Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Interaction of Magnesium Hydride Clusters with Nb Doped MgO Additive Studied by Density Functional Calculations

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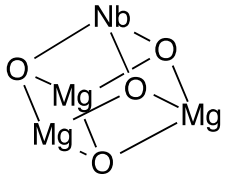
1. Electronic structure of Mg_3NbO_4 cation

The cationic Mg_3NbO_4 cluster has a C_{3v} symmetric structure as shown below.



Its possible electronic configurations in the frontier orbital levels are shown in Fig. S1 accompanied with the corresponding molecular orbitals. $1a_1$ orbital mainly consists of Nb d orbital, whereas $2a_1$ orbital extending over the entire cluster is a combination of Mg and Nb atomic orbitals. The degenerate e symmetric orbitals consist of Nb d orbital and Mg hybrid atomic orbitals. If the electronic configuration of the cluster is assumed to be a closed-shell, the most stable $1a_1$ orbital is doubly occupied. However, the difference in energy between these orbitals is not large enough, the triplet state having two singly occupied orbitals could be more stable. The present calculations showed that the triplet state shown in Fig. S1b bearing two singly occupied orbitals (SOMOs) and degenerated lowest unoccupied orbitals (LUMOs) is the most stable. These SOMOs and LUMOs are expected to play a role in interacting with other molecules. Hereafter, $1a_1$ and $2a_1$ orbitals are called SOMO1 and SOMO2, respectively.

When the hydrogen molecule coordinates to a metal atom, its binding mechanism is discussed in terms of donation and back-donation as shown in Fig. S2. Because the occupied boding σ orbital does not have a node, electron donation from it is possible to the vacant metal orbital without a node. Opposite to this, back-donation occurs from the occupied metal orbital

with a node to the unoccupied σ^* orbital. In addition, note that, because the Mg cation has formally no valence electrons, back-donation from the Mg cation is not taken into account.

