First Principles Investigations on how Site Preference and Entropy Affects the Stability of \((\text{Eu}_x\text{M}_{1-x})_2\text{Ge}_2\text{Pb}\) \((\text{M} = \text{Ca, Sr, Ba})\) Polar Intermetallics

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First Principles Investigation on how Site Preference and Entropy Affects the Stability of $(\text{Eu}_{x}M_{1-x})_{2}\text{Ge}_{2}\text{Pb}$ (M = Ca, Sr, Ba) Polar Intermetallics

TYSON TERPSTRA, a JAMES HOOPER a,b, AND EVA ZUREK a,*

a Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260-3000, USA

b Department of Theoretical Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Krakow, Poland

*All correspondence regarding this work should be directed to ezurek@buffalo.edu
Abstract  Density functional theory calculations have been carried out to analyze the factors contributing to the stabilities of a set of recently synthesized quaternary polar intermetallic compounds, \( \text{(Eu}_x\text{M}_{1-x})_2\text{Ge}_2\text{Pb} \) with \( M = \text{Ca}, \text{Sr} \) and \( \text{Ba} \). Experiments showed that these preferentially crystallized with \( \text{Pbam} (M = \text{Ca}) \) or \( \text{Cmmm} (M = \text{Sr}, \text{Ba}) \) symmetry. We systematically explored how the electronic energies of these structures depended upon how they were “colored” by the Eu/M ions, for a wide composition range. It was found that whereas there was very little site preference in the electronic energies of these structures depended upon how they were “colored” by the Eu/M ions, for a wide composition range. It was found that whereas there was very little site preference in the electronic energies of these structures depended upon how they were “colored” by the Eu/M ions, for a wide composition range.

Keywords  Polar intermetallic compounds, first-principles calculations, coloring problem, site preference, entropy, Gibbs free energy

1. Introduction

Compounds containing an electropositive metal (e.g. an alkali, alkaline earth or rare earth metal) and an electronegative post-transition metal (e.g. a group 13-16 element) often yield insulating or semiconducting compounds whose bonding can be understood using electron-precise counting schemes such as the Zintl concept. Recently, there has been tremendous interest in the synthesis of metallic compounds comprised of these constituents because of their interesting properties including superconductivity and thermo-electricity. These polar intermetallic materials bridge the gap between pure ionic and pure metallic compounds as described by the van Arkel-Ketelaar triangle, demonstrating wide structural diversity. For example, it was previously shown, in a subset of rare earth metal germanides, that the germanium atoms, which become formally reduced, assemble into different suites of polyanionic lattices such as Ge\(_2\) dimers seen in Ln\(_2\)MgGe\(_2\) and Ln\(_3\)Li\(_4\)Ge\(_4\) (Ln = lanthanide or rare earth element), one dimensional zigzag chains in LnLiGe\(_2\), cis-trans chains in Ln\(_2\)Li\(_2\)Ge\(_3\), or the two dimensional layers seen in Ln\(_3\)Ge\(_5\) and EuGe\(_2\). Despite the large differences in chemistry, the above patterns can be distilled into combinations of much more simply understood structures, which, are “colored” according to properties such as atomic size, electronegativity, and the number of valence electrons.

Recently, the synthesis, structural characterization and magnetic properties of the structurally related polar intermetallic compounds \( \text{(Eu}_1-x\text{M}_x)_2\text{Ge}_2\text{Pb}, M = \text{Ca}, \text{Sr}, \text{Ba}, \) have been reported. These compounds were found to crystallize in one of two structure types, both which can be viewed as 1:1 intergrowths of the CsCl and AlB\(_2\) fragments. The first structure type (sI) assumed the Pbam space-group and contained a trans-butene-like [Ge\(_4\)] anionic fragment, whereas the second structure (sII) was comprised of one-dimensional zigzag germanium chains, \( _1^\text{\infty} \text{[Ge}_2\text{]} \), and adopted Cmmm symmetry. The ternary MGe\(_2\)Pb compounds were never obtained, and the quaternaries could only be synthesized in narrow composition ranges wherein the alkaline earth metals constituted \( \sim 15\% \) of the electropositive elements. Whereas \( \text{(Eu}_1-x\text{Ca}_x)_2\text{Ge}_2\text{Pb} \) only crystallized in the sI structure and \( \text{(Eu}_1-x\text{Sr}_x)_2\text{Ge}_2\text{Pb} \) always assumed Cmmm symmetry, the barium containing compound crystallized preferentially in the sII structure, but the sI arrangement was at times found as the minor product, depending on the \( \text{Ba}:\text{Eu} \) ratio in the starting material. These syntheses were carried out at temperatures approaching up to 1100 K. Our in-depth Density Functional Theory (DFT) analysis of the electronic structure of these metallic compounds confirmed that sI contains the first-realization of an extended system exhibiting covalent Ge-Ge and Ge-Pb bonds.

