

# Phase Stability and Thermoelectric Properties of Alkali-Metal Doped Group IV Clathrate Compounds.

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## ABSTRACT

The relationship between phase stability and structure of alkali metal doped clathrate compounds of C, Si and Ge is investigated by a combination of first principles band structure calculations and qualitative tight binding theory. The current study of compounds of the general formula  $A_nX_m$  (A=alkali metal, X=group IV element) is to develop principles to design, via computer simulation, new and more efficient thermoelectric materials. It is found that  $X_{40}$  and  $X_{172}$  may also form stable compounds which are energetically similar to those for known materials. These new phases are characterized by calculation of Seebeck coefficient which indicates that favorable conditions for high thermoelectric efficiency exist in these phases at low dopant concentrations.

**Keywords:** Thermoelectric Materials, Ab Initio calculations, Band Structure, Clathrate Compounds.

## 1 INTRODUCTION

First-principles calculations may be used to obtain an accurate description of the structure and physical properties such as elastic constants. Often these simulations do not readily allow for the identification of the underlying physical principles which govern why the complex structures are formed or why some materials are harder or more ductile than others. On the other hand, the alloy designer or solid state chemist can make and understand their properties by the proper use of simple models such as the Zintl concept or Meidema's rules and structure maps [1]. Thus, the answer to the question of why intermetallic phases form with a particular structure and stoichiometry is still elusive. A fundamental step in understanding phase stability, and ultimately predicting what phase may be obtained for a given stoichiometry, is to understand on a qualitative level the structure of phase diagrams. From the point of view of theory, this type of paradigm would be useful in materials science to act as an aid in studies by complementing computationally intense first principles studies. At present, first principles methods based upon Density Functional Theory {DFT} are now capable of providing accurate enough description of solids to be able to discriminate the total energies of different phases to within fractions of an electron volt. Yet, to indiscriminately search through a host of possible phases using DFT methods

can be extremely demanding upon resources. What is therefore required is an approach to qualitatively screen out structures, either by fast low level calculations or by simple *rules of thumb*.

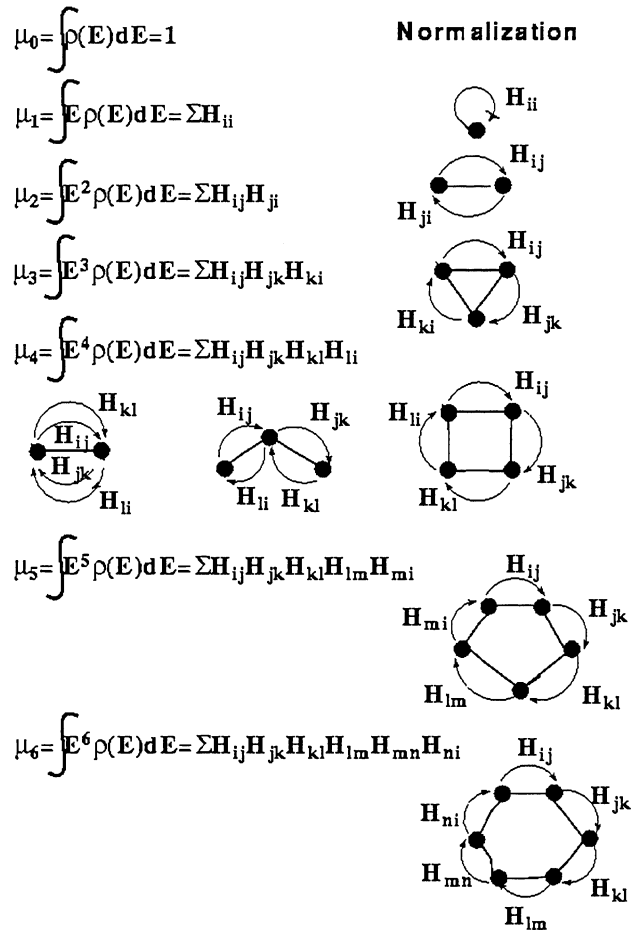


Figure 1: Definition of moments  $\mu_n$  and schematic representation of the relevant structural information contained within these parameters. Summations are over all indices of the Hamiltonian matrix elements.

