Comparing the influence of cation order and composition in simulated Zn(Sn, Ge)N$_2$ on structure, elastic moduli, and polarization for solid state lighting

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ABSTRACT

Alloying and site ordering play complementary roles in dictating a material’s properties. However, deconvolving the impacts of these separate phenomena can be challenging. In this work, we simulate structures of Zn(Sn, Ge)N$_2$ with varied Sn content and site ordering to determine the impacts of order and composition on structural and electronic properties. We assess the formation enthalpy, lattice parameters, elastic constants, spontaneous polarization, and piezoelectric coefficients. In mostly disordered structures (order parameters ranging from 0.2 to 0.4), the formation enthalpy exhibits local extrema as a function of the order parameter, deviating from the more linear trends seen in both fully disordered and fully ordered systems. This anomalous deviation from the otherwise linear trend in formation enthalpy with order manifests in each of the other properties calculated. This range of order parameters of interest may be caused by a transition in the ordering of the quaternary material similar to phase changes seen in ternary compounds but stretched over a region including 20% of the order parameter range. Most parameters calculated are more sensitive to order than to composition in the limited composition range tested; however, the lattice parameter $c$, piezoelectric coefficient $e_{33}$, and elastic moduli $C_{12}$, $C_{13}$, and $C_{23}$ are more sensitive to composition. Of the properties compared, the piezoelectric coefficients are influenced most significantly by changes in both the composition and order parameter. Lattice parameters undergo the smallest changes with order and composition, but these small differences appear to impart large trends in the other properties. Better understanding the effects of disorder and group IV alloying in Zn(Sn, Ge)N$_2$ allows for more accurate modeling of characteristics of this material system for solid state lighting and other applications.

INTRODUCTION

Site disorder in materials is of rising interest for controlling properties in electronic devices. In photovoltaics and solid state lighting, this static type of ordering can cause deviations in the absorption and carrier mobility to reach the desired characteristics for a layer in a device. The degree of ordering in these solids depends on the processing of the material whereby disorder can be “frozen in” to a material’s crystal structure even when ordering is thermodynamically favored.

In recent studies of ZnGeN$_2$ as an active layer in light emitting diodes, site disorder has been assessed to determine how the structural and electronic properties change with the order parameter of a structure. A more common means of controlling these properties in electronics has historically been to employ alloying. Alloying with relevant ionic species and manipulating site order offer different challenges and benefits in different material systems and can also be used in tandem to achieve desired effects. Site disorder and alloying have been studied extensively in ZnGeN$_2$ and ZnSnN$_2$, but separating the effects of composition and order on properties remains a challenge. ZnSnN$_2$ and ZnGeN$_2$ are fully miscible across their composition range largely due to their shared crystal structure and similar
ionic species. Figure 1 provides the crystal structure shared by ZnSnN$_2$ and ZnGeN$_2$. The group IV site on which alloying between Sn and Ge occurs is labeled as Sn/Ge. Site disorder occurs on the cation sublattice sites containing the group IV and group II (Zn) sites. The degree of order is calculated as $S = r_\alpha + r_\beta - 1$, where $r_\alpha$ is the fraction of site $\alpha$ occupied by species $\alpha$ and $r_\beta$ is the fraction of site $\beta$ occupied by species $\beta$ (i.e., Zn on Zn sites and group IV elements on group IV sites). This study considers the impact of heterovalent disorder but does not consider the impact of aliovalent disorder on the group IV site. This choice is based on experimental demonstrations of highly disordered ZnSnN$_2$ and ZnGeN$_2$ from both our group and other thin film demonstrations.

For solid state lighting, a tunable bandgap is desired for emission at green and amber wavelengths and both disorder and group IV site alloying with Sn in ZnGeN$_2$ are possible ways to achieve this bandgap (ideally without sacrificing other desirable properties). Many studies have sought to answer how stoichiometry in ZnGeN$_2$ controls properties as well as how oxygen, a common dopant and contaminant, affects the order parameter and properties of the separate Sn- and Ge-based systems. Differing conclusions have been drawn for ZnSnN$_2$ and ZnGeN$_2$. For instance, O incorporation appears to narrow the bandgap of ZnGeN$_2$ due to repulsion between N p- and Zn/Ge d-orbitals. The inclusion of O strongly impacts ordering due to its preference for bonding to Zn over Ge, driving disorder in the system. Interestingly, in ZnSnN$_2$, O plays the opposite role of increasing bandgap along with higher zinc composition, while disorder noticeably narrows the bandgap. Differences between the Zn(Sn, Ge)N$_2$ ternary constituents complicate our understanding of the group IV alloyed system.