Herein, DFT calculations are employed to understand the factors that are important in determin-
ing which structure types are adopted in the aforementioned quaternary polar intermetallic compounds, whose compositions differ mainly in the identity of the alkaline earth element. Whereas the electronegativities of Ca, Sr and Ba vary only slightly, these alkaline earths have vastly different ionic radii (0.99, 1.12 and 1.34 Å, respectively, as compared to 1.09 Å for Eu in the 2+ oxidation state). The ionic size differences hint that the way in which the lattices are “colored” by the M/Eu atoms may be important in understanding which structures are assumed. In addition, we will consider the role that configurational and vibrational entropy play in determining the preferred structure type. Understanding the factors that influence which polymorph is adopted may lead to the rational design of compounds with desired structural characteristics and unique chemical bonding.

2. Computational Details

First principles DFT calculations were performed using the Vienna ab initio Simulation Package (VASP) version 5.2.12. The projector augmented wave (PAW) method was employed for the treatment of electronic core states along with a plane wave basis set with an energy cutoff of at least 500 eV. The Ge 4s/4p, Pb 6s/6p, Ca 3p/4s, Ba 5s/5p/6s, Sr 4s/4p/5s and Eu 5p/6s electrons were treated explicitly. The gradient-corrected exchange and correlation functional of Perdew-Burke-Ernzerhof (PBE) was adopted. The Γ-centered Monkhorst-Pack scheme was used to generate k-point grids, and the number of divisions along each reciprocal lattice vector chosen was such that the product of this number and the real lattice constant was 50-60 Å. These computational settings have been previously used to successfully interrogate the bonding within (Eu$_{1-x}$M$_x$)$_2$Ge$_2$Pb, M = Ca, Sr.[25] Phonon frequencies and thermodynamic properties of select phases were calculated in the harmonic approximation using the phonopy package on supercells which contained at least 160 atoms. The thermal entropy is defined as the negative of the change in Helmholtz free energy over the change in temperature:

$$S_{qm} = -\frac{\delta F}{\delta T} = \frac{1}{2T} \sum_{q_v} \hbar \omega(q_v) \coth \left( \frac{\hbar \omega(q_v)}{2k_B T} \right) - k_B \sum_{q_v} \ln \left( 2 \sinh \left( \frac{\hbar \omega(q_v)}{2k_B T} \right) \right)$$

(1)

where $T$ is the temperature, $q_v$ is the q-point of interest, $\hbar$, $\omega$, and $k_B$ are the reduced Planck constant, angular frequency of the phonon mode, and Boltzmann constant respectively; coth and sinh are hyperbolic trigonometric functions. The primitive cells were generated using the standard representation from the AFLOWLIB website (http://www.aflowlib.org), and the supercells were constructed directly from these.

To explore the coloring problem, as addressed in the main text, the initial structures and stoichiometries were constructed by hand and were limited to a simulation cell with eight possible sites for M and Eu cations. The stoichiometries with four M atoms and four Eu atoms in the simulation cell, i.e. a 50% M dopant concentration, were explored systematically by generating and modeling all of the symmetry-in equivalent ways to distribute the M and Eu atoms in the cell. The 25% M and 75% M dopant concentration cells were also explored systematically. For the rest of the M dopant concentrations that were considered, the initial structures were built by removing or adding one M atom from the nearest lowest-energy or highest-energy 50% M or 25% M simulation cell. The optimized coordinates of select structures are given in the Supplementary Information.

3. Results and Discussion

The sI and sII structures can best be differentiated from one another by considering the structure of the Pb/Ge sublattices and, also, by looking at the nature of the chemical environment that surrounds each cationic M/Eu site, depictions of which can be found in Fig. 1 and Fig. 2. The Pb/Ge sublattice in the sI structure, pictured in Fig. 1, consists of butadiene-like fragments that are made up of four Ge atoms and each fragment is capped by two Pb atoms. The arrangements of these Pb/Ge chains result in
two distinct chemical environments being available for the M/Eu atoms to populate. The two distinct
sites that are available to the cations (the “A” and “B” sites) are represented in Fig. 1 by drawing the
polyhedra that are formed around each site when the surrounding Pb and Ge atoms are used as the
vertices; it can easily be seen that the shape of each polyhedron is different in the relaxed sI structure.
The arrangement of the infinitely extended zigzag chains of Ge in the higher symmetry sII structure
however, Fig. 2, lead to only a single type of polyhedron encapsulating a cationic “A” site.

**Fig. 1.** (left) Extended crystalline structure of the lowest energy coloring compound for sI with a 1:1 Ba:Eu ratio.
It has been colored to emphasize the arrangement of Pb (green), Eu (purple), Ba (red), and Ge (gray) atoms. The
upper and lower panels present the same views, but in the former the polyhedra surrounding the metal cations are
highlighted, whereas the latter emphasizes the polyhedra around the tetrel elements. (right) The preferred chemical
environment around each chemical species present in sI represented as space filling polyhedra. (bottom, right) A
schematic depiction of the Pb capped butadiene Ge fragments in the Pb/Ge sublattice.

