

## Structural and electronic properties of aggregates and crystals formed from Ti@Si<sub>16</sub>, Sc@Si<sub>16</sub>K, and V@Si<sub>16</sub>F super-molecular units: a first principles study

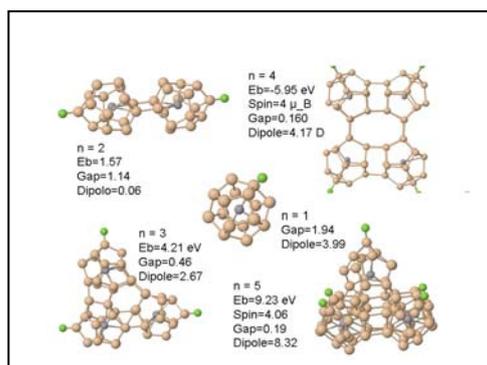
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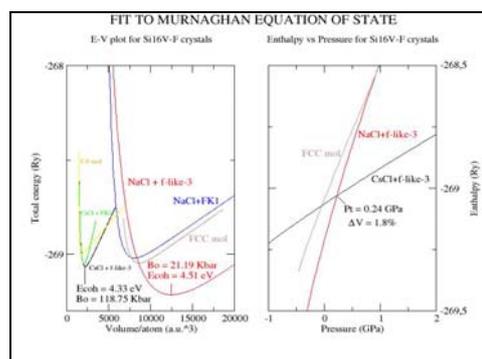
**Abstract** – The cage-like M@Si<sub>16</sub> clusters (M = Sc, Ti, V<sup>+</sup>) have been proposed as basic units to construct optoelectronic materials due to their large Homo-Lumo gap (> 1.5 eV) [1]. In this work, we have studied by means of first principles calculations the formation of aggregates and bulk crystal phases built from super-atom molecular units like Ti@Si<sub>16</sub>, Sc@Si<sub>16</sub>K and V@Si<sub>16</sub>F

Firstly we have studied the trends in the formation of [Ti@Si<sub>16</sub>]<sub>n</sub>, [Sc@Si<sub>16</sub>K]<sub>n</sub>, and [V@Si<sub>16</sub>F]<sub>n</sub> 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<sub>4d</sub> isomer of M@Si<sub>16</sub>, instead of the ground state Frank-Kasper T<sub>d</sub> symmetry of the isolated M@Si<sub>16</sub> 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 [Si<sub>16</sub>VF]<sub>n</sub> (n = 1-5).

With respect to bulk phases we have found meta-stable sc, fcc, bcc, NaCl, CsCl, and hcp (this only for TiSi<sub>16</sub>) structures built from Ti@Si<sub>16</sub>, Sc@Si<sub>16</sub>K, and V@Si<sub>16</sub>F super-molecules. The orientation of the molecule in the cell plays a critical roll. Ti@Si<sub>16</sub> reaches the largest cohesive energy for the bcc crystal with the FL isomer as basic unit. The preferable meta-stable crystal phase of Sc@Si<sub>16</sub>K is again the bcc one. Instead, for V@Si<sub>16</sub>F the NaCl structure, formed by V@Si<sub>16</sub> (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@Si<sub>16</sub>F crystals with D<sub>4d</sub> and T<sub>d</sub> symmetry of V@Si<sub>16</sub> superatom. A phase transition from NaCl to CsCl structure occurs at 0.24 GPa. Other extended systems, like wires and nanotubes composed of M@Si<sub>16</sub>-Z units, have been studied.



**Figure 1:** The (V@Si<sub>16</sub>F)<sub>n</sub> aggregates (n = 1-5) with fullerene-like D<sub>4d</sub> structure of the V@Si<sub>16</sub> superatom.



**Figure 2:** Fit to Murnaghan equation of state for V@Si<sub>16</sub>F crystals with D<sub>4d</sub> and T<sub>d</sub> structures of V@Si<sub>16</sub> 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.