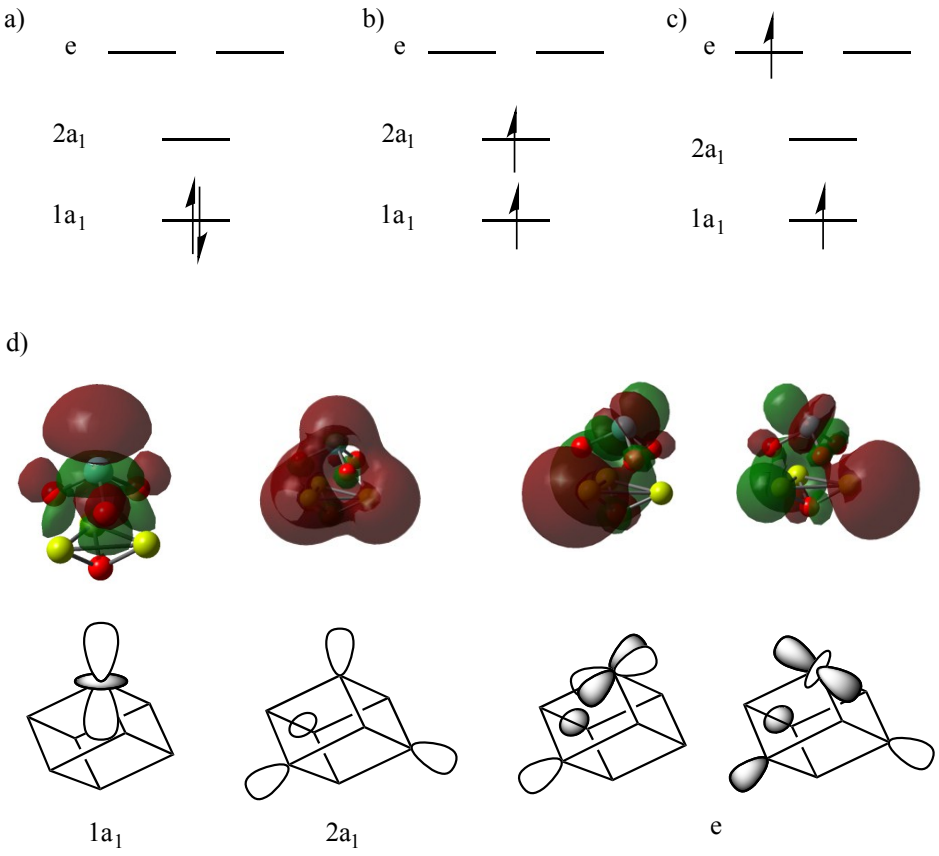


Fig. S1. Possible electronic configurations of Mg_3NbO_4 cation in the low-lying electronic states, a) $^1A_1$, b) $^3A_1$, and c) ^3E, and d) the relevant molecular orbitals.

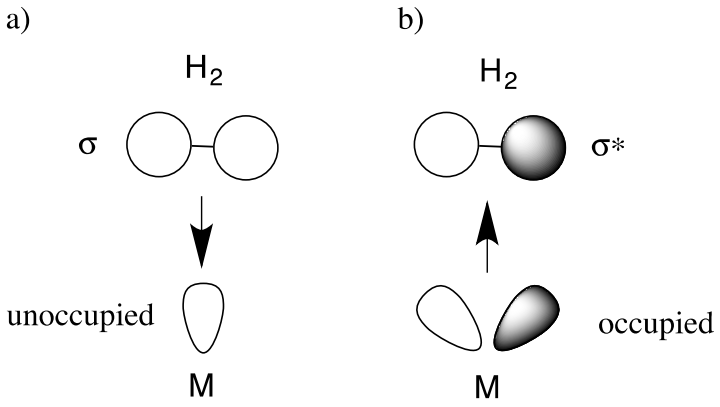


Fig. S2. (a) Electron donation from and (b) back-donation to the hydrogen molecule.

2. Electronic structure of Mg_3NbO_4 –H_2

The above argument and the shape of molecular orbitals shown in Fig. S1 suggest that, when the hydrogen molecule attacks the Mg atoms, the hydrogen molecule would interact with the $2a_1$ and e orbitals of Mg_3NbO_4 to donate electrons. Because the $1a_1$ orbital has only small lobes on the Mg cations, it does not participate into the interaction. The orbital correlation diagram for this case is

shown in Fig. S3a. The σ orbital of the hydrogen molecule interacts with the $2a_1$ orbital as well as the e orbitals to form the orbital φ_1 representing the electron donation between Mg and the hydrogen molecule. The shapes and energies of the singly occupied orbitals φ_2 and φ_3 are similar to those of the $1a_1$ orbital and one of the e orbitals of Mg_3NbO_4. This is because they do not interact with the hydrogen molecule. When the hydrogen molecule attacks the Nb cation, the interactions are different as shown in Fig. S3b. While the σ orbital of the hydrogen molecule similarly interacts with the $2a_1$ orbital, the orbital representing the back-donation from the Nb d orbital to the σ^* orbital (φ_7) is occupied by an electron. The singly occupied $1a_1$ orbital consisting of the d orbital with a proper nodal character realizes the back-donation to the σ^* orbital of the hydrogen molecule. Accordingly, the larger binding energy in the attack of the hydrogen molecule to Nb in Mg_3NbO_4 than that in the attack to Mg can be ascribed to the contribution from the back-donation. This also accounts for the longer H-H bond distance.