This work analyzes simulated Zn(Sn, Ge)N$_2$ structures to differentiate the effects of the composition and ordering in this material system. The simulations utilize the results of prior Monte-Carlo simulations of group II/IV site disorder, assuming random Ge/Sn mixing at the group IV positions. We also limit the anion sublattice to N to focus on alloying and disorder on the cation sublattice without the influence of O and other potential dopants/defects.

This method allows for quick calculations of properties based on prior Monte Carlo simulations of ordering in the structure and avoids the need to train new cluster expansions. Figure 1 shows the wurtzite-derived crystal structure shared by ZnGeN$_2$ and ZnSnN$_2$. We focus on concentrations of Sn from 0% to 12.5% as this is the range of alloying sought for green and amber emission.

METHODS

Structure generation

The structures used in this work were adapted from those published in Ref. 36. Initially generated using Monte-Carlo simulations to accurately produce ordering effects. Ten representative ZnGeN$_2$ structures with varied order parameter were selected from that prior work and are reproduced here. We then randomly replaced 3.125%, 6.25%, 9.75%, and 12.5% of the Ge in each of these structures with Sn to simulate alloying on the group IV site and allow for a comparison of composition and site order. Fifty structures in total were used in this work, each containing 128 atoms. This method of ion replacement for generating structures is not as robust as training cluster expansions and performing Monte-Carlo simulations for combined site disorder and alloying because ion replacement provides a smaller set of structures to compare than could be generated with new Monte Carlo simulations. However, the replacement technique for structure generation avoids significant computational cost, which would require more than ten times the resources needed for similar investigations of ZnGeN$_2$ and ZnSnN$_2$.

First principles calculations

All first principles calculations performed for this work follow the same methods as Ref. 36. Supercells were relaxed in volume, shape and ionic positions using density functional theory (DFT) following the Perdew–Burke–Ernzerhof (PBE)-type generalized gradient approximation (GGA). For 128 atom supercells, the gamma-point-only version of the Vienna Ab-initio Simulation Package (VASP) was used along with a single, gamma-centered k-point. In the cluster expansion training set, 6 k-point grids were used for 16 atom cells and 8 atom cells, respectively. A maximum energy of $10^{-5}$ eV and force of 0.02 eV Å$^{-1}$ were set for each atom as convergence criteria for ionic relaxation. The Coulomb potential, $U = J$, was set to 6 eV for the Zn d orbital (DFT+U) to describe the correct consistent with the prior literature following the Dudarev approach. Kresse–Joubert projector augmented wave datasets were used with pseudopotentials from VASP version 4.6 (Ge_d, N_s, Sn_d, and Zn) and an energy cutoff of 380 eV.

Following the initial relaxation of supercells, properties were determined with more precise energy and force convergence criteria of $10^{-8}$ eV and 0.001 eV Å$^{-1}$ per atom, respectively. The finite differences approach was used to calculate elastic moduli and polarization. Polarization was calculated from Born effective charge, lattice parameters, and displacements of cation layers.

MATERIAL PROPERTIES

By examining different properties of Zn(Sn, Ge)N$_2$, we can identify relationships with structure and order as well as identify...
which variables are strongly connected to general trends in device-relevant material parameters and local anomalies with respect to order parameter. The structures chosen for this dataset are representative of ZnGeN$_2$ structures selected from Ref. 36. The formation enthalpy of these structures remains negative across the ranges in composition and order parameter simulated as shown in Fig. 2 indicating the miscibility of the two systems in agreement with experiment. There is a strong trend between the Sn content and formation enthalpy, whereby the increased fraction of Sn raises the formation enthalpy. The ordered structure exhibits the lowest formation enthalpy for all compositions as expected; however, each composition also exhibits a local minimum around $S = 0.2$ and a local maximum at $S = 0.3$. These extrema also appear in the other properties simulated, but in none so pronounced as in the formation enthalpy. This region of order parameter roughly corresponds to the onset of a phase transition described previously in ZnGeN$_2$. Further study is needed to better identify the reasons for this change in the property slope.

Figure 3 shows the lattice parameters of the orthorhombic supercells of Zn(Sn, Ge)N$_2$ used in this work. While $a$ increases with the order parameter, $b$ decreases due to the similar sizes of Zn and Ge, and the disparate sizes of Zn and Sn. The change in the crystal structure is consistent with the transition from a more wurtzite-like structure in the disordered extreme to the orthorhombic cell in the ordered configuration of both ZnSnN$_2$ and ZnGeN$_2$. The changes in lattice parameters with composition are also consistent with the lattice parameters measured for reactive sputtered films in Ref. 25. The changes in $a$ and $b$ nearly balance the volume of the cell; however, when $a$ and $b$ are averaged for “wz” wurtzite from “or” orthorhombic parameters as $a_{wz} = \frac{a_{or} + b_{or}}{2}$, where $a_{or} > b_{or}$, we find that $a_{wz}$ is larger at low order parameters. This decrease in $c = c_{wz} = c_{or}$ highlights a shrinking trend in the volume of the unit cell as the material tends toward order. This trend has been noted previously by Adamski et al. The trends in lattice parameters as they change with order are consistent across all compositions simulated. However, in each lattice parameter plot, there is a kink in the trend between $S = 0.2$
and $S = 0.3$. Within this range, $a$, $b$, and $c$ each temporarily reverse the larger trend.

