

# Effects of Chlorine and Fluorine on the Vibrational Properties of Nanoporous Germanium: A Theoretical Approach

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## Extended Abstract

Since the discovery of photoluminescence in nanoporous silicon in 1990, nanoporous semiconductors have attracted much attention due to their different properties and potential applications. Compared to porous silicon, nanoporous Germanium (pGe) has been less studied, due to its difficult synthesis that involves a bipolar electrochemical etching in hydrochloric acid, compared to the rather simple synthesis of porous Silicon. However, pGe has been used in optoelectronics as photodetector, battery electrode for energy storage and backside reflector for photovoltaics. However, the theoretical characterization of this material is still scarce, this kind of investigation could be of the utmost importance in order to accelerate the development of applications using this nanostructured material, especially the determination of their vibrational properties which could indicate the stability of this material and its thermodynamic properties which are crucial for electronic and thermoelectric applications, also vibrational spectroscopies such as Raman and Infrared are intrinsically linked to the vibrational properties, by modelling these spectrums experimental investigations have a valuable resource for comparison since these are two of the most used non-destructive characterization techniques. In this work we study the vibrational properties of pGe using the first principles density functional perturbation theory and the supercell scheme [1,2]. The nanoporous structures are modelled by removing columns of atoms of the [001] direction from an otherwise perfect Ge crystal, then the surface dangling bonds are passivated with hydrogen atoms. The surface H is then replaced by F and Cl to elucidate the effects of these atoms on the vibrational properties of the pGe. Three pore sizes are modelled: 1.1, 1.4, and 1.6 nm, with the morphology chosen so that only single dangling bonds are present on the pore surface. This model has the advantage that it considers the interconnected nature of the porous network, that gives rise to the partial quantum confinement in these structures. The results show that the H-passivated porous structures are stable since there are no imaginary frequencies in their vibrational spectrum, having frequencies up to  $2000\text{ cm}^{-1}$ . When chlorine is introduced, the phonon spectrum gets compressed to lower frequencies with the highest being  $700\text{ cm}^{-1}$ . Finally, F showed many imaginary frequencies, therefore this passivation scheme is deemed unstable. For the stable structures further analysis was performed, showing that the modes with the highest Raman activity are the Ge-H stretching ones, contrary to the infrared spectrum where the highest intensity peaks are located in Ge-H and Ge-Cl bending modes frequencies. These results could be important in the characterization of pGe with techniques such as Raman and IR.

## References

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