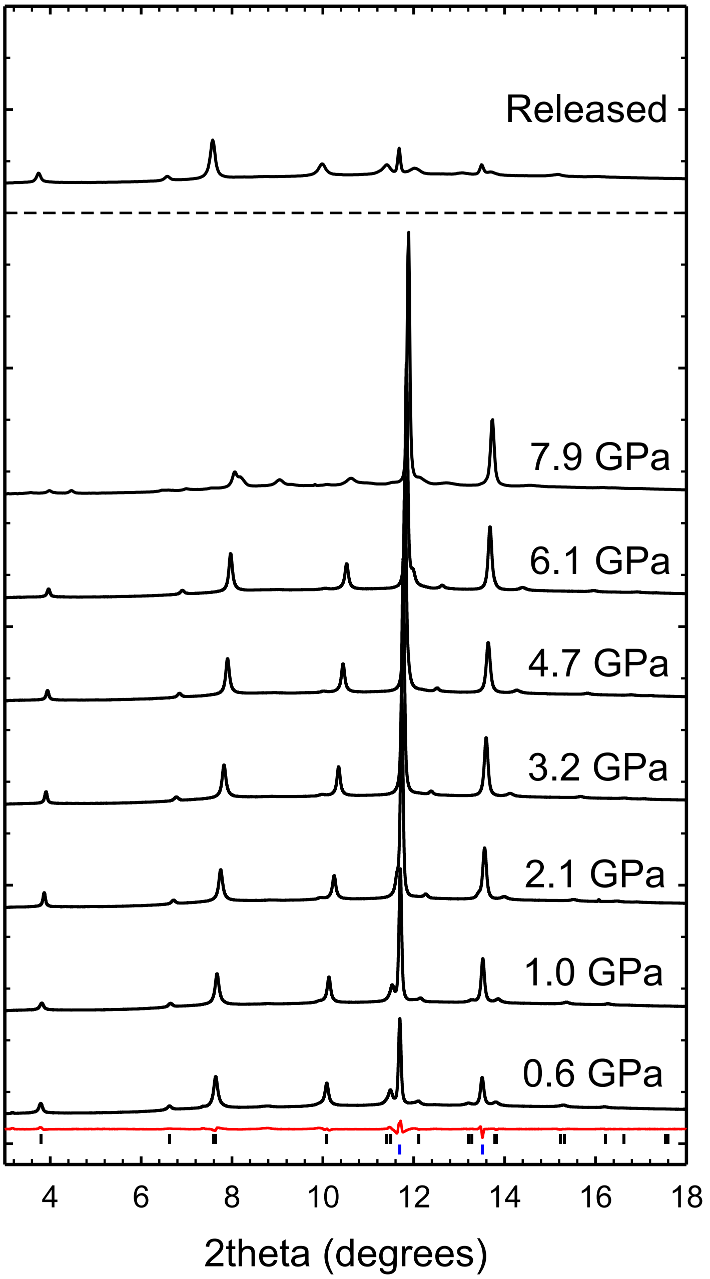

Fig. S1. Selected powder XRD patterns of BiTeBr at different pressures up to 8 GPa. Backgrounds have been subtracted and patterns shifted in vertical for comparison. Observed (solid circles) and Le Bail calculated and difference (solid lines) XRD profiles of the low-pressure phase of BiTeBr at 0.6 GPa are shown.