In order to computationally explore any potential site preference of the metal cations over the available sites, i.e.
the coloring problem, we carried out DFT geometry optimizations of differently colored simulation cells with Eu_{8-x}M_{x}Ge_{8}Pb_{4} stoichiometries. Different stoichiometries were considered by
varying the amount of the alkaline earth metal, x, from 0 to 8 so that we could sample the ternaries as well as a broad range of quaternary compositions. Even though the alkaline earth metals in the synthesized compounds constituted less than 50% of the electropositive elements, consideration of a wide stoichiometry range allowed us to more thoroughly probe the effect of the cationic size on the site preference. For each quaternary composition, most of the possible distributions of the alkaline metal and Eu over the cationic sites were systematically explored with respect to symmetry, as described in Sec. 2. This procedure allowed us to investigate the stability of the quaternary structures with respect to the stoichiometry (ie. the M:Eu ratio in each structure) and the coloring (ie. where the M:Eu atoms lie in each structure).

The results are summarized in Fig. 3, which provides the reaction energy, \( \Delta E_{\text{rxn}} \) (at 0 K and not
including zero-point energy corrections), associated with the reaction of the most stable ternary sI or sII compounds to form the quaternary ones. For comparison we note that the formation of ternary sII-Ba$_8$Ge$_8$Pb$_4$ from the binary Cmcm-BaPb and Pnma-BaGe$_2$ structures reported in the literature\cite{31} was calculated to be endothermic by 0.14 eV per Ba$_8$Ge$_8$Pb$_4$ formula unit. Moreover, with the exception of the Sr and Ba sII polymorphs, we find at least one coloring for which the quaternaries are more stable than the ternaries at each composition. These results are consistent with the experimental observations that the ternary phases could not be synthesized.\cite{25}

The solid line in the plots represents the “convex hull”, which is the set of line segments joining $\Delta E_{\text{rxn}}$ below which no other $\Delta E_{\text{rxn}}$ points lie.\cite{32} All of the structures whose $\Delta E_{\text{rxn}}$ lie on the hull are thermodynamically stable. Thus, according to the electronic energies alone, all of the Ca-sI stoichiometries, all of the Sr-sI stoichiometries except for the 12.5% and 25% compositions, the 50% Ba-sI and the 50% Ca-sII systems are thermodynamically stable phases. However, the electronic energies of the sI structures that did not lie on the hull were not more than 3-4 meV/atom away from it; an amount that can easily be overcome by zero point energy or finite temperature effects.

The reaction energies suggest that the quaternary sI structure types are the most stable, neglecting configurational entropy and finite temperature effects. However, in experiments only the Ca and Ba based quaternaries were found to crystallize in the sI structure. In addition, none of the colorings we considered for the Ba sII phase, which is the major product observed experimentally, were found to have favorable reaction enthalpies for any of the compositions considered. The phase with a 75% Ba dopant concentration was the closest to being favorable with a $\Delta E_{\text{rxn}}$ value near 0.10 eV/cell. Thus, the 0 K energies do not appear to explain the experimentally characterized structures very well, particularly in how the sI structure is favored for every quaternary coloring.
Fig. 3. Reaction energies ($\Delta E_{\text{rxn}}$) for various M:Eu stoichiometries of the (left) sI and (right) sII structures according to the reaction given at the top of the figure, where M = Ca, Sr, Ba. The vertical lines are connected to highlight the results obtained for a single M:Eu ratio, but each point along a line represents a different arrangement (coloring) of the M and Eu atoms throughout the cationic sites. The solid lines connecting stoichiometries represent the convex hull for each phase.

The first column of Table 1 provides the difference in energy between the sI and sII ternary structures (upper panel), as well as the difference in energy between the most stable colorings for the 50% alkaline-earth-metal doped quaternary sI and sII structures (middle panel). A positive value indicates sI is favored. For the ternaries, the sI polymorph is the most stable for the Ca-based phases. Larger cations tend to stabilize sII, and it becomes the most stable polymorph for Ba. This suggests that the sII structure is better able to accommodate cations with a larger size and/or simulation cells with a larger volume. Moreover, sI is preferred for all of the quaternaries, but the difference in energy between sI
Table 1. Energy of sII relative to sI for various ternary (X/X) and quaternary (X/Y) systems. The quaternary Ca/Eu, Sr/Eu, and Ba/Eu structures correspond to the lowest energy 1:1 M:Eu colorings that were found for sI and sII. In the third column we provide the difference in the energies of the 50% sI structure colored such that all of the “A” sites contain the same electropositive atom, and the “B” sites contain the other electropositive atom. The fourth column reports the shortest Pb-Ge distances (see the Pb capped butadiene-like Ge chains shown in Fig. 1) for the most and least stable colorings of the sI structure (i.e., the structures used to compute $E_{site A} - E_{site B}$).

