Compositional Dependence of Uniaxial Zero Thermal Expansion and Zero Linear Compressibility in Metal-Organic Framework MIL-122 (Al, Ga, In)

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Electronic properties of MIL-122(Al, Ga, In)

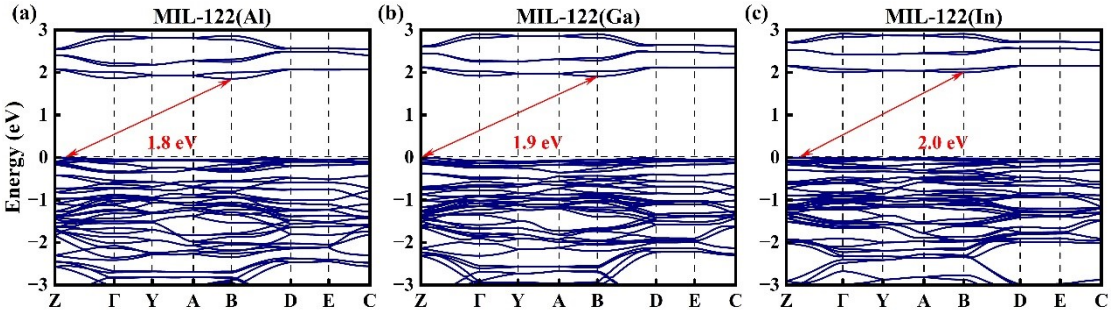


Figure 1s Calculated band structure along high-symmetry points of (a) MIL-122(Al), (b) MIL-122(Ga), and (c) MIL-122(In). The Fermi level is set to 0 eV.

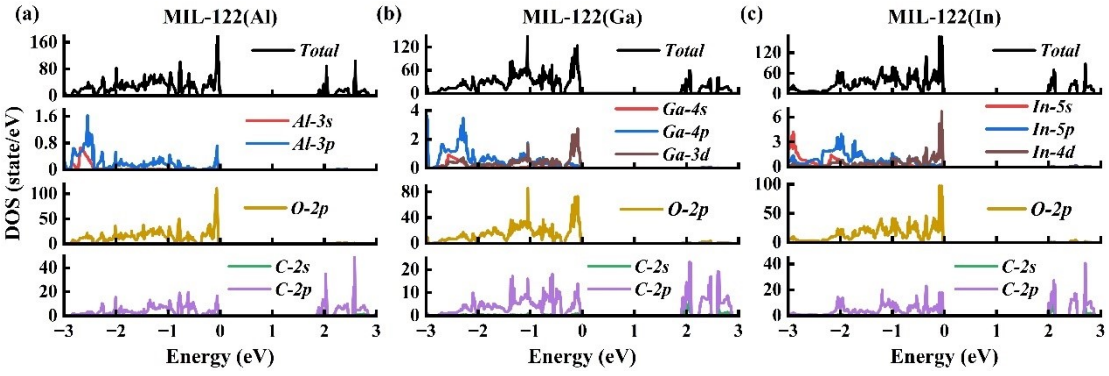


Figure 2s Calculated total and partial density of states (DOS) of (a) MIL-122(Al), (b)

MIL-122(Ga), and (c) MIL-122(In). The Fermi level is set to 0 eV.

The variations in the electronic band gaps of MIL-122(Al, Ga, In) are illustrated in Fig. 1s. It is observed that as the radius of metal atoms increases, the calculated band gap gradually increases, manifested as 1.8 eV for MIL-122(Al), 1.9 eV for MIL-122(Ga), and 2.0 eV for MIL-122(In). The Z and B points respectively constitute the valence band top (VBT) and conduction band bottom (CBB) of the indirect bandgap of MIL-122(Al, Ga, In). It should be noted that actual bandgaps may be larger than our calculated values due to underestimation by GGA approximation. The total and partial density of states (DOS) of MIL-122(Al, Ga, In) are compared in Fig. 2s. We have noticed that the conduction bands of MIL-122(Al, Ga, In) are only composed of the C 2p states, while the upper valence bands are primarily derived from the strong hybridization between Al 3p and O 2p states, Ga 3d and O 2p states, and In 4d and O 2p states, respectively. In addition, the interaction between the C 2p and O 2p states also contributes to the valance band of these systems.

Phonon density of states of MIL-122(Al, Ga, In)