The goal of the current work is to provide just such a qualitative approach based upon a simple tight binding model and analysis of the structure-phase stability relationship via the method of moments[1-3]. This theory allows the energy to be factored into meaningful parameters which are related to local geometrical motifs. This is achieved by the direct link between phase stability and the

moments,  $\mu_n$  ( $n=0,1,2,\dots$ ), of the electronic density of states (DOS). Within a tight binding description of electronic structure, these moments are intimately connected to local structural features and thus are the perfect parameters by which to relate the crystal structure topology to the total electronic energy of the system; see Fig 1. For example,  $\mu_2$  is related to the coordination number,  $\mu_3$  is related to the number of triangular arrangements of atoms,  $\mu_4$  is connected to squares and bond angle effects,  $\mu_5$  and  $\mu_6$ , among other things, reflect the contribution of pentagons and hexagons respectively [1-3]. The moment analysis provides a unique insight into the local structural motifs that stabilize them. In general, at low electron count, the preferred structural features are triangular faces, hexagons are favored around the half filled band, followed by squares and chains at increasing numbers of valence electrons [4-5]. These insights into the energy-structure relationship form the key to bridging the gap between the simple model concepts and first-principles methods.

The objective of this work is to demonstrate how a relatively simple tight binding scheme may be exploited as a practical tool to complement first principles studies of novel materials. Here theoretical simulations are applied to understand the phase stability of group IV clathrate structures [5,6] which are of interest as potential high temperature thermoelectric materials due to several desirable characteristics. In these phases resonant phonon scattering [5], whereby the localized vibrations of the alkali metal couple effectively with the phonon modes of the clathrate framework, can lower the overall thermal conductivity. By removal of some of the alkali metal atoms a scheme by which the doping level may be systematically altered and thus the electronic component of thermal power may also be maximized. Here, we investigate the phase stability and thermal power of alternate clathrate structures which as yet have not been observed experimentally but may be suitable for the high temperature thermoelectric application.

## 2 THEORETICAL METHODS

Throughout this work we employ the second moment scaled Huckel tight binding model which has met with great success in rationalizing the structural trends in solid state phases [3]. The method has been compared with ab initio electronic structure theory [7] such that that relative performance and weaknesses are well documented. The structures which we have used for all tight binding simulations are obtained from fully optimized geometries of empty cage clathrates at the DFT level. For the tight binding analysis, each main group atom is modeled by including the valence s and p atomic orbitals. The alkali and alkali earth atoms are assumed to have transferred all valence electrons to the main group atoms and thus considered to act only as point charges. We have verified this assumption at the DFT level of theory in our previous

work [5]. A mesh of at least 1000 k-points over the symmetry-inequivalent portion of the Brillouin Zone (BZ) was used to insure convergence of moments and energies.

In order to both validate the theoretical predictions of the simpler tight binding model and to obtain high quality descriptions of the structure and properties of these phases we have performed first-principles calculations based on DFT. In particular, the core electrons were modeled via an ultrasoft pseudopotentials [8] and the valence electrons were expanded in a basis set of plane waves with a cutoff energy of 1.5 times that of the recommended value for convergence to high accuracy. A Monkhorst-Pack [9] 10X10X10 mesh of k-points was used for BZ integration with the exception of the  $X_{136}$  and  $X_{172}$  ( $X=C, Si, \text{ and } Ge$ ). For these latter phases the large size of the unit cells allowed for use of a smaller 6X6X6 k-mesh. Results were obtained within the local density (LDA) approximation. DFT calculations were performed with the Vienna Ab Initio Software Package (VASP) [10].

Thermoelectric figure of merit, ZT, of a material is governed by the equation,  $ZT=TS^2\sigma/\kappa$ , where S is the temperature dependent Seebeck Coefficient,  $\sigma$  is the electrical conductivity and  $\kappa$  is the thermal conductivity. For crystals S(T) can be calculated, within the approximation of constant relaxation time from the equation  $S(T)=L^1/eTL^0$ , where,  $L^0=(e^2/3h)\sigma$ , and for metals at low temperature,  $L^1=-(\pi^2/3e)k^2T[\partial\sigma(E)/\partial E]_{E=EFermi}$ . Thus, the Seebeck coefficient is related to the inverse of electrical conductivity and the first derivative of conductivity near the Fermi energy. In general S is largest in systems where there are weakly dispersive partially occupied bands. Thus structures with flat bands in and around the Fermi level will be the best candidates to obtain large values of S. Transport properties of the  $X_{40}$  phases were modeled via a similar prescription to our previous work on Na-doped Si-clathrate phases [5,11].