<table>
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<th>Cations (X/Y)</th>
<th>$E_{dII} - E_{dI}$ (eV/cell)</th>
<th>$E_{site A}^X - E_{site B}^X$ (eV/cell)</th>
<th>Pb-Ge distances (Å)</th>
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<tr>
<td>Ca/Ca</td>
<td>0.344</td>
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<td>2.99</td>
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<tr>
<td>Eu/Eu</td>
<td>0.217</td>
<td>-</td>
<td>2.99</td>
</tr>
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<td>-</td>
<td>3.02</td>
</tr>
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<td>Ba/Ba</td>
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<td>-</td>
<td>3.03</td>
</tr>
<tr>
<td>Cu/Eu</td>
<td>0.415</td>
<td>0.374</td>
<td>2.98, 3.02</td>
</tr>
<tr>
<td>Sr/Eu</td>
<td>0.263</td>
<td>-0.261</td>
<td>2.94, 3.09</td>
</tr>
<tr>
<td>Ba/Eu</td>
<td>0.276</td>
<td>-0.777</td>
<td>2.88, 4.29</td>
</tr>
<tr>
<td>Sr/Ca</td>
<td>-</td>
<td>-0.589</td>
<td>2.91, 3.13</td>
</tr>
<tr>
<td>Ba/Ca</td>
<td>-</td>
<td>-0.684</td>
<td>2.86, 4.37</td>
</tr>
<tr>
<td>Na/Y</td>
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<td>2.89, 3.12</td>
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<tr>
<td>K/Y</td>
<td>-</td>
<td>0.274</td>
<td>2.81, 4.90</td>
</tr>
<tr>
<td>Rb/Y</td>
<td>-</td>
<td>-0.121</td>
<td>2.94, 5.28</td>
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and sII decreases for the Sr and Ba ions. This, again, suggests that the larger ions are more suited to the sII structure.

The most stable and least stable colorings for the 50% doped quaternary sI structures were always found to be those that exclusively color each site, “A” or “B” as labeled in Fig. 1, with either Eu or the alkaline earth metal dopant. The middle column of Table 1 lists the difference in energy between the two extremes, where $E_{site A}^X$ refers to the energy of the configuration that places the X atoms on A sites and $E_{site B}^X$ places the X atoms on B sites; thus, a positive value means that atom X prefers site B. The magnitude of the spread in energies is the smallest for Sr (0.26 eV/cell), which correlates with the similar radii of the two cations (Sr$^{2+}$, 1.12 Å and Eu$^{2+}$, 1.09 Å). It is only somewhat larger for Ca (0.37 eV/cell), and it more than doubles (0.78 eV/cell) for the largest cation Ba$^{2+}$.

The large $E_{site A}^X - E_{site B}^X$ value for X = Ba is significant because it suggests that there is a much larger energy penalty for placing Ba at an unfavorable B site than there is for placing Ca at an unfavorable A site or Sr at an unfavorable B site. This large energy penalty implies that, under the high-temperature conditions used in experiment, the distribution of Ba atoms may be more restricted. As a simple demonstration of this effect, we now discuss the configurational entropy that is associated with placing the cations over the available cationic sites in both structures, sI and sII, for the two extreme cases: 1) where there exists no particular M site preference in the sI structure, and 2) where there is such a site preference to the extent that the alkaline earth metal cation, M, must exclusively occupy one site or the other; note that, for now, we ignore the interaction between the cations and the Pb/Ge sublattice and the interactions between the cations themselves. We use the Boltzmann entropy formula, $S = k_B \ln(\Omega)$, as an estimation of the configurational entropy ($S/k_B$), which is dependent on only the number of available sites and number of atoms available to statistically populate them.

If there exists no particular M site preference in the sI structure, then there are an equal number of ways to distribute the M atoms throughout the eight available sites in our sI and sII simulation cells. As such, with no site preference, the 50% M sI and sII phases are estimated to have the same configurational entropy ($S/k_B = \ln(\frac{\Omega}{4!}) = 4.25$). In the case of an extreme M site preference in the
50% sI phase, the four M atoms must occupy the four preferential sites available and, since there is only a single way to arrange the M atoms to accomplish this, \( S/k_B = \ln\left(\frac{4!}{8}\right) = 0 \). Therefore, the configurational entropy will tend to favor the 50% sII (\( S/k_B = 4.25 \)) over 50% sI (\( S/k_B = 0 \)). At 1100 K, this difference in configurational entropy amounts to \( T\Delta S = 0.403 \text{ eV/cell} \), which is easily comparable with the difference in energy between the most stable sII and sI structures of M/Eu in Table 1. In fact, the 0.403 eV/cell entropy contribution stabilizes the sII structure if the energy of the lowest-energy coloring and the configurational entropy contributions are summed together; \( (E - TS)_{\text{II}} - (E - TS)_{\text{I}} \) is found to be 0.012 eV/cell for Ca, -0.143 eV/cell for Sr, and -0.123 eV/cell for Ba. The stabilization of sII for Ba and Sr and the continued stabilization of sI for Ca is consistent with the major products that were characterized experimentally.