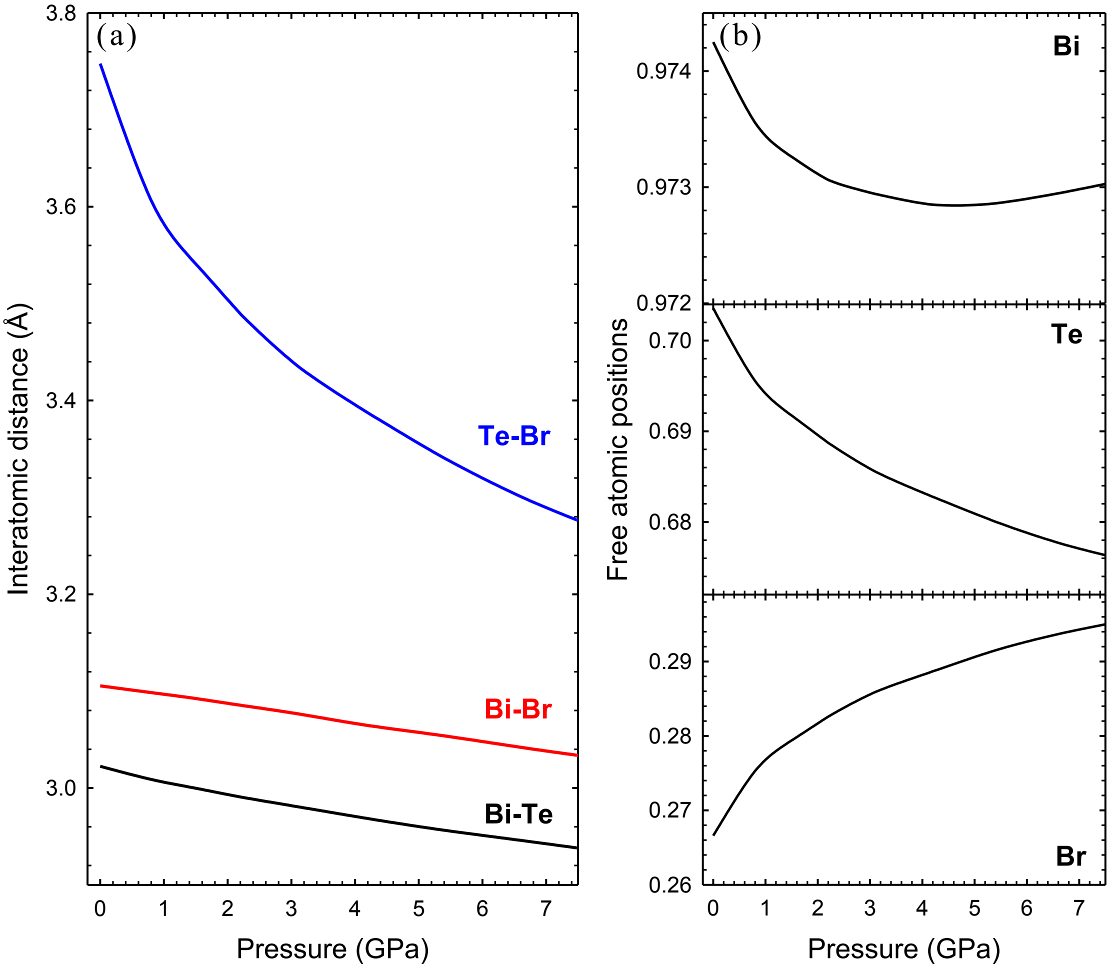

Fig. S2. Pressure dependence of the theoretical Bi-Te, Bi-Br and Br-Te distances (a) and z coordinate of the atomic position of Bi, Br, and Te (b) in BiTeBr.

Vibrational properties under pressure

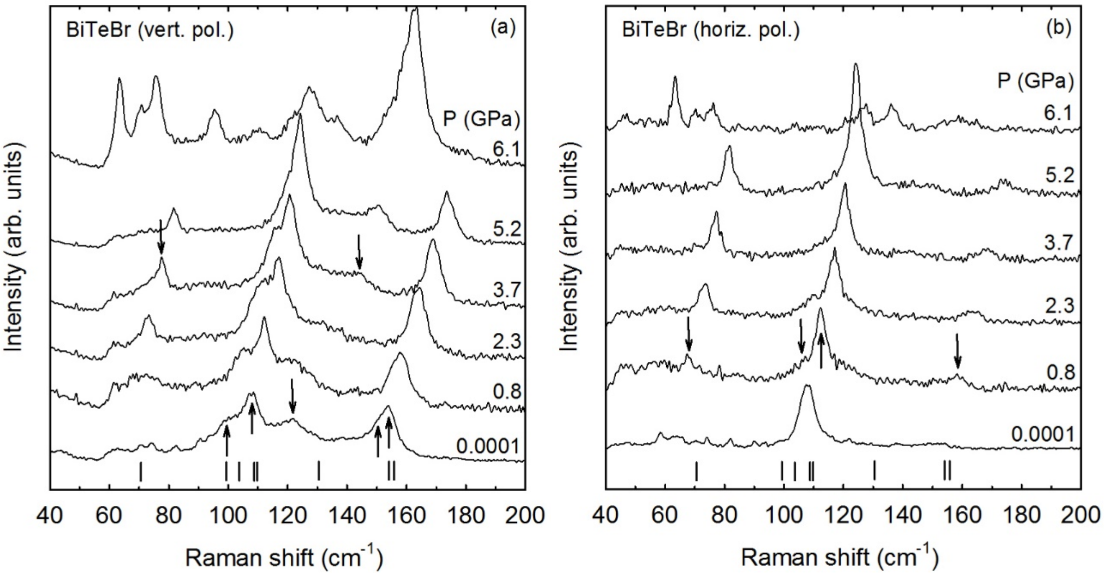

Fig S3. Experimental RS spectra of BiTeBr at selected pressures for vertical polarization (a) and horizontal polarization (b). Arrows indicate the position of first-order Raman modes of BiTeBr. Theoretical frequencies of the first-order Raman-active modes are marked at the bottom for comparison.