## 3 RESULTS AND DISCUSSION

We begin this discussion with a description of the cage framework of the clathrate phases as illustrated in Fig 2. The structures are: the sodalite structure  $X_{12}$  ( $X=C, Si, Ge$ ) which is composed of both 4 and 6 member rings.  $X_{34}$  a hexagonal structure seen in methane hydrate compounds which contains 4, 5, and 6 member rings.  $X_{38}$  seen in mercury amalgams [12] consisting of 3 and 4 member rings.  $X_{40}$  proposed as a structure of porous diamond [13] with only 5 and 6 member rings. Finally  $X_{172}$  which has similar types of cages as  $X_{40}$  and is observed for bromine hydrate [14]. In addition, we compare these phases to the framework of the known clathrate phases  $X_{46}$  and  $X_{136}$  both of which contain 5 and 6 member rings and the diamond structure  $X_8$  which is a known elemental form of C, Si and Ge and contains only 6 member rings.

A useful measure of the phase stability of these phases is the relative energy of the undoped lattices of these phases

as given in Table 1. The  $X_8$  structure is the lowest in energy for C, Si and Ge. The next lowest in energy are the known phases  $X_{46}$  and  $X_{136}$ . What is most surprising is that  $X_{40}$  and  $X_{172}$  are only a few hundredths of an eV/atom higher in energy than these former two phases. The  $X_{34}$  phase is higher in energy than these phases but much less than either the  $X_{12}$  or  $X_{38}$  structures. Finally, it is noted that the simple tight binding scheme predicts identical structure trends as the full DFT calculations with the exception that the energy differences are larger especially for the least stable phases. However, the tight binding calculations are less computationally demanding and thus may serve as a quick method by which phases may be screened.

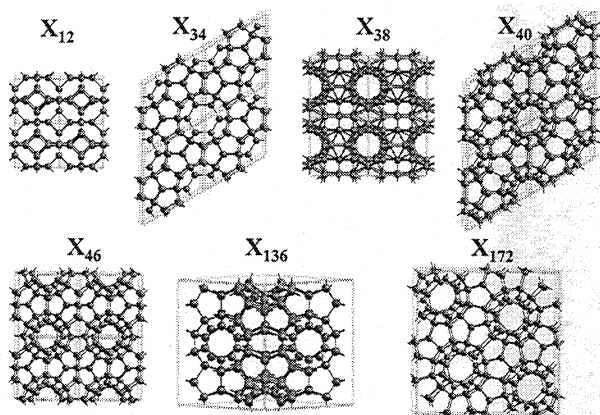


Figure 2: Clathrate structures. All cages are left unfilled to highlight the structure of the group IV element framework.

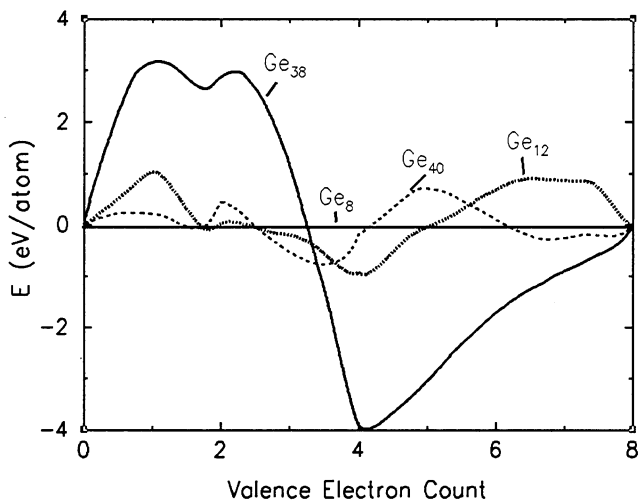


Figure 3: Energy difference curves for the  $Ge_{12}$  (solid line),  $Ge_{38}$  (dashed line) and  $Ge_{40}$  (long dash line) phases relative to the diamond structure.

The tight binding schemes offers one other advantage in that the structures may be studied at any desired electron count in order to assess the energy dependence on the number of valence electrons. Such a calculation is depicted

in Fig. 3 where the total electronic energy is plotted as a function of the number of valence electrons for the  $Ge_{12}$ ,  $Ge_{38}$  and  $Ge_{40}$  phases relative to  $Ge_8$ . The convention of these curves is that the structure with the highest energy for a given electron count is most stable at that electron count. The relationship of the shape of these curves to the moments has been fully developed elsewhere [4]. In general, the number of nodes (including the two end points) in these curves is equal to the moment which is most responsible for the energy difference between two structures. Thus, the  $Ge_{12}$  structure is less stable than diamond at around 4 electrons per atom due largely to a 4th moment effect which results from the presence of the square faces. The  $Ge_{38}$  structure is favored at low electron counts due to the large number of triangles ( $\mu_3$  effect) and thus unstable around 4 valence electrons. The  $Ge_{40}$  phase however is stable above 4.2 e<sup>-</sup>/atom due to the 5 member rings and thus like the known phases may be stabilized by doping. It is noted that  $Ge_{172}$  exhibits the same behavior as  $Ge_{40}$  largely due to the similarity in their structures. The same trends are found for Si and C as well. In general, structures with either four or three member rings are not energetically compatible for electron counts around 4 e<sup>-</sup>/atom as compared with structures consisting of 5 and 6 member rings.

