Supplementary Information for

Tuning the performance of a Mg negative electrode through grain boundaries and alloying toward the realization of Mg batteries

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Atomic structures of the grain boundaries with different rotating angles

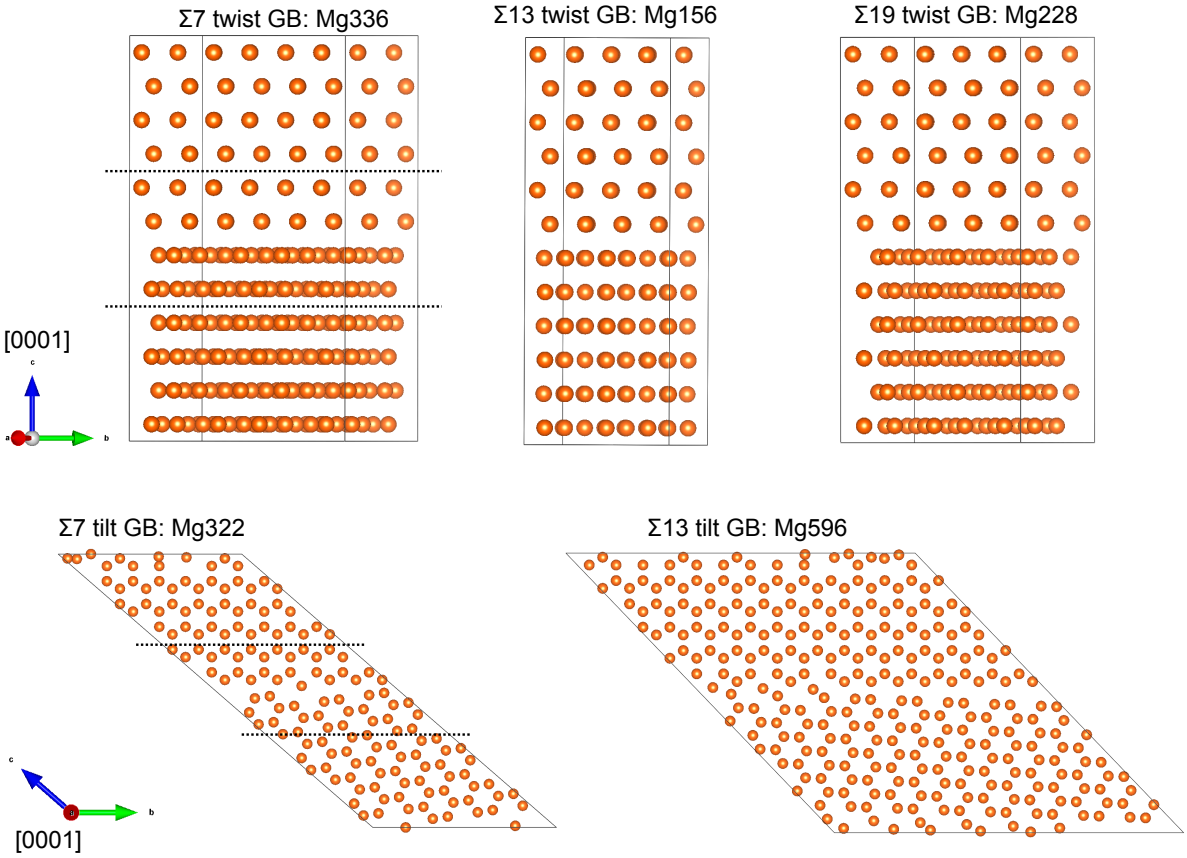
The (0001) Mg surface has been found to be the most energetic-favorable surface.[1,2] Thus, we focus on the twist and tilt grain boundaries (GBs) with [0001] rotating axis. In this work, we consider the GBs with coincident site lattices (CSL) because it was suggested to be more stable.[3,4] In the Mg hexagonal close-packed (hcp) structure on the [0001] direction, some specific rotating angles can yield CSL GBs, denoted by sigma (Σ) notation, where Σ is the reciprocal density of coincidence sites. The rotating angles and the corresponding Σ values are listed in Supplementary Table 1. The rotating angles marked in bold are the ones selected for generating GBs in this work. We have also examined the effect of the distance between the two grains in the calculation cell in terms of total energy, as shown in Supplementary Table 2. Because the total energy per atom increases with the distance, we chose not to add extra distance between the grains, the final atomic structures of twist and tilt GBs with different rotating angles were built via pymatgen.analysis.gb.grain module in Pymatgen[5] and shown in Supplementary Figure 1. We did not consider the Σ19 tilt GB in this work because the number of atoms of Σ19 tilt GB is over 1,000 that exceeds our calculation capacity.