Comparison with other layered compounds

It is interesting to compare the Raman mode frequencies and pressure coefficients of BiTeBr and BiTeI (see **Table II** of manuscript). It can be observed that the measured pressure coefficients for the different modes are rather similar in both compounds. As regards the low-frequency modes, it is known that in layered materials the lowest-frequency E and A modes are usually related to shear vibrations between adjacent layers along the *a-b* plane and to vibrations of one layer against the others along the *c* axis, respectively. In layered InSe and GaSe, the low-frequency E mode exhibits a much smaller pressure coefficient than the other three modes whereas the low-frequency A mode displays the largest pressure coefficient. For example, the E and A modes with frequencies around 40 (60) cm^{-1} and 116 (133) cm^{-1} in InSe (GaSe) have pressure coefficients of 0.68 (0.85) cm^{-1}/GPa and 5.41 (5.78) cm^{-1}/GPa, respectively **[1,2]**. Usually, the small pressure coefficient of the low-frequency E mode in layered materials is ascribed to the weak bending force constant due to weak van der Waals forces between the neighboring layers. On the other hand, the large pressure coefficient of the low-frequency A mode is due to the extraordinary increase of the stretching force constant between neighboring layers due to the strong decrease of the interlayer distance **[1,2]**. A similar behavior is found in layered topological insulators Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 **[3-5]**. However, BiTeBr and BiTeI behave in a slightly different manner because the low-frequency E^1(TO) mode has a similar pressure coefficient than the rest of the optic modes and the low-frequency $A_1{}^1$(TO) mode has not so large pressure coefficient as expected. Therefore, the relatively large and similar pressure coefficients of the low-frequency E^1(TO) and $A_1{}^1$(TO) modes in BiTeBr and BiTeI suggest that interlayer forces in these compounds are stronger than common van der Waals forces in other layered compounds. We think that this could likely be due to the strong polarity of bismuth tellurohalides **[6]**. Moreover, the rather similar pressure coefficients of these two modes in BiTeBr and BiTeI also suggests that bending and stretching interlayer bonds tend to harden at similar rates with pressure in both compounds; i.e., the anisotropy in the properties along the layers and perpendicular to the layers is not so high as in other layered compounds and tend to disappear at a similar rate with increasing pressure in both compounds.

As regards the high-frequency modes, we must note that the high-frequency E^2 and $A_1{}^2$ modes in BiTeBr and BiTeI have high and rather similar pressure coefficients (between 4 and 5 cm^{-1}/GPa), as expected for strong ionic-covalent intralayer bonds. This result is in good agreement with the similar bond distances and bond compressibilities of both intralayer Bi-Te and Bi-Br distances shown in **Fig. S2(a)**. Furthermore, the pressure coefficients of the high-frequency E and A modes in BiTeBr and BiTeI are larger than those in α-Sb_2Te_3, α-Bi_2Te_3 and α-Bi_2Se_3 **[3-5]**. Noteworthy, a comparison of Grüneisen parameters of the high-frequency Raman modes of both families, assuming bulk moduli around 20 GPa in BiTe*X* compounds and around 50 GPa in the Bi_2Se_3 family, yield values of around 0.7 for the former and larger than 1.1 for the latter. This result means that the anharmonicity of intralayer ionic-covalent forces in both families is different and the intralayer forces evolve in different way with compression in both families as already observed for the interlayer forces.