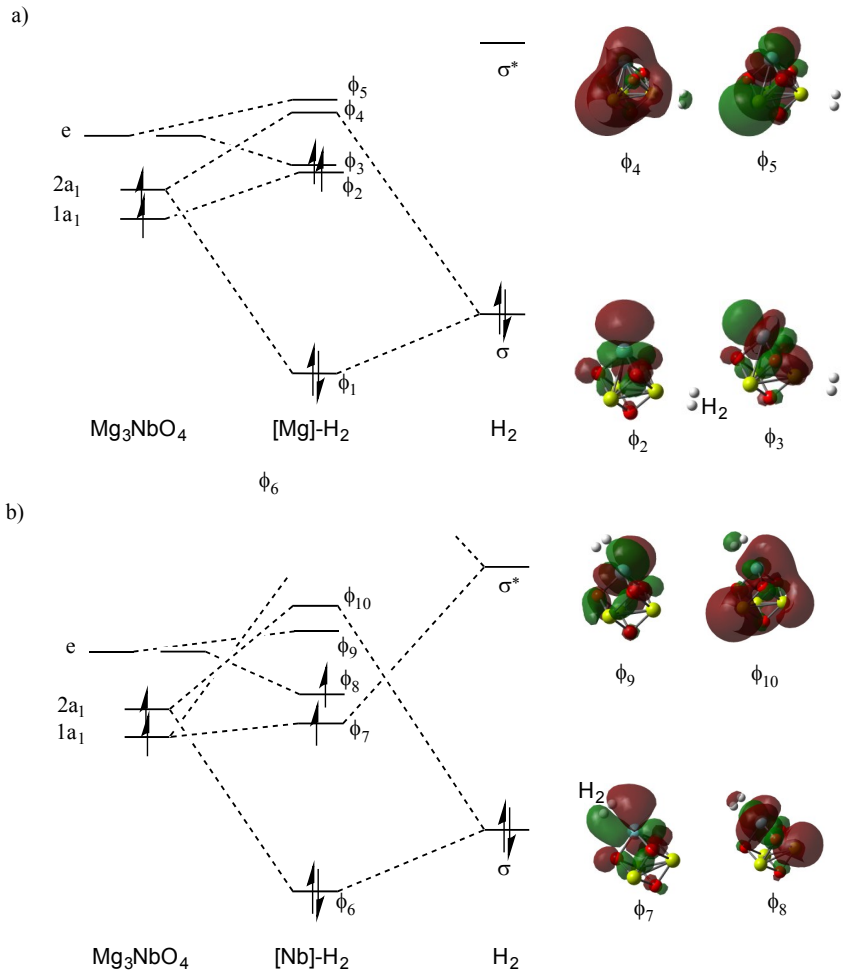
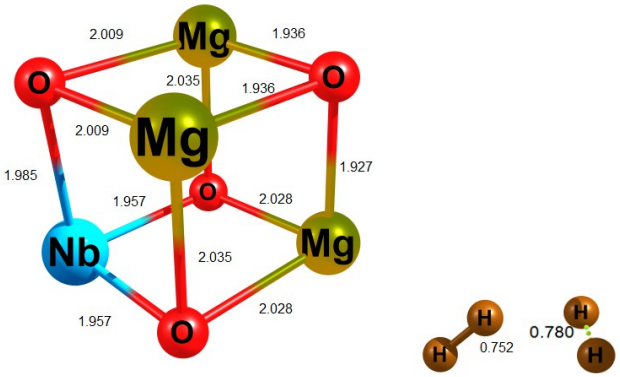
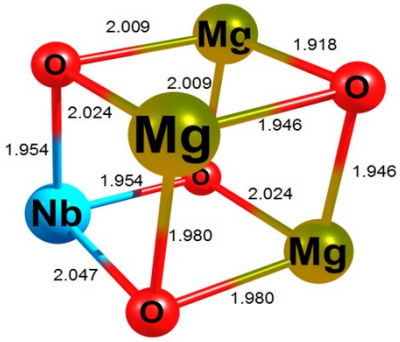


Fig. S3. Orbital correlation diagram for the attack of the hydrogen molecule to a) Mg and b) Nb in Mg_3NbO_4 cation.