n	C	Si	Ge
DFT (LDA)			
8	0.00	0.00	0.00
12	0.46	0.26	0.22
34	0.20	0.11	0.08
38	2.16	0.54	0.43
40	0.18	0.11	0.06
46	0.16	0.09	0.05
136	0.12	0.07	0.04
172	0.17	0.09	0.05
Tight binding			
8	0.00	0.00	0.00
12	2.01	1.06	0.92
34	0.51	0.28	0.27
38	3.62	4.56	3.89
40	0.18	0.18	0.19
46	0.15	0.15	0.16
136	0.10	0.11	0.13
172	0.15	0.15	0.16

Table 1: Relative energies (eV/atom) of  $X_n$  phase ( $X=C, Si$  and  $Ge$ ). See text for explanation of calculational methods

To understand why  $X_{40}$  and  $X_{172}$  have not been observed even though their energies are compatible with known phases it is necessary to examine the size of the cages found within these materials. Both frameworks consists of 20, 24 and 26 member polyhedra into which electron donating

atoms may be intercalated. However, the disparity in size between these cages is large and it would require either a ternary or quaternary stoichiometry to provide the ions to fit within the cages. For example, for Ge the 26 atom cage is large enough to accommodate Rb atoms but the remaining two cages can only accommodate atoms no larger than K and Na. Since, to our knowledge, no such quaternary phases have been studied it is not surprising that these structures have not been observed.

To investigate the thermal power of these phases we have calculated the Seebeck Coefficient,  $S$ , for fully optimized phases of  $\text{Na}_3\text{K}_2\text{Rb}_2\text{Si}_{40}$  and  $\text{Na}_3\text{K}_2\text{Cs}_2\text{Ge}_{40}$ , both phases which may result from the above mentioned doping scheme. Similar to the known clathrate phases at high doping levels these species are calculated to have low values of  $S$  at 300K of about 5-10 ( $\mu\text{V}/\text{K}$ ) and thus would not be useful high temperature thermoelectrics. However, as in our previous [5] study it was found that an estimate of  $S$  for variable concentrations may be obtained by assuming a rigid band model (derived from the empty cage) and monitor  $S$  as a function of Fermi energy. This function is plotted for three such hypothetical band fillings in Fig. 4 for the  $\text{Si}_{40}$  lattice. The thermal power is almost 25 times higher than the fully loaded structure at 300 K for the lowest doping level  $0.03 e^-/\text{Si}_{40}$  unit and falls off rapidly to only a factor of 10 increase for  $0.5 e^-/\text{Si}_{40}$ . In practice this would require extremely low doping levels which is an identical situation as found for the known phase with the  $\text{Si}_{46}$  structure.

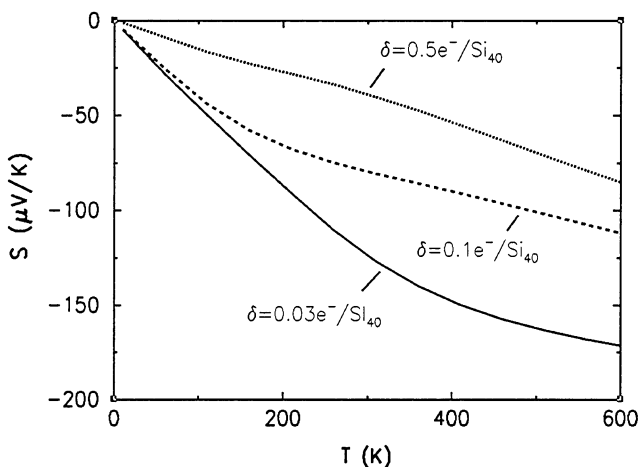


Figure 4: Seebeck coefficient for  $\text{Si}_{40}$  phase with valence electron count increased by  $\delta$  electrons.

## 4 CONCLUSIONS

The  $\text{X}_{172}$  and  $\text{X}_{40}$  structures are found to be likely candidates for stable phases assuming that they are synthesized by a combination of both large and small alkali-metal cations. However, like the  $\text{X}_{136}$  and  $\text{X}_{46}$  the

thermal power of these phases is found to be low at maximum doping hence removal of alkali metal atoms after formation would be required to maximize this property. Extensions of this study to examine hole doping and other framework elements are in progress.

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