Discussion about possible Electronic Topological Transition

As regards the possible ETT in BiTeBr, we must mention that in a previous work **[7]** it was reported that the E^2(TO) mode, usually the most intense one in BiTeBr and BiTeI **[2]**, showed a strong decrease in linewidth between room pressure and 4 GPa. This feature was interpreted as indicative of the occurrence of an ETT near 4 GPa, similar to that observed in several topological insulators (Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3) **[3-5]**. Our measurements of the full width at half maximum (FWHM) of this Raman mode in BiTeBr (see **Fig. S4**) also shows an initial strong decrease of the FWHM between room pressure and 1 GPa; however it has a different pressure dependence than that reported in BiTeI **[7]**. We have interpreted FWHM changes in BiTeBr as due to its particular morphology of the two-phonon density of states and the way the frequency of the first-order mode sweeps the two-phonon density of states as pressure increases **[8]** rather than the existence of an ETT around 1 GPa. It must be stressed that the change in the FWHM between room pressure and 1 GPa is much smaller than that observed in topological insulators **[3-5]**. Therefore, our RS measurements do not support the existence either of a pressure-induced IPT or ETT in our samples of BiTeI-type BiTeBr.

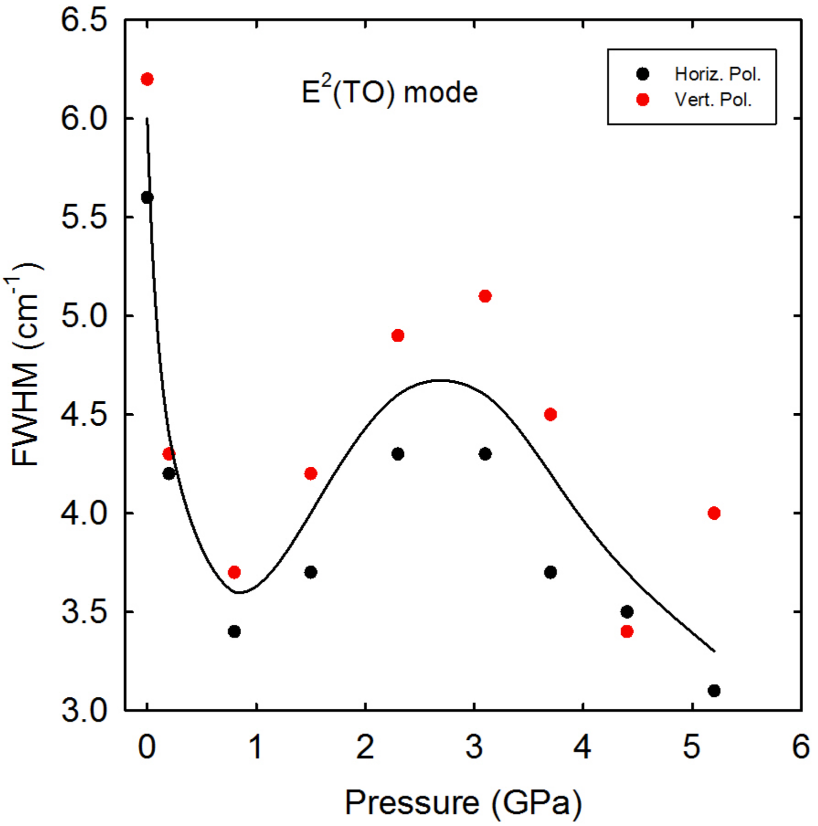

Fig. S4. Experimental pressure dependence of the full width half medium (FWHM) of the E^2(TO) Raman-active mode. Solid line is just a guide to the eyes.