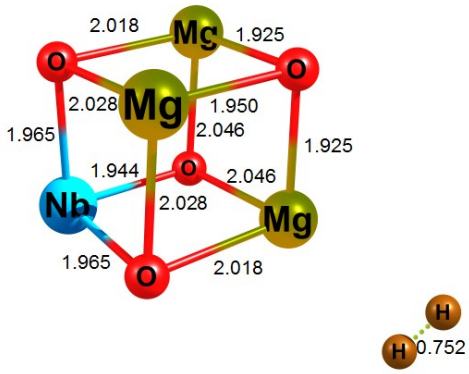
3. Optimized structures of $Mg_3NbO_4 – mH_2$ (m = 1 – 4) for category I and II



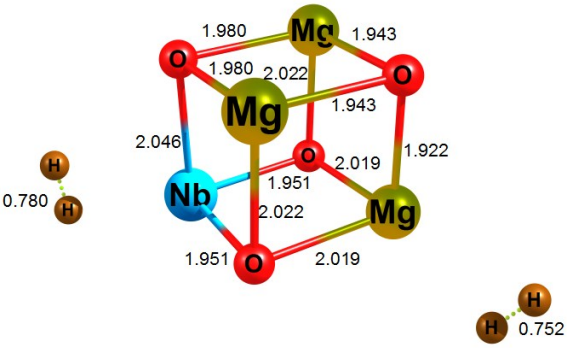
Mg_3NbO_4-1H_2 (H_2 towards Mg)



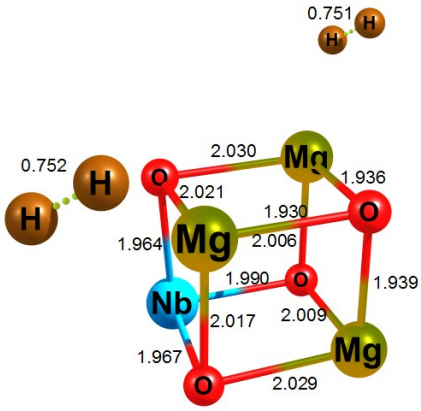
Mg_3NbO_4-1H_2 (H_2 towards Nb)



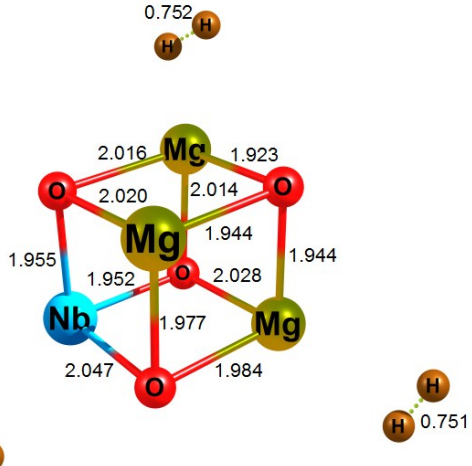
Mg_3NbO_4-2H_2 (one H_2 towards Mg)



Mg_3NbO_4-2H_2 (one H_2 towards Nb)

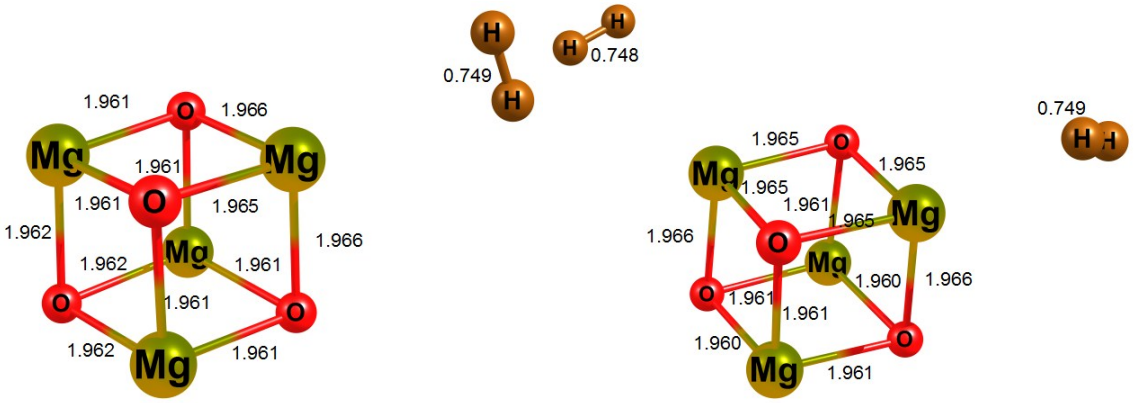


Mg_3NbO_4-3H_2 (one H_2 towards Mg)