Entropic trends that differ from energetic trends can also be seen when 25% M stoichiometries are considered. For the 25% stoichiometry, there are now two M atoms to distribute throughout the eight available cationic sites in the simulation cells. Therefore, \( S/k_B = \ln\left(\frac{8!}{2!2!2!2!}\right) = 3.33 \) for 25% M stoichiometries in the absence of any type of site preference, which is roughly 20% lower than what was observed for the 50% stoichiometry. With the consideration of a strong site preference for sI, however, the two M atoms in the 25% M stoichiometry still possess some degree of flexibility in distribution throughout the four available sites in the simulation cell, this flexibility in distribution results in a non-zero \( S/k_B = \ln\left(\frac{4!}{4\times4}\right) = 1.79 \). The significance of this result is that, at 1100 K for example, \( TS \) favors the 25% M stoichiometry of our sI model by 0.154 eV/cell over the 50% M sI stoichiometry. The stabilization of M concentrations that are less than 50% is consistent with experiment.

Furthermore, the difference in \( S/k_B \) between sII and sI for 25% M concentrations still favors sII over sI by 0.146 eV/cell at 1100K. This difference is not enough to offset the difference in energy between the most stable sII and sI structures of Ba and Sr; \( (E - TS)_{\text{II}} - (E - TS)_{\text{I}} \) is found to be 0.174 eV/cell for Ca, 0.094 eV/cell for Sr, and 0.114 eV/cell for Ba. But it does suggest that the configurational entropy term still partially cancels out the energetic preference for sI and that the sI structure is most stable for Ca > Ba > Sr, which is consistent with sI being the major product for Ca, the minor product for Ba, and not a product for Sr.

Although the configurational entropy arguments described above can be used to rationalize, to some degree, the major products and the sub 50% M dopant concentrations in structures with a pronounced site preference, the simple assumption that the sI structure has a strong site preference and sII does not is an oversimplification considering the spread in energies for different colorings of each stoichiometry in Fig. 3. The spread in energies for each stoichiometry is always larger in sII than it is in sI, but it is quite clear, especially for Ba, that the energies of sII are affected by the manner in which the cations are arranged. Furthermore, it was previously shown with electronic structure calculations that the Ca cations are not inert and interact significantly with the Pb/Ge sublattice.[31]

Herein, we find that the coloring of the quaternary simulation cells does indeed have a dramatic influence on not only the 0 K energies, but also on the geometric nuances and bonding within the Pb/Ge sublattice. To illustrate this, in Table 1 we provide the nearest neighbor Pb-Ge distances that cap the ends of the characteristic Pb···Ge-Ge-Ge···Pb molecular fragments in the sI structure, see Fig. 1, in the lowest and highest energy coloring of the 50% sI structures. The largest difference between these distances is found for the Ba/Eu system, which correlates with the largest mismatch between the sizes of the cations. Indeed, the Pb-Ge distance of 4.29 Å found in the high-energy coloring is much too large to be considered a bond and depicts how the arrangement of Ba atoms in that coloring forces the Pb atom to “bond” with the other Ge-Ge-Ge-Ge fragment in the simulation cell. Furthermore, the Pb-Ge distances are affected least for the Ca/Eu system, which coincides with Ca/Eu having the smallest ions and, interestingly, with the system for which sI is actually the major product.

To further explore the relationship of the relative sizes of the ions with the apparent site preference and with the perturbations in the Pb-Ge distances, we also looked at hypothetical quaternary models of sI built solely from alkaline earth metal cations, specifically Ca/Sr, Ca/Ba, and Sr/Ba, and models
of sI built with Yttrium, Y (Y$^{3+}$ radius is 0.893 Å$^{[26]}$), and doped with alkali metals. The combination of Y with alkali cations preserves the formal net +4 charge from the cation pairs and allows the alkali series to be explored in an analogous way to the alkaline earth metal series with Eu. The $E_{X}^{\text{site A}}$, $E_{X}^{\text{site B}}$ values and the variations in Pb-Ge distances between them are shown for these model systems in the bottom panel of Table 1. It is seen once more that heavier atoms prefer the A site in sI, ie. $E_{X}^{\text{site A}}$, $E_{X}^{\text{site B}}$ becomes more negative for Na$\rightarrow$K$\rightarrow$Rb, and that K/Y and Rb/Y behave similarly to Ca/Eu and Sr/Eu, which we note because the K/Ca and Rb/Sr pairs sit next to each other on the periodic table. The distortions in the Pb-Ge sublattice are also influenced more as Na$\rightarrow$K$\rightarrow$Rb and, furthermore, are affected much more drastically than they are in the M/Eu systems. This provides further evidence showing that the cationic layers certainly have a strong influence on the nature of the Pb/Ge interactions. Such trends are of course not particular to these lead germanide systems. The relationship between a number of intermetallic compounds and their cations’ differences in size have been well-studied, with particular focus on how well the cations “fit” into the chemically distinct sites that are available in a given lattice.$^{[33,34]}$ The sI and sII structures discussed here relate particularly well, for example, with Li$_{2}$Ni$_{2}$Mg$^{[35]}$ and U$_{3}$Si$_{5}^{[36]}$ which possess similar types of building blocks, specifically the square and trigonal M/Eu prisms which surround each Ge and Pb atom, see Fig. 1 and Fig. 2.

