

Structural and electronic properties of aggregates and crystals formed from Ti@Si₁₆, Sc@Si₁₆K, and V@Si₁₆F super-molecular units: a first principles study

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Abstract – The cage-like M@Si₁₆ clusters (M = Sc, Ti, V⁺) have been proposed as basic units to construct optoelectronic materials due to their large Homo-Lumo gap (> 1.5 eV) [1]. In this work, we have studied by means of first principles calculations the formation of aggregates and bulk crystal phases built from super-atom molecular units like Ti@Si₁₆, Sc@Si₁₆K and V@Si₁₆F

Firstly we have studied the trends in the formation of [Ti@Si₁₆]_n, [Sc@Si₁₆K]_n, and [V@Si₁₆F]_n aggregates as their size increases, going from linear to planar to three dimensional arrangements. The more favourable configurations for n ≥ 2 are those formed from the fullerene-like (FL) D_{4d} isomer of M@Si₁₆, instead of the ground state Frank-Kasper T_d symmetry of the isolated M@Si₁₆ unit. These units are joined preferably by Si-Si bonds between the Si atoms of their square facets and can form linear (wires), planar (multilayer), and three dimensional aggregates with several arrangements. In all cases the Homo-Lumo gap for the most favourable structure decrease with the size n. Trends for the binding energy, dipole moment, and other electronic properties are also discussed. Figure 1 shows the structure of the aggregates [Si₁₆VF]_n (n = 1-5).

With respect to bulk phases we have found meta-stable sc, fcc, bcc, NaCl, CsCl, and hcp (this only for TiSi₁₆) structures built from Ti@Si₁₆, Sc@Si₁₆K, and V@Si₁₆F super-molecules. The orientation of the molecule in the cell plays a critical roll. Ti@Si₁₆ reaches the largest cohesive energy for the bcc crystal with the FL isomer as basic unit. The preferable meta-stable crystal phase of Sc@Si₁₆K is again the bcc one. Instead, for V@Si₁₆F the NaCl structure, formed by V@Si₁₆ (FL) and F as the two atom cell components, results to be more bound. We further study the electronic and structural properties of these materials at finite temperature and pressure. Figure 2 shows the fits to Murnaghan equation of state for V@Si₁₆F crystals with D_{4d} and T_d symmetry of V@Si₁₆ superatom. A phase transition from NaCl to CsCl structure occurs at 0.24 GPa. Other extended systems, like wires and nanotubes composed of M@Si₁₆-Z units, have been studied.

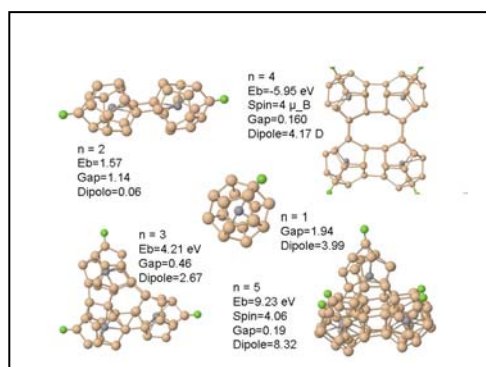


Figure 1: The (V@Si₁₆F)_n aggregates (n = 1-5) with fullerene-like D_{4d} structure of the V@Si₁₆ superatom.

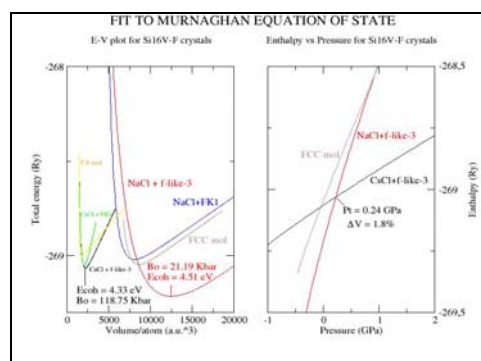


Figure 2: Fit to Murnaghan equation of state for V@Si₁₆F crystals with D_{4d} and T_d structures of V@Si₁₆ superatom.

References

- [1] K. Koyasu et al, *J. Phys. Chem. A*, **111** (2007) 42. *ibid*, *J. Chem. Phys.*, **129** (2008) 214301.
 [2] M. B. Torres, E. M. Fernández, and L. C. Balbás, *Phys. Rev. B*, **75** (2007) 205425.