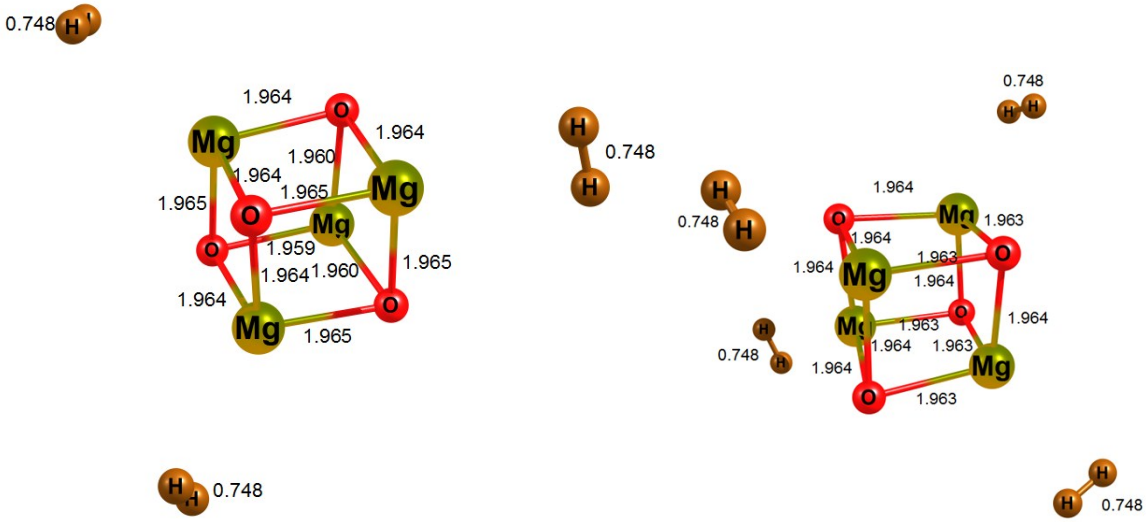


Mg_3NbO_4-3H_2 (one H_2 towards Nb)

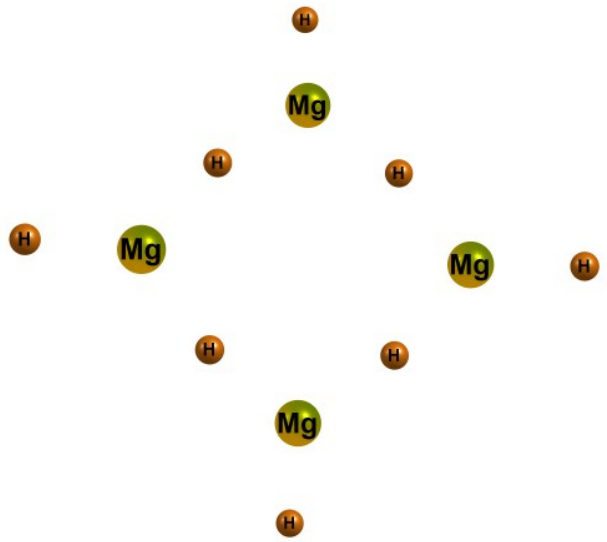
4. Optimized structures of Mg_4O_4 – mH_2 (m = 1 – 4)



