Supplementary Information for:

High pressure effect on electronic structure and thermoelectric properties of BiCuSeO: First-principles calculations

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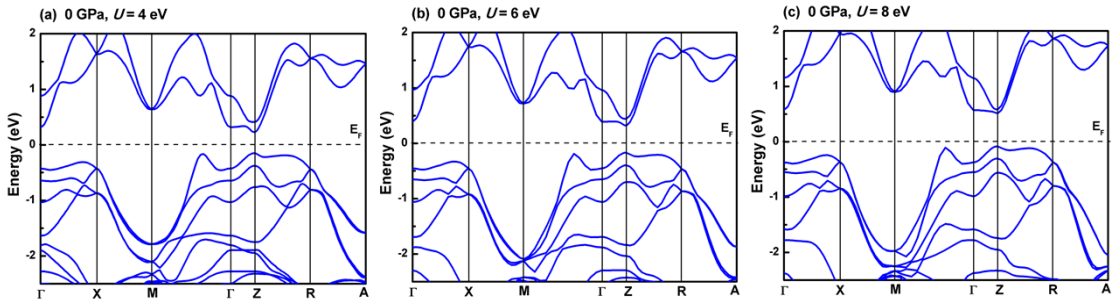

Fig. S1 Calculated band structures of BiCuSeO at 0 GPa under different *U* parameters. (a) 4 eV, (b) 6 eV, (c) 8 eV. The Fermi levels are set to zero.

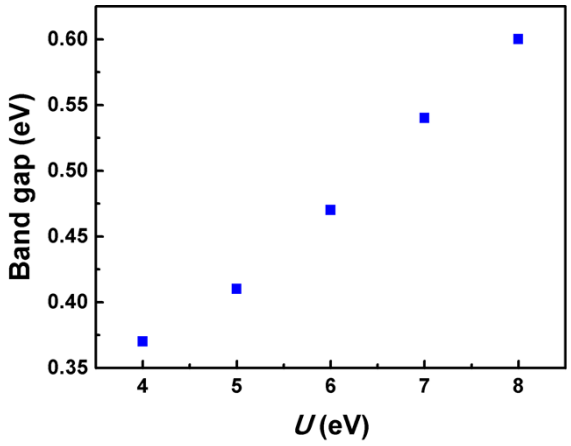

Fig. S2 Calculated band gaps of BiCuSeO at 0 GPa under different *U* parameters.

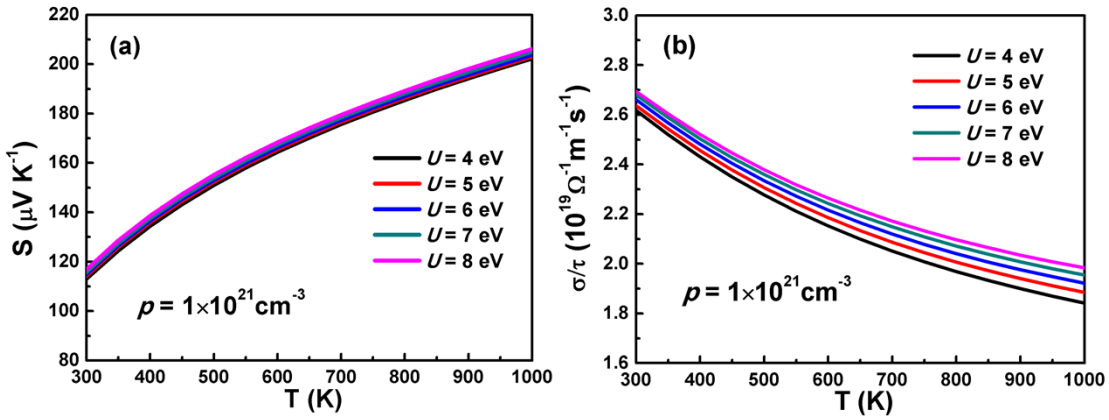

Fig. S3 Calculated (a) Seebeck coefficient and (b) electrical conductivity of BiCuSeO at 0 GPa under different *U* parameters.