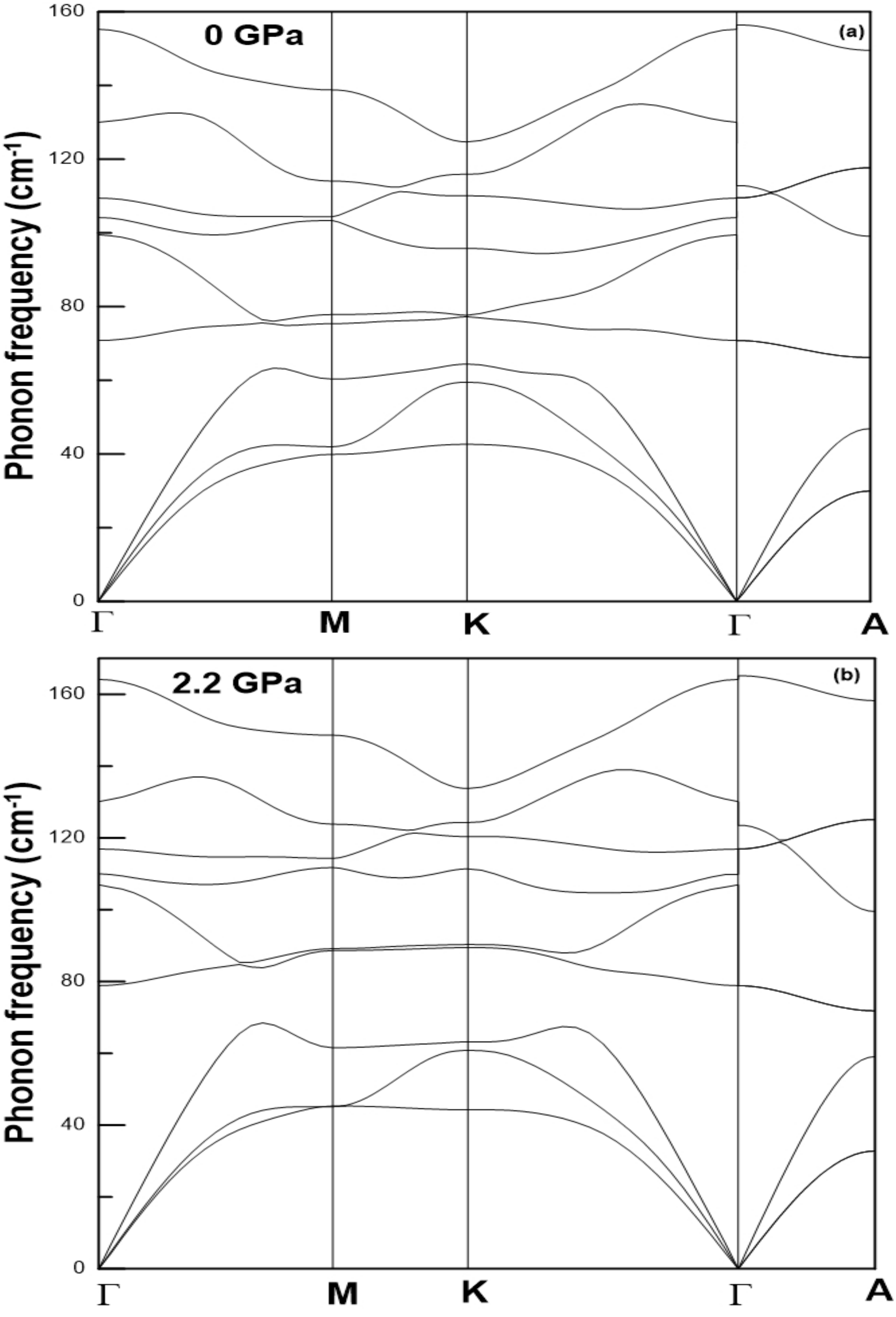

Fig. S5. Phonon dispersion curves of BiTeBr along the whole Brillouin zone at room pressure (a) and 2.2 GPa (b).

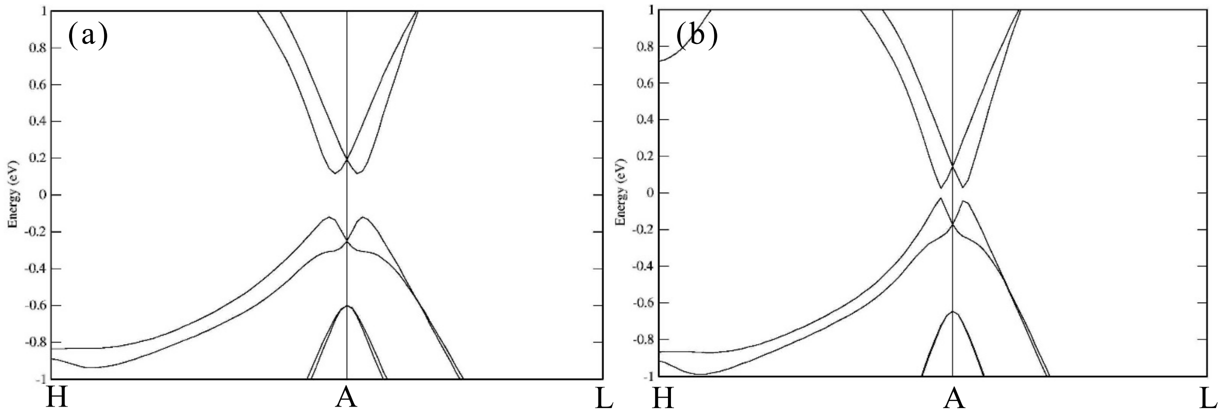

Fig. S6. Detail of the electronic band structure of BiTeBr along the H-A-L directions at room pressure (a) and 2.2 GPa (b).

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