Mg_4O_4-$1H_2$ Mg_4O_4-$2H_2$



Mg_4O_4-$2H_2$ Mg_4O_4-$3H_2$



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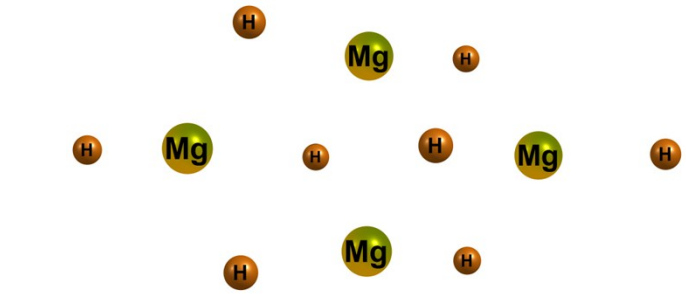
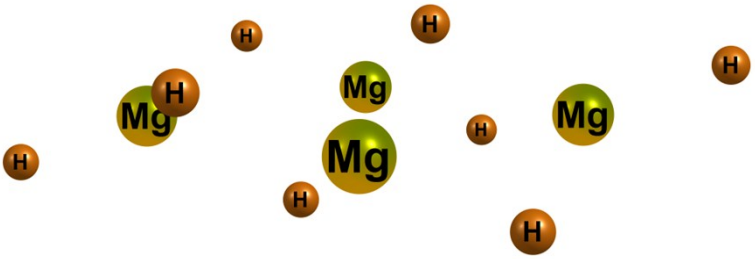


Top view



Side view

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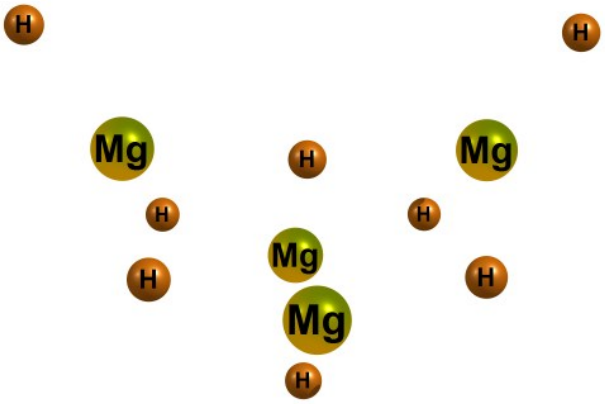

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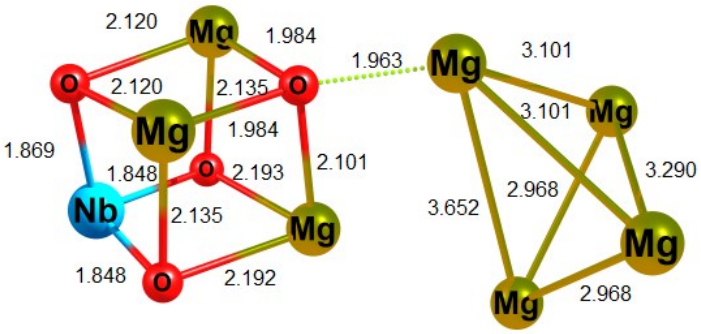
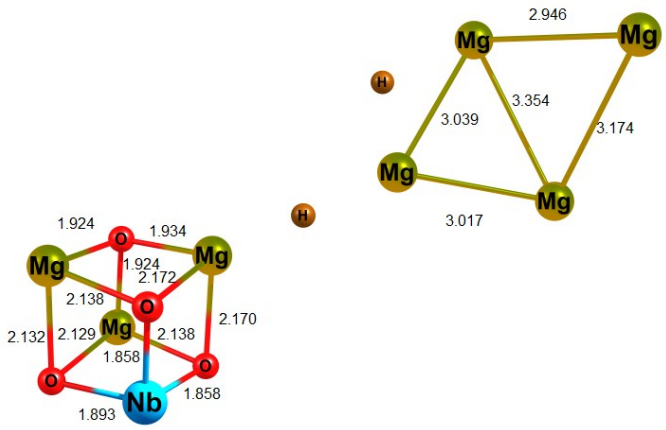
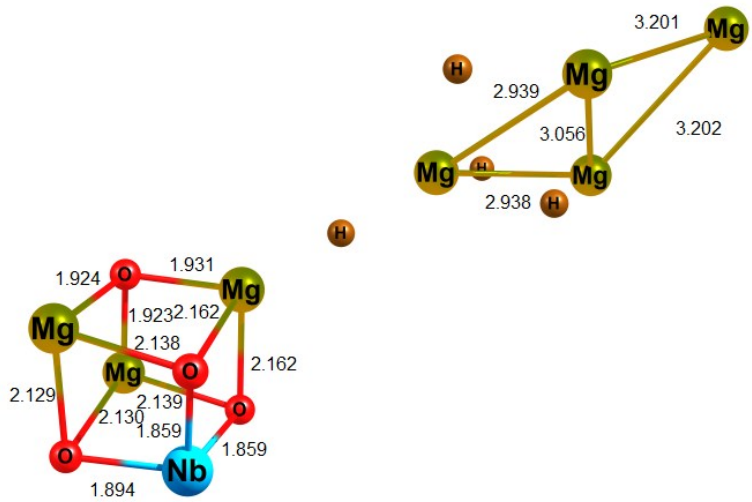
5. Three different isomers of Mg_4H_8 clusters



