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Real and Virtual Polymorphism of Titanium Selenide with Robust Interatomic Potentials - Electronic Supplementary Information

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Electronic Supplementary Information

The following gives a brief description of the findings regarding TiSe_2 clusters. The clusters have been generated using our PSM IP model and a GA approach. The structures have been fully re-optimised and compared with a DFT approach.

We have also tested the performance of our PSM IP to reproduce the structure and energy of several gas phase TiSe_2 clusters. We emphasize, however, that the current PSM IP were fitted to reproduce the experimental crystal structure and physical properties of bulk TiSe_2 with no aim to predict accurately the properties of TiSe_2 clusters. The chemical bonding, coordination number and local environment may differ significantly between bulk and clusters, and the same would most likely apply regarding their physical properties. Therefore, this exercise is purely illustrative. We have obtained the low energy $(\text{TiSe}_2)_n$ ($n = 2, 3, 4$) clusters at the PSM IP level using a GA approach as used in refs. 1–3 with the KLMC code.^{1,4,5} In total, 25 low energy clusters were obtained and their structures were fully reoptimised at the DFT level using the all-electron, full potential electronic structure code FHI-aims.⁶ A light basis set of numerical atom-centered orbitals (approximately equivalent to triple-zeta plus polarisation Gaussian type basis sets)⁷ was used. The zero order regular approximation (ZORA)^{8,9} was used to take into account scalar-relativistic effects. Figure 1 shows the energy references for TiSe_2 clusters. For the 5 $(\text{TiSe}_2)_2$ clusters, only 3 unique ones were left after DFT optimisation. As seen in Figure 1, PSM IP based structures 3 and 4 converged to DFT structures 1 and 2, respectively. The energy difference between these two clusters is, however, very small (ca. 0.0011 eV). For $(\text{TiSe}_2)_3$, there are only 6 unique configurations at the DFT level, with those ranked 3 and 4 with the PSM IP converging to structure 1 at the DFT level, whereas those ranked 8 and 9 with the PSM IP converged to the one ranked 5 with DFT.

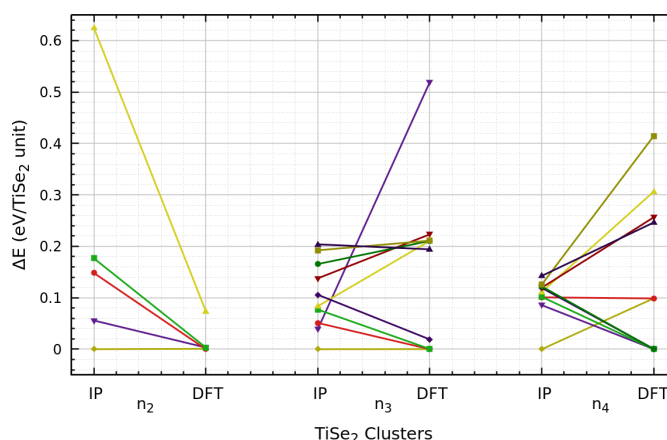


Fig. 1 Energy map ranking of the 25 TiSe_2 clusters for 3 different cluster sizes $n = 2, 3, 4$.

In $(\text{TiSe}_2)_4$, there are 9 DFT unique configurations. In general, we conclude that there are some structural changes in the PSM IP based $(\text{TiSe}_2)_n$ clusters when compared to those optimised with DFT. However, realistic low energy cluster candidates were predicted by our new PSM IP even though the fitting process did not include any information regarding undercoordinated ions. These new PSM IP, therefore, can be used as an efficient filter for finding low DFT energy structures not only for crystalline systems but also for clusters.

Notes and references

- 1 T. Lazauskas, A. A. Sokol and S. M. Woodley, *Nanoscale*, 2017, **9**, 3850–3864.
- 2 T. Lazauskas, A. A. Sokol, J. Buckeridge, C. R. A. Catlow, S. G. E. T. Escher, M. R. Farrow, D. Mora-Fonz, V. W. Blum, T. M. Phaahla, H. R. Chauke, P. E. Ngoepe and S. M. Woodley, *Phys. Chem. Chem. Phys.*, 2018, **20**, 13962–13973.
- 3 D. Mora-Fonz, T. Lazauskas, S. M. Woodley, S. T. Bromley, C. R. A. Catlow and A. A. Sokol, *J. Phys. Chem. C*, 2017, **121**, 16831–16844.
- 4 S. M. Woodley, *J. Phys. Chem. C*, 2013, **117**, 24003–24014.
- 5 M. R. Farrow, Y. Chow and S. M. Woodley, *Phys. Chem. Chem. Phys.*, 2014, **16**, 21119–21134.
- 6 V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren,

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- K. Reuter and M. Scheffler, *Comput. Phys. Commun.*, 2009, **180**, 2175–2196.
- 7 O. Lamiel-Garcia, K. C. Ko, J. Y. Lee, S. T. Bromley and F. Illas, *J. Chem. Theory Comput.*, 2017, **13**, 1785–1793.
- 8 C. Chang, M. Pelissier and P. Durand, *Phys. Scr.*, 1986, **34**, 394–404.
- 9 E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1994, **101**, 9783–9792.