We estimated the effect of the *U* parameter on the electronic structures and transport properties of BiCuSeO before the calculations. The typical electronic structures of BiCuSeO at 0 GPa under different *U* parameters are shown in Fig. S1. As we can see, the band structure characteristics are all similar except that the band gap increases as the *U* parameter increases. The band gaps of BiCuSeO under

different *U* parameters are reported in Fig. S2, it can be seen from Fig. S2 that the band gaps grows almost linearly with the *U* parameters. The transport properties of BiCuSeO under different *U* parameters are reported in Fig. S3. We can easily see that the Seebeck coefficient within the range of the considered temperature have remained largely unchanged under different *U* parameters, and the electrical conductivity have changed very little. The results show that thermoelectric properties of BiCuSeO are determined by the band features, not by the band gaps. That is, the *U* parameter has little influence on thermoelectric properties of BiCuSeO.

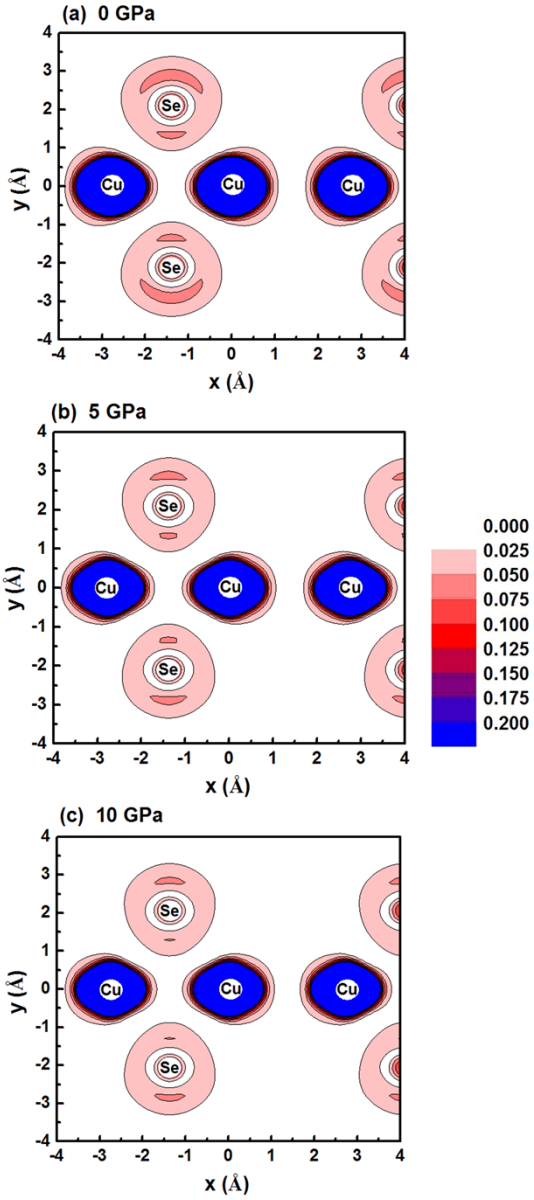

Fig. S4 Contour plots of the partial charge density in the upper portion of the valence bands (–2 ~ 0 eV) of BiCuSeO on the Cu–Se–Cu plane at different pressures. (a) 0 GPa, (b) 5 GPa (c) 10 GPa. The Fermi levels are set to zero. The unit of charge density is e/Å^3.

To analyze the changes of the conductive network for holes transport in *p*-type BiCuSeO, the antibonding states between Cu 3*d* and Se 4*p* are also estimated by using partial charge density distribution. The partial charge density on the Cu–Se–Cu plane of BiCuSeO in the upper portion of the valence bands at different pressures are shown in Fig. S4. From the contour plots of the partial charge density at zero pressure, obvious antibonding characteristics between Cu and Se atoms can be concluded because of a zero-charge-density gap between them, which is consistent with

literature[1,2] and our earlier work.[3] As the Se 4*p* orbitals become localized with enhanced external pressure, the Cu–Se antibonding states become more hybridized under pressure, and it will lead to electrical conductivity of *p*-type BiCuSeO increase with increasing pressure.

1 H. Hiramatsu, H. Yanagi, T. Kamiya, K. Ueda, M. Hirano and H. Hosono, *Chem. Mater.*, 2007, **20**, 326.

2 E. S. Stampler, William C. Sheets, Mariana I. Bertoni, W. Prellier, T. O. Mason and K. R. Poeppelmeier, *Inorg. Chem*., 2008, **47**, 10009.

3 D. Zou, S. Xie, Y. Liu, J. Lin and J. Li, *J. Mater. Chem. A*, 2013, **1**, 8888.