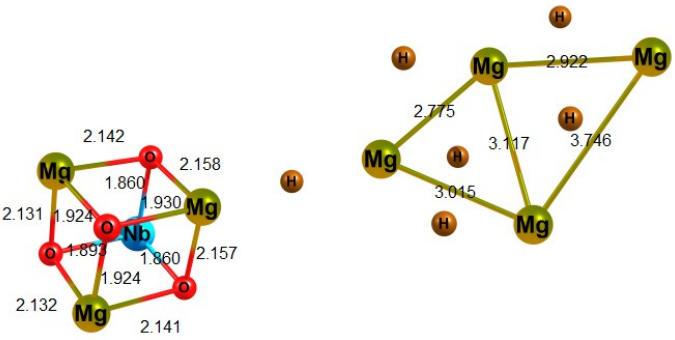
Mg_3NbO_4-Mg_4



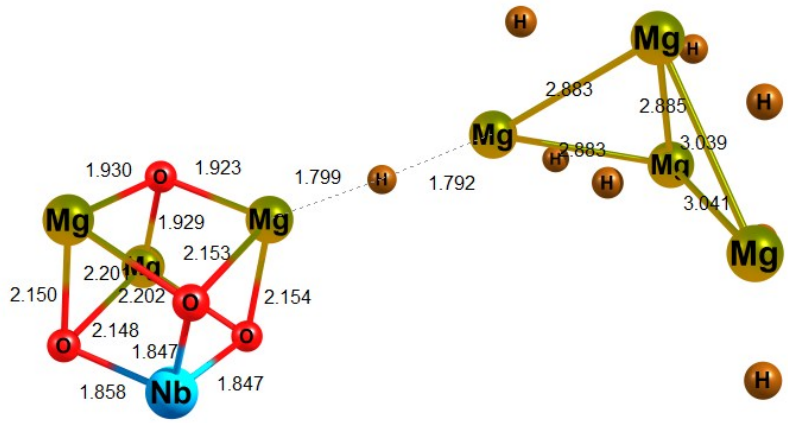
Mg_3NbO_4-Mg_4H_2



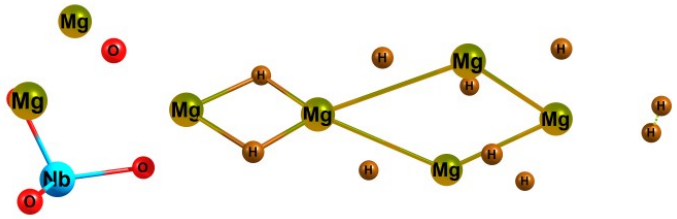
Mg_3NbO_4-Mg_4H_4



Mg_3NbO_4-Mg_4H_6



Mg_3NbO_4-Mg_4H_8



Mg_3NbO_4-Mg_4H_{10}

6. Optimized complex structures of $Mg_3NbO_4 – Mg_4H_x$ (x = 0, 2, 4, 6, 8, 10) system