Supplementary Material

1. Computational methods

The first-principle calculations were performed by the application of DFT method with the combination of Vanderbilt-type ultrasoft pseudopotential and a plane-wave expansion of the wave functions [1] implemented in the CASTEP [2] module of Materials Studio 6.0 [3]. The self-consistent ground state of system was determined by using a band-by-band conjugated gradient technique to minimize the total energy of the system with respect to the plane-wave coefficients. The electronic wave functions were obtained in a density-mixing minimization method [4] for the self-consistent field calculation and the structures were relaxed using the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) [5] method. The cutoff energy of plane waves was set to 340 eV. Brillouin zones sampling was carried out by using the Monkhost−Pack scheme with a *k*-point grid of 1 × 3 × 1. The values of the kinetic energy cutoff and the *k*-point grid were determined to ensure the convergence of total energies.

The initial crystal was taken from Zhang *et al*. (CCDC 1042895) [6] and designed to the following computations. All the calculations are on the basis of the same experimental crystal structure of NTO/TZTN. The total energy of the system was converged less than 1.0×10^{-5} eV, the residual force less than 0.03 eV·Å^{-1}, the displacement of atoms less than 0.001 Å, and the residual bulk stress less than 0.05 GPa. Single point energies calculations were conducted at the B97-D/6-311++G** level of DFT with Gaussian 09 [7] suite. Previous studies showed that the performance of B97-D for H-bond systems is exceptionally good [8-10].

References

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2. Density of states (DOS)

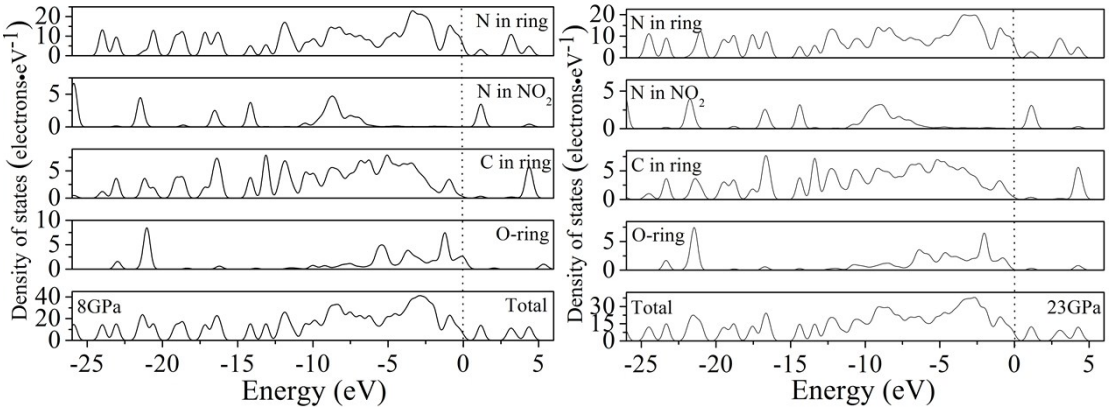

Fig. 1 The atom-resolved DOS and PDOS of cocrystal NTO/TZTN at 8 GPa, and 23 GPa.