To summarize thus far, our calculations suggest that neither the reaction energies shown in Fig. 3 nor the computed configurational entropies as discussed above account entirely for the sI/sII product distribution observed in experiment. Two interesting trends, however, emerge:

1. Ca/Eu- doped systems are particularly suited for the sI structure, as seen by: (i) the large energy difference between sII and sI in the ternary forms in Table 1, and (ii) the trend that the Ca and Eu cations both suit the “B” site building block, which is not found in the sII structure.

2. There is a clear relation between the ion-sizes and/or site-preferences on the nature of the Pb/Ge interactions in both structures. The strongest bonding interactions in sI and sII are, by a considerable margin, the Ge-Ge bonds along the zigzag chains in sII and along the Pb-$\cdots$Ge$_{4}$$\cdots$Pb molecular chains in sI. The variability in the Pb-Ge distance in sI was demonstrated in Table 1 and similar distortions are observed in sII as well. In the ternary sII structures the variance between nearest neighbor Ge-Ge distances is nearly zero, ~2.59 Å, in Ba$_{4}$Ge$_{8}$Pb$_{4}$ for example. However, even in the lowest energy 50% Ba sII structure, Fig. 2, the Ge-Ge bond distances along the Ge-chains vary from 2.51 to 2.56 Å and the Ge-Ge-Ge angles along the chain vary between 103-109°.

Since the synthesis of these quaternary lead germanides was carried out at high temperatures ($T \geq 1000$ K), it should be expected that the 0 K energies may be insufficient for rationalizing which structures were formed. We have already shown, for instance, that the configurational entropy tends to favor different structures than the electronic energies. This leads to the question of whether or not the entropy contributions to the Gibbs free energies may be important. Phonon frequency calculations were therefore carried out on the lowest energy colorings of the 1:3 (25%) and 1:1 (50%) M:Eu ratios of sI and sII to see whether the computed finite temperature contributions to the Gibbs free energies could, themselves, affect which structures were predicted to be the most stable.

Fig. 4 illustrates the difference in the free energies between the sI and sII structures as a function of temperature. First, the relative stabilities of the sII and sI Ba$_{4}$Eu$_{4}$Ge$_{8}$Pb$_{4}$ models will be addressed, since the 0 K reaction energies do not predict the major experimental product, sII, to be stable. Let us start by considering the compounds containing a 1:1 ratio of Ba:Eu. At temperatures up to 1510 K the sI structure is favored over the higher symmetry sII phase, whereas at higher temperatures sII has a lower free energy. It is to be expected that as the temperature increases the vibrations become progressively more anharmonic. Moreover, small errors in the entropy will lead to larger errors in the $TS$ contribution to the Gibbs free energy at higher temperatures, as compared to lower ones. However, it is the trends, rather than the computed transition temperatures, which are important. Clearly, with increasing temperature the differences in the free energies between the sI and sII phases diminish, until at very high temperatures sII becomes preferred. Therefore, it seems reasonable to suggest that if
the potential energy barrier to interconvert between sII and sI is suitably large, then finite temperature effects may play a key role in determining which structure is the major product formed.

It can also be seen in Fig. 4 that sII becomes favored over sI for the 50% Ca and Sr structures at increasing temperature. Moreover, the temperature at which the stability of these structures reverses decreases with decreasing mass of the alkaline earth metal. The results are consistent with the sII structure being formed in the high temperature synthesis for the strontium based quaternary, but contradict the fact that only the sI polymorph is formed for the calcium containing compound. Furthermore, the temperature at which the free energies of the two structure types becomes equivalent is much lower than what was seen for Ba. At room temperature the energy difference between the sI and sII structures is much larger for the Ca-based quaternaries than the Sr-based ones, with sI being favored. It is possible, for example, that the smaller size and mass of the Ca atoms, relative to that of Ba and Sr, lower the energy barrier for the interconversion between sI and sII structures as the samples are cooled down, but such processes are not explored in any detail in this work.