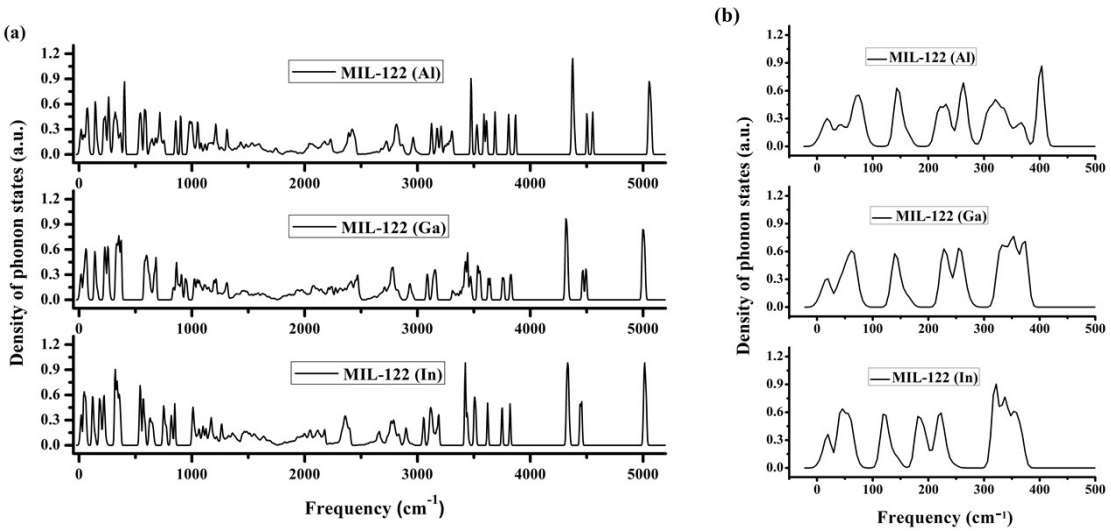
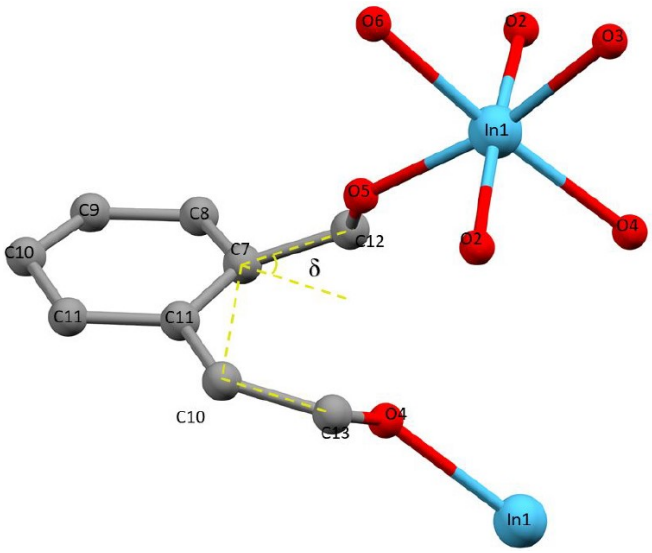


Figure 3s Calculated phonon DOS of MIL-122(Al, Ga, In) in (a) the entire frequency range and in (b) the low-frequency range.

The Phonon DOS of all compounds have been shown in Fig. 3s. Slight phonon imaginary frequencies exist, which we cannot eliminate within the QHA accuracy. High-order anharmonic interactions have a very good effect on dealing with material imaginary frequencies. However, this type of calculation is quite expensive and time-consuming. As a material with numerous atoms, it is unrealistic to use precise high-order anharmonic calculations for MOFs. So, to balance accuracy and efficiency, we have to choose QHA calculation. Although phonon imaginary frequencies exist, their proportion in the entire frequency range of the compound is tiny, so their influence on physical properties is very limited.

The pressure dependence of local structure in MIL-122(In)

At present, only the high-pressure experimental data [30] of MIL-122(In) is available. The evolution of the key bond length and angle in MIL-122(In) with pressure is shown in Fig. 4s.



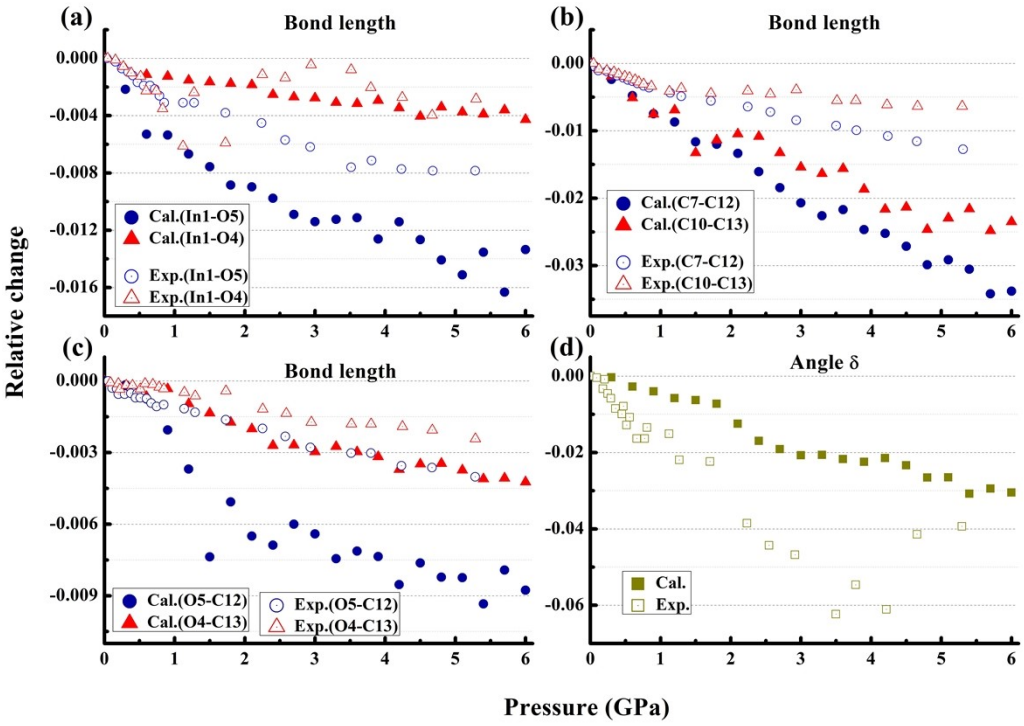


Figure 4s The evolution of the key bond length and angle in MIL-122(In) with pressure, compared with the experimental data [30].