Supporting Information:

A density-functional theory approach to the existence and stability of molybdenum and tungsten sesquioxide polymorphs

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**S1: DFT technicalities**

To ensure well-converged structures, the *k*-point grid was increased until the number of *k*-points multiplied with the number of atoms was greater than 5000. A further increase of the *k*-points resulted in marginal changes in the total energies of only about 1 J/mol. Such small changes are irrelevant for our investigation, as the lowest observed energy difference between two structure types is about 1 kJ (Sm2O3 to Sb2O3) and in all other cases at least 1.4 kJ/mol. The final *k*-point grid for all structures is listed in Table 1.

Table 1: Details of the k-point mesh and the number of k-points in the irreducible Brillouin zone for all investigated polymorphs of Mo2O3 and W2O3.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| starting structure | atoms/cell | *k*-point mesh | *k*-points | atoms x *k*-points |
| Ag2O3 | 10 | 30 x 30 x 30 | 816 | 8160 |
| Al2O3 | 30 | 20 x 20 x 6 | 242 | 7260 |
| Au2O3 | 40 | 5 x 9 x 24 | 195 | 7800 |
| Bixbyit | 80 | 10 x 10 x 10 | 76 | 6080 |
| Fe2O3 | 40 | 16 x 9 x 7 | 180 | 7200 |
| Ga2O3 | 20 | 6 x 24 x 9 | 364 | 7280 |
| GdFeO3 | 20 | 16 x 12 x 10 | 378 | 7560 |
| La2O3 | 5 | 18 x 18 x 12 | 1037 | 5185 |
| Rh2O3 | 20 | 14 x 15 x 10 | 384 | 7680 |
| Sb2O3 | 20 | 19 x 8 x 17 | 450 | 9000 |
| Sb2S3 | 20 | 7 x 27 x 10 | 336 | 6720 |
| Sm2O3 | 30 | 5 x 25 x 9 | 299 | 8970 |
| V2O3 | 20 | 9 x 15 x 11 | 400 | 8000 |

**S2: Metal bonds in the corundum type**

A bonding study of the energetically favored corundum type structure was performed to analyze the nature of the metal-metal interaction. The DOS showed a small amount of electron density at the Fermi level for both compounds (Mo2O3 and W2O3). The shortest Mo‒Mo distances are 2.7 and 2.9 Å while the equivalent W‒W distances in the corundum structure are 2.7 and 3.0 Å. The calculated pCOHP (projected Crystal Orbital Hamilton Population) data clearly evidence that the short M‒M interactions (2.7 Å) are of bonding nature while the longer interactions also include antibonding contributions.

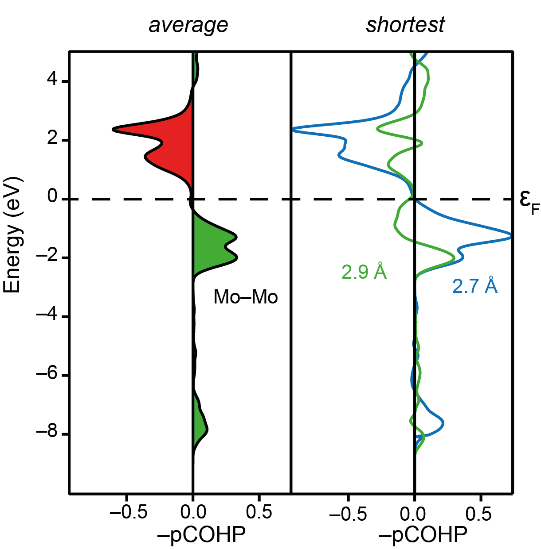
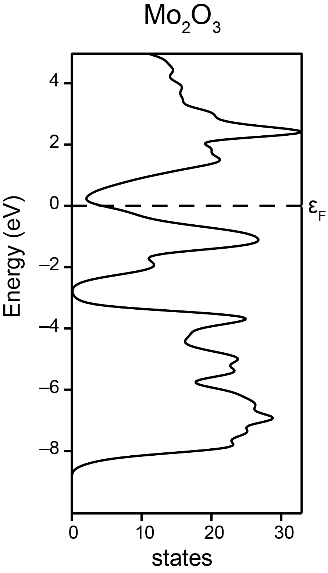


Figure 1: Calculated DOS (left) and pCOHP (right) of corundum-type Mo2O3.

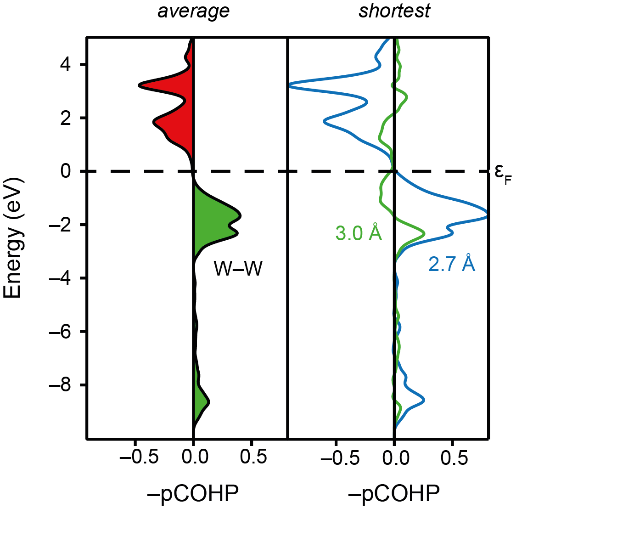
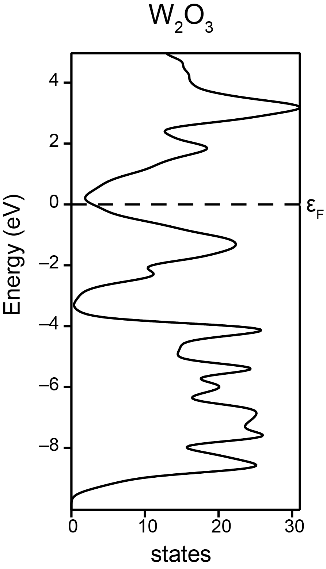


Figure 2: Calculated DOS (left) and pCOHP (right) of corundum-type W2O3.