Supplementary Table 1. Rotating angles and the corresponding Σ values that can yield CSL grain boundaries on [0001] direction in the hcp structures.

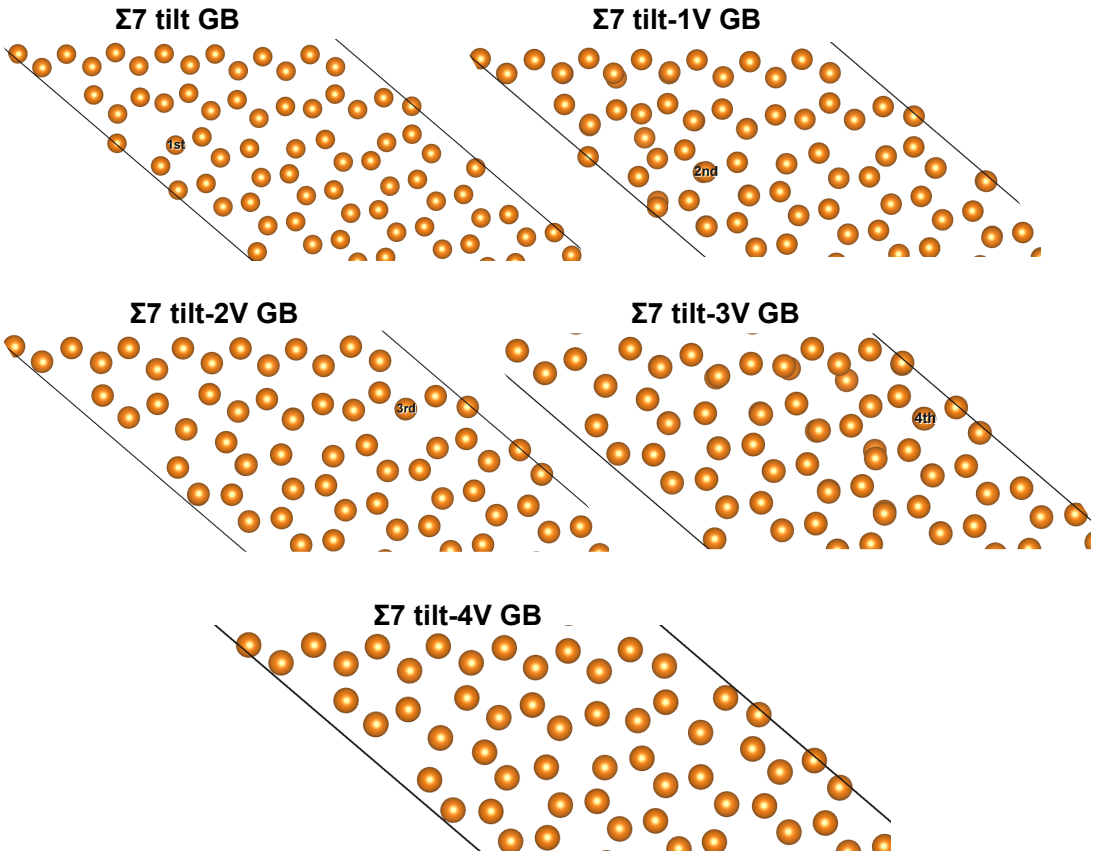
Σ	Rotating angle (^{0})
7	**21.79**
	38.21
	81.79
13	27.80
	32.20
	87.80
19	**13.17**
	42.83
	73.17

Supplementary Table 2. The energy change in Σ7 tilt GB when the additional distance between the two grains is changed (atomic structure shown in Supplementary Figure 1).