This anomaly in the cell shape and volume seems to suggest the formation of a new phase based on the degree of order. However, evidence from a prior publication on ZnGeN$_2$ only weakly supports the formation of a separate phase with only some properties showing phenomena at $S = 0.25$. Other prior work more strongly suggests an ordering change in ZnGeN$_2$, but also indicates that order parameters between $S = 0.3$ and $S = 0.9$ would be difficult to physically isolate. A closer look at these order parameters in the ZnSnN$_2$/ZnGeN$_2$ family of materials lies outside the scope of this article; future studies may illuminate the reason for this abrupt change in lattice parameters and other properties.

The elastic moduli of Zn(Sn, Ge)N$_2$ are plotted together for the axial directions in Fig. 4. For $C_{11}$, these values are further differentiated by the composition to better understand how the moduli change with ordering. $C_{11}$ sees the least change with ordering and least pronounced local extrema around $S = 0.25$. $C_{11}$ remains similar at its ordered and disordered extremes, dropping in the magnitude from $S = 1$ to $S = 0.6$ with its minimum (of the data collected) at $S = 0.6$. $C_{22}$ is the greatest at $S = 1$, decreasing to its minimum at $S = 0.3$ and rising to a local maximum at $S = 0.2$. Similarly, $C_{33}$ drops from its maximum at $S = 1$ to a wide array of values depending on the composition at $S = 0.3$. A local maximum in $C_{33}$ also occurs at $S = 0.2$.

The non-axial moduli exhibit similar relationships with order parameter to the axial moduli. $C_{13}$ and $C_{23}$ generally decrease as the order parameter increases; $C_{44}$, $C_{55}$, and $C_{66}$ increase as the order parameter increases; and $C_{12}$ remains relatively the same independent of the order parameter. Like the axial moduli, the nonaxial moduli each also exhibit local peaks around $S = 0.2$ and $S = 0.3$.

In $C_{33}$, compositions varying from 0% to 12.5% Sn/(Sn+Ge) reveal different trends at different order parameters. In the ordered system, a higher Sn content leads monotonically to a higher elastic modulus, $C_{33}$. However, this trend does not remain consistent for any of the other order parameters sampled. At $S = 0.8$ for instance, 2% Sn first lowers the modulus relative to 0% Sn before increasing

![FIG. 4. Elastic moduli of Zn(Sn, Ge)N$_2$ plotted for varied order parameter and composition.](image-url)
for each subsequent increase in Sn. The relationship between the elastic modulus and composition is more convoluted at lower order parameters. Some of these structures with lower order parameters undergo oscillations in elastic moduli as the fraction of Sn increases. This different relationship for each order parameter yields a wide range of elastic moduli between $S = 0.2$ and $S = 0.3$ and much narrower ranges below $S = 0.2$ and at $S = 1$.

Along with the elastic moduli, polarization constants can be used to better understand the interaction of one material with another at a coherent interface. The spontaneous polarization of a material depends on the structure and ionic species and must be calculated based on these.\textsuperscript{36,50} In Fig. 5, increasing Sn content slightly lowers the spontaneous polarization; however, this effect is only expected to be significant at interfaces with materials with very similar polarization. Based on spontaneous polarization values from Fig. 5 and Ref. 36, these values have an uncertainty at a given order parameter of 3%. Additionally, while incorporating a small amount of Sn into a ZnGeN\textsubscript{2} structure lowers spontaneous polarization constants by around 1%, further incorporation of Sn has a lesser effect. The uncertainty in $P_g$ for a structure with a set order parameter, but variable ion configuration reaches a maximum at $S = 0.3$. While the trend of lower $P_g$ for higher Sn content generally holds even at $S = 0.3$, the difference in ion configurations results in a relatively wide 0.01 C/m\textsuperscript{2} disparity between the most Sn-rich compositions. This disparity for a single composition and single order parameter indicates that the exact ion configuration plays a large role in spontaneous polarization in the range $0.2 < S < 0.4$ and $S$ alone is not a strong predictor of $P_g$ in this range.

The piezoelectric coefficients dictate