Another important consideration is the composition ranges that could be synthesized for these quaternaries. In all cases the mole fraction of europium exceeded that of the alkaline earth metal so that the M:Eu ratios in the synthesized structures were closer to the 1:3 compositions. As illustrated in Fig. 3 the lowest energy coloring of the Ca-sI 25% stoichiometry lies on the convex hull, so it is thermodynamically stable. The variance of the 0 K energies for the 25% alkaline earth compositions is smaller than for the 50% ones, and we wondered how this, coupled with the changes in the phonon

Fig. 4. Relative Gibbs free energies for the lowest energy colorings of the sI and sII structures with (left) 1:3 and (right) 1:1 ratios of M:Eu. The dashed lines represent the crossover temperature at which structure favorability, sI or sII, switches. Relative energies reported are per the stoichiometry given in each inset.
modes that are caused by the geometric differences induced by unsymmetrical occupation of the “A” and “B” sites, would affect the free energy.

The free energy differences between sI and sII in the lowest energy 25% colorings are also shown in Fig. 4 and, as speculated, they are qualitatively different from the 50% colorings. The observed trends correlate very well with the experimental preference of sI for Ca, sII for Sr, and sII for Ba. The main qualitative difference for the Ca containing compounds is that whereas the sI structure becomes progressively favored at higher temperatures for the 1:3 stoichiometry, the opposite trend is observed for the 1:1 ratio. The relative free energies of the sI and sII structures in the 25% Sr and Ba compositions follow the same trend observed for the 50% stoichiometries: the sII structure becomes progressively more stable as the temperature is increased. The two Sr polymorphs are nearly thermoneutral at 1100 K; their free energies differing by only 2.1 meV/atom. The Ba containing structures strongly favor the sII phase, except at low temperature. The free energy difference between the Ba sI and sII phases at the synthesis temperature is just over double that calculated for the Ca based compound at 1.88 eV/cell in favor of the sII structure.

Fig. 5. Thermal entropies as a function of temperature for the lowest energy colorings of (top) Ca, (middle) Sr, and (bottom) Ba (left) 1:3 and (right) 1:1 M:Eu sI and sII structures. The inset legend indicates both the number of M atoms (2 or 4) considered within the unit cell and their relative positioning within the cationic sites (site A or site B).

The above results illustrate that the thermal (vibrational) entropies are important in determining which phases are the most stable. Fig. 5 compares the entropic contributions to the free energies of sI and sII as a function of temperature. With the exception of the 25% Ca compounds, the entropy of sII rises more quickly than that of sI with increasing temperature, and this is the reason why the Gibbs free energies increasingly favor the formation of the latter at higher temperatures. The crossover
point between sI and sII depends on the relative 0 K electronic energies, and on how the difference in the entropies changes as a function of temperature. For example, even though at 0 K the difference in energy between the two polymorphs is about the same for the 50% and 25% Sr-based compounds, the crossover temperature is lower for the latter because the difference in the thermal entropy between the two structure types rises more rapidly with increasing temperature than that of the former. Whereas the entropy of the sI and sII 50% Ba-containing systems remain quite similar throughout the temperature range studied, for the 25% compositions the sII entropy rises much more quickly than that of sI. This in part explains why the transition between the two phases is predicted to occur at much higher temperatures for the 50% as compared to the 25% stoichiometry.

In order to better understand the factors affecting the thermal entropies – and in particular the lower entropy of sII vs. sI for the 25% Ca-based structures, we plotted the phonon densities of states (DOS) and projected phonon DOS for the more experimentally relevant 1:3 M:Eu composition range in Fig. 6. In general, the heavier the element the lower the vibrational frequencies associated with its motions. This is most obvious upon comparison of the center of gravity of the projected DOS of the alkaline earth metals (Ba < Sr < Ca). The high-frequency Ge-based modes are most likely a result of the stretching of the Ge-Ge bonds, whereas the low frequency ones are in part coupled with the motions of the heavier elements.

As low frequency modes are larger contributors to the thermal entropy, we proceeded to analyze variations in the integrated phonon DOS to better understand the trends observed in the thermal entropies in Fig. 5. Such an integration allowed us to determine which polymorph had a greater abundance of low frequency, versus high frequency modes. The cutoff between the two frequency regimes was chosen to be 150, 140 and 130 cm$^{-1}$ for the Ca, Sr and Ba based compounds, because these are frequencies at which the total phonon DOS for the two structure types was found to be low. This revealed that Ca-sI had a higher number of low frequency modes than Ca-sII (50.0 vs. 47.3), consistent with the higher thermal entropy of the former in Fig. 5. The low-frequency regime in Sr-sI contained nearly the same number of modes as Sr-sII (53.4 vs. 52.6) in-line with the fact that the thermal entropies of the two polymorphs are nearly the same. The Ba sI phase has substantially fewer (48.1) low frequency modes than sII (52.8), and this correlates with the latter having a progressively larger thermal entropy at higher temperatures. It should be noted that whereas for the Ca-based systems the majority of the Ca modes lie above the high frequency division, most of the Sr and Ba modes are shifted below the low/high frequency divisions that we defined because of their heavier masses.