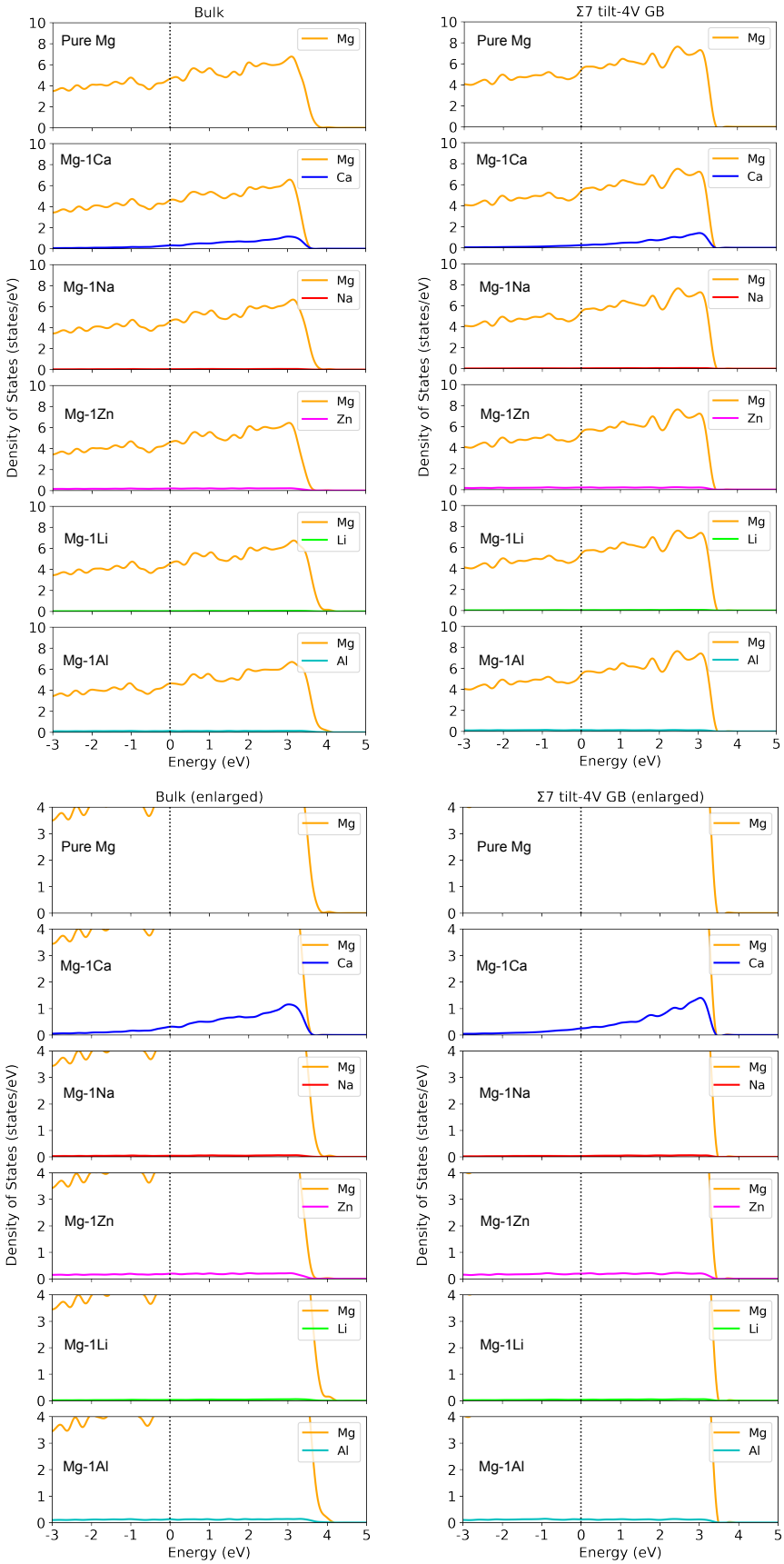
Additional distance between the two grains (Å)	Total energy (eV)	Number of atoms	Total Energy per atom (eV/atom)
0	**-69.44**	**49**	**-1.42**
1	-75.60	55	-1.37
2	-74.16	56	-1.32



