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# Cage disorder and gas encapsulation as routes to tailor properties of inorganic clathrates

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ABSTRACT

Inorganic clathrates with the type II crystal structure are of interest as potential materials for high temperature thermoelectric applications. In this study we present ab initio calculations for the electronic and phonon properties of several Sn type II clathrate compositions with partial Ga substitution on the framework, empty cage $Sn_{136}$, and compounds of $Sn_{136}$ filled with inert Xe atoms. It is found that cage disorder due to atomic substitution and guest encapsulation affect the fundamental characteristics of these materials in profound ways. We determine that the stability of these materials is enhanced by the presence of guests and lack of direct Ga–Ga bonds in disordered clathrates. Inert Xe atoms provide a unique opportunity to preserve the overall electronic structure of $Sn_{136}$ and take advantage of the loosely bound guest rattling for enhanced phonon scattering. The calculated energy bands and density of states, as well as phonon band structure and mode Gruneisen parameter, enable further analysis of type II Sn clathrates and reveal interesting structure-property relations.



## 1. Introduction

Clathrate materials have cage-like structures characterized by tetrahedrally coordinated environments with $sp^3$-bonded framework lattices. The family of group IV clathrates and their unique properties have been studied extensively in the past several years, as this interest being motivated by their applications in thermoelectricity, superconductivity, and photovoltaics [1–5]. Inorganic and gas hydrate clathrates are in fact analogous in structure, with classifications of different types available [1,6].

Much of the work to date has focused on the role of the guest atoms inside the clathrate voids. The rattling of such guests (typically alkaline and alkaline-earth species) leads to phonon anharmonic scattering. This is an effective way to reduce the lattice thermal conductivity, a goal that is desirable for thermoelectricity [1,5]. The encapsulation of fillers from the first two columns of the periodic table results in ionic bonding with the framework. In many instances, this process reduces the band gap and in some cases it transfers the materials to a metallic state, this being problematic for thermoelectricity. Changing the framework composition is an alternative way of altering their physical properties. This particular direction has only recently begun to be investigated more systematically as the cage atoms can be partially substituted with lower valent atoms, such as Ga, In, and Al [7,8]. The mixed cage structural composition is important not only for the electronic properties but also for the phonon dynamics, as shown in type I clathrates [9,10]. We note that despite the significant body of research on various cage materials in the past several years, more work is needed in order to synthesize clathrates with low thermal conductivity and semiconducting transport for thermoelectric applications.

Exploring clathrates of different compositions shows that the frameworks can be categorized by symmetry of the constituent polyhedra, which can encapsulate different types of guests typically with atoms from group I or II [11]. It is also possible that the guest occupants are methane or noble gas atoms that weakly interact with the framework. The possibility of putting gaseous atoms inside the inorganic clathrate voids can lead to new pathways for property tuning. Due to their weak interaction with the framework, one envisions that nobel gas inserts may not significantly affect the band structure (thus the semiconducting behavior is preserved), but they can reduce the thermal conductivity at the same time. This would be a much desired scenario for thermoelectricity. Previous investigations have shown that Xe-filled type I clathrates, such as

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$Xe_8Si_{46}$, are ultimately unstable [12]. It was also found that the cages of type II clathrates, such as $Si_{136}$ and $Ge_{136}$, are generally too small to accommodate inert gas guests [13]. Another possibility to design clathrate properties is to utilize mixed cage materials [14]. Most of the work thus far has focused on type I clathrates [1,9]. However, it would be beneficial to further explore strategies of atomic substitution on frameworks beyond such systems [15] in combination with suitable guest atoms in order to achieve reduced thermal conductivity with a semiconducting transport behavior.

The goal of this research is to advance our fundamental understanding of type II Sn-based clathrates. We note that although type I Sn clathrates have been extensively studied over the past two decades [16–18], researchers have only recently begun working on type II Sn materials [19]. To advance the science of these systems and stimulate further experiments, here we investigate several type II Sn clathrates using first principles density functional theory (DFT) simulations. These include the empty cage $Sn_{136}$, several compounds with partial Ga substitution on the framework with various guest atoms, and several compositions of $Sn_{136}$ filled with Xe atoms. Several features found here reveal interesting structure-property relations, specifically, our simulations clearly show the stabilizing role of the guest atoms, which can also interact strongly with the clathrate framework. It turns out that the location of the Ga atoms on the framework is also a stability factor, which in turn can influence the electronic structure and charge transfer. Of particular interest are the Xe filled $Sn_{136}$, which show little electronic guest-cage interaction. The phonon properties are also calculated for the various materials. The phonon density of states, phonon band structure, and mode Gruneisen parameter help us give a microscopic picture of the vibrational characteristics of type II Sn clathrates.

## 2. Methodology

Here we perform electronic structure calculations utilizing DFT simulations via the VASP package [20,21]. This is a state of the art code that relies on the projector-augmented wave method with a plane-wave basis set and periodic boundary conditions. The exchange-correlation energy is calculated with the Perdew–Burke–Ernzerhof (PBE) function [22]. The unit cells for the considered materials (described in Results and Discussions Section) take advantage of the inherent symmetries of each composition. Ionic relaxation are performed with 367 eV cutoff. The force and total energy difference relaxation criteria are $10^{-4}$ eV/Å and $10^{-8}$ eV, respectively. The cell is allowed to change shape and volume during the structural relaxation with $9 \times 9 \times 9$ k-mesh. The tetrahedron integration method with Blöchl correction is used for the self-consistent calculations on the same k-grid. Also, the VESTA software package is utilized to perform the crystal structure and the electron localization function [23].