![Fig. 6.](https://mc06.manuscriptcentral.com/cjc-pubs)
We also analyzed the phonon DOS for the 50% stoichiometries, see Fig. 7, in order to understand why the thermal entropies of the 25% and 50% Sr and Ba based structures followed the same trends, whereas the two stoichiometries for the Ca containing compounds did not. Visual inspection of Fig. 6 and Fig. 7 revealed that the only structure for which the vibrational frequencies exceeded 250 cm$^{-1}$ was the 50% Ca-sI polymorph, suggesting that this system may have a particularly low thermal entropy. We again integrated the number of modes using the previously mentioned cutoff defining the low frequency regime. Whereas the Sr and Ba based 50% quaternaries followed the same trends as the 25% stoichiometries (the low frequency regime contained 50/52 Ba sI/sII and 52.5/52 Sr sI/sII modes), for Ca the opposite trend was observed. That is, the sII structure had slightly more low frequency modes (45.2) than sI (44.4). This suggests that sII will become preferred at higher temperatures, completely in-line with the behavior of the thermal entropies in Fig. 5. Thus, our DFT calculations revealed that the correct trends in the free energies of the (Eu$^{1-x}$M$_x$)$_2$Ge$_2$Pb M = Ca, Sr, Ba polar intermetallics can only be obtained when using structure models that have approximately the same compositions as the experimentally synthesized phases, and the lowest energy colorings.

4. Conclusions

First-principles calculations have been carried out to determine why (Eu$^{1-x}$M$_x$)$_2$Ge$_2$Pb with M = Sr and Ba preferentially crystallize in a structure with Cmmm symmetry (sII), whereas (Eu$^{1-x}$Ca$_x$)$_2$Ge$_2$Pb assumes a Pbam structure (sI). Whereas the sI phase has two different classes of site symmetries, sII contains only a single site that can be occupied by the cations. We have explored the “coloring problem”, that is how the Eu/M can be distributed among these sites. Calculations on a wide stoichiometry range illustrated that within sI the smaller “B” site exhibited a pronounced preference for smaller cations, whereas the larger “A” site does not show much preference for any of the cations considered herein, instead it happily accepts Ca, Sr, Ba and Eu ions alike with a minimal penalty to the electronic energy. The way in which the sI structure is colored has a dramatic effect on the Pb–Ge distances within the Pb···Ge–Ge–Ge···Pb molecular fragments in the sI structure.

Because the electronic energies of the most stable sI and sII colorings alone could not account for the experimentally observed product ratios, we considered the role that entropy may have on the structures that are formed. For phases containing 1:3 (25%) and 1:1 (50%) M:Eu ratios without a site-preference for the Eu/M atoms the configurational entropy of sI and sII was approximately the same. When a site-preference was assumed, the sII structure had a larger configurational entropy than sI. With the exception of the 25% phase with a site-preference, the sII structure always had a higher...
configurational entropy than sI. Clearly, the configurational entropy is an important factor in dictating which structures are formed, but it also could not explain all of the experimental observations.

In addition to the enthalpic penalty imposed by a mismatching of cations and the sites within which they lie, as well as the configurational entropy, the thermal entropy contributions to the free energy were found to play a role in phase preference and stability. For the 25% structures, the thermal entropy contribution to the free energy supports the experimentally observed product ratios for each compound; favoring the sI phase for Ca, and the sII phase for both Sr and Ba at the experimental synthesis temperature. Additionally, based on the configurational entropy, when a marked site preference exists the 50% colorings show a trend towards stabilization of the sII phase over sI. The degree of sII stabilization, at the synthesis temperature of 1100K, is enough to overcome the enthalpic difference between the sI and sII phases for Sr and Ba supporting the observed sII product preference for each cation. A rationalization for M dopant concentrations less than 50% can be provided through considering the configurational entropy contributions of the 25% coloring systems in the presence of a large site preference. These findings highlight the importance of computing the free energies when considering phase stability for systems, particularly so for those synthesized at high temperatures.

Finally we note that the systems studied herein meet the criterion for differential fractional site occupation (DFSO) stabilized materials introduced by Franzen et al.\cite{37-40} The M/Eu ions can have mixed site occupancies within the “A” and “B” sites illustrated in Fig. 1 and Fig. 2, and a pronounced site preference of the metals within the “A” sites, as determined by the atomic radius, is apparent. As a consequence the phases adopted depend upon the interplay of entropic stabilization of systems with mixed site occupations, and the enhanced bonding within the compounds that occurs when the ions occupy the most favorable configuration of sites. The main difference being that whereas the parent structures for DFSO stabilized compounds discussed by Franzen and co-workers do exist (although in a different structure type), the ternary MGe$_2$Pb compounds could not be obtained in any structure type.

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