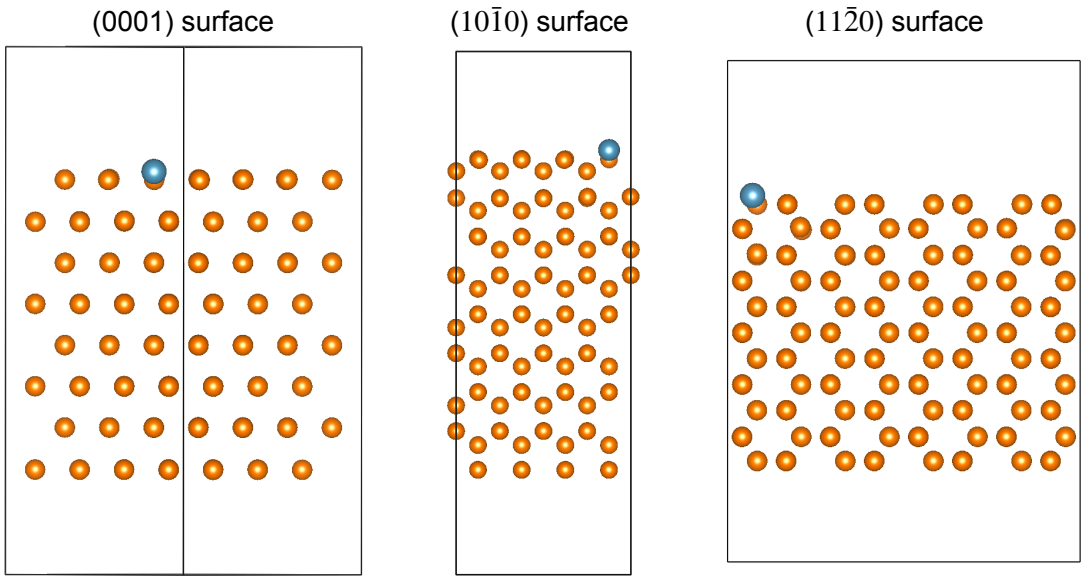
Supplementary Figure 1. Atomic structures of the [0001](0001) twist GB and [0001]($10\bar{1}0$) tilt GB with different rotating angles. The Mg atoms in between the dashed lines in Σ7 twist GB and Σ7 tilt GB were removed one at a time or replaced by the dopant to calculate the vacancy formation energy of the Mg atoms.



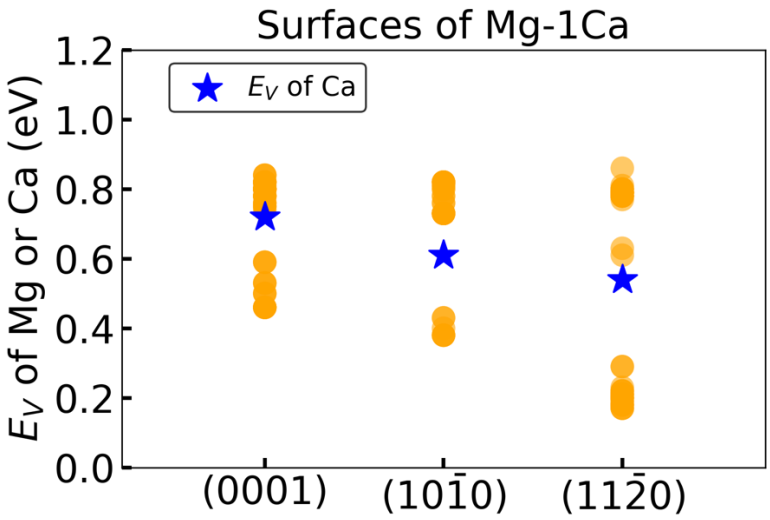
Supplementary Figure 2. The atomic structures of the defective tilt GBs investigated in this work. The notation, 1V, means one Mg atom has been removed from the cell, and so on. The Mg atoms marked as 1st represent the atom with a negative and the smaller vacancy formation energy and will be removed spontaneously. The vacancy formation energies of all the Mg atoms become positive until four Mg atoms are removed (Σ7 tilt-4V GB), the calculation results can be found in Figure 1 (b) in the main text.



Supplementary Figure 3. Projected density of states of the bulk structures (left) and the Σ7 tilt-4V GB structures of Mg and Mg-alloys.



Supplementary Figure 4. Favorable positions of the Ca atom at three Mg surfaces and the optimized structures. All the atoms in the top four layers were selected and removed one at a time to calculate the vacancy formation energy.



Supplementary Figure 5. Vacancy formation energy (Ev) of Mg atoms and Ca atom at three surfaces, the corresponding structures are shown in Supplementary Figure 4.