Structure Discrimination of Sn_NGa with N = 9–15

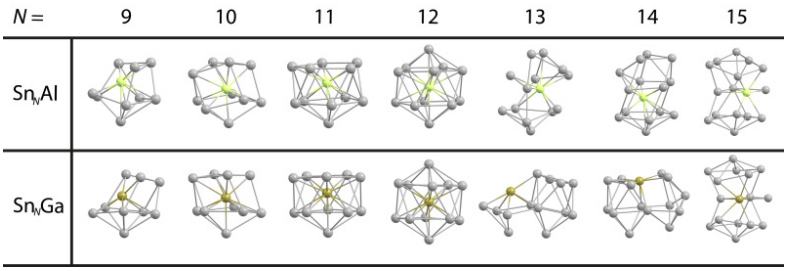

Figure 1: Predidcted ground state structures (GM) for Sn_NGa with N = 9–15 at the PBE0/def2-TZVPP level of theory in comparison to their previously calculated Sn_NAl counterparts. Tin atoms are displayed as gray spheres while the gallium atom is shown in yellow and the aluminum atom in green.

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Project Term
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Clusters
Lichtenberg Cluster Darmstadt

Software
GAUSSIAN, ORCA, NWChem, Quantum ESPRESSO

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Introduction

Since semiconductors are fundamental for modern technologies, the research is focused on such materials and their miniaturization in particular. The investigation of materials at the sub-nanoscale becomes mandatory because the opto-electric properties change significantly with size and chemical composition. By changing these properties, band gaps can be tuned and typical metal-like tin becomes semiconductive. Furthermore, tin forms very stable cages and can be doped with most elements from the periodic table. In a previous project aluminum-doped tin was investigated in quantum chemical calculations to understand the geometric and electronic structures of these nanosystems. In this project, the doping atom is exchanged by gallium which is in the same group in the periodic table and is, therefore, very similar to aluminum. By calculating gallium-doped tin clusters and comparing them to aluminum-doped tin clusters, the influence on the dopant can be investigated. The predicted geometric structures can then be compared to experimental data generated by electric and magnetic molecular beam deflection experiments.

Methods

Energetically-favored geometries were generated using a plane-wave Density Functional Theory-based (pw-DFT) Genetic Algorithm (GA) developed in our group. Calculations for all clusters are performed with an applied Ultrasoft-Rabe-Rappe-Kaxiras-Joannopoulos pseudopotential for both elements and an energy cut-off of 30 Ry. Electrons which are explicitly described are calculated with a Methfessel-Paxton-smearing. These calculations are performed using the Quantum Espresso software package. From the generated pool of structures candidates in the energy range of 2 eV are optimized on the PBE0/def2-TZVPP level of theory with the quantum chemistry program NWChem and verified with frequency analyses. The

latter is carried out with the quantum chemistry program ORCA and Gaussian16.

Results

Within this project the geometrical structures of Sn_NGa with N = 9–15 were calculated and further optimized. We calculated vibrational frequencies to verify the found structures and calculated dipole moments for isomers within an energy range of about 0.1 eV relative to the energy of the predicted global minimum. With the help of the dipole moments and the moments of inertia given by the geometric structures these candidates are compared to experimental data. It was possible for most of the investigated clusters to successfully assign one of the candidates to the experimental electric beam deflection profiles. However, for the $Sn_{12}Ga$ cluster only one candidate is found within the considered energy range which cannot completely explain the experimental data. This is very similar to the observation of the $Sn_{12}Al$ data for which also only one structure could be found that could not explain the experimental deflection profile entirely.

Discussion

The calculated structural geometries show a very similar growth pattern to their Sn_NAl counterparts which was confirmed for most species by electric beam deflection experiments. Although, the structural motifs found for both systems of the same cluster size are very similar, the energetic order of the isomers differs for N = 13 and 14 for which more than one isomer was found within the considered energy range. Just like for the $Sn_{12}Al$ cluster, only a spherical structure was found within the considered energy range showing a center of inversion. Therefore, no beam broadening should be observed in the electric beam deflection. The experimental data, however, indicate a nonpolar and polar fraction simultaneously present in the molecular beam of which the nonpolar fraction must be the geometric structure with a center of inversion. Although, the latter can be assigned to the found global minimum of $Sn_{12}Ga$, the asymmetric isomer is still unknown.

Publications

Rivic, F.; Fuchs, T. M.; Schäfer, R.: "Discriminating the influence of thermal excitation and the presence of structural isomers on the Stark and Zeeman effect of AlSn12 clusters by combined electric and magnetic beam deflection experiments.", Phys. Chem. Chem. Phys., 23(16), 9971–9979, (2021) https://doi.org/10.1039/d1cp00351h

Rivic, F.; Lehr, A.; Fuchs, T. M.; Schäfer, R.: "Joint electric and magnetic beam deflection experiments and quantum chemical studies of MSn12 clusters (M = Al, Ga, In): on the interplay of geometric structure and magnetic properties in nanoalloys.", Faraday Discussions, 242, 231–251, (2023) https://doi.org/10.1039/D2FD00091A

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