The phonon properties in terms of vibrational density of states (vDOS) and phonon dispersion spectra for the considered structures are calculated with the PBE functional using the PHONOPY package [24]. For this purpose, finite atomic displacements with an amplitude of 0.01 Å are introduced in the simulated structures. The atomic forces within the supercell are calculated using VASP followed by phonon frequency calculations from the dynamical matrix represented in terms of the force constants. The mode Gruneisen parameter, defined as $\gamma_i = -\partial \ln(\omega_i)/\partial \ln(V)$ for each phonon mode with frequency $\omega_i$ ($V$ is the volume of the lattice), is also calculated. For this purpose, phonon calculations for the equilibrium volume and two additional volumes that are slightly larger and smaller, are calculated in order to compute the logarithmic derivate in $\gamma_i$.

## 3. Results and discussion

### 3.1. Structure and stability

Type II clathrates are described by the general chemical formula $A_8B_{16}X_{136}$ (A = Cs, Rb; B=Na, K, Ba; X = Si, Ge or Sn) and form in the $Fd\bar{3}m$ cubic space group with 136 tetrahedrally coordinated atoms (X) forming the framework of the unit cell with two types of cages: eight hexakaidecahedra [$5^{12}6^4$] and sixteen dodecahedra [$5^{12}$] [1]. "Guest" atoms can be accommodated inside each cage, where two types of atoms can occupy the different polyhedra. It is also possible to have either [$5^{12}6^4$] or [$5^{12}$] occupied, or the same type of guest atoms are in both cages. Clathrates with partially substituted cages are feasible as well ($Y_mX_{136-m}$, where the Y atoms are also tetrahedrally coordinated in the framework) where charge transfer from the guests to the cage is balanced.

The focus of this investigation are type II Sn-based clathrates. Although $Ba_{16}Ga_{32}Sn_{104}$ with Ga and Sn being on the framework have been synthesized almost three decades ago [25], only recently have researchers started investigating these materials. Structural data and transport property measurements of compounds synthesized by various methods have been reported showing intriguing structure-property relations [18,26–29]. First principles simulations on a handful of materials have also been performed showing much reduced band gaps and/or transfer to metallic states upon alkaline and earth-alkaline atoms cage insertion [30,31]. The phonon dynamics for a few materials has also been reported [32,33].

To obtain broader and more systematic insight into the basic science of these systems we consider $Sn_{136}$, $Ga_{40}Sn_{96}$, $Cs_8Ba_{16}Ga_{40}Sn_{96}$, $K_2Ba_{16}Ga_{30}Sn_{106}$, $K_8Ba_{16}Ga_{40}Sn_{96}$, $Xe_8Sn_{136}$, $Xe_{16}Sn_{136}$, and $Xe_{24}Sn_{136}$. The variety of these compositions gives an excellent opportunity to compare and contrast properties of clathrates with empty cages, partially substituted framework, and cages hosting various guests. Using the inherent symmetries of the $Fd\bar{3}m$ space group the conventional unit cell of the empty $X_{136}$ system can be reduced to a primitive unit cell with 34 atoms, $X_{34}$ [23,34]. Similar four-fold reduction can be applied to $A_8B_{16}X_{136}$ where the Wyckoff positions for the cage sites are 96g, 32e and 8a, while the Wyckoff's positions for the guest atoms are 16c and 8b. Reducing the number of atoms is especially useful for better computational efficiency. The Ga substitution in the mixed cage systems, however, leads to many possibilities where the Ga atoms could reside. Considering $Ga_{40}Sn_{96}$, for example, there are $\binom{34}{10} \approx 10^8$ ways of possible arrangements. For many Ga concentrations the reduction to a primitive cell is not possible, but for a handful of cases ($Ga_8Sn_{128}$, $Ga_{32}Sn_{104}$, and $Ga_{40}Sn_{96}$), the construction of a primitive cell can be done. To study these types of arrangements in what follows we take advantage of the primitive unit cell of $Ga_{40}Sn_{96}$. We further distinguish between the following possibilities of the Ga atoms arrangements: (i) a substitution by placing the Ga atoms in symmetric 32e and 8a Wyckoff positions; (ii) a random substitution with some direct Ga–Ga bonds; (iii) a random substitution with no direct Ga–Ga bond.

Fig. 1 displays some of the studied structures after the ab initio relaxation process. We find that the randomly substituted empty $Sn_{96}$ framework with Ga are not stable. A snapshot of the computational process for $Ga_{40}Sn_{96}$ at some intermediate step is given in Fig. 1b showing distortion of the lattice when compared to the $Sn_{136}$ system (Fig. 1a). The $Ga_{40}Sn_{96}$ eventually becomes severely twisted which leads to breaking of the crystal lattice. Our calculations indicate that the guest atoms in the [$5^{12}$] and [$5^{12}6^4$] cages remove this distortion and stabilize the structure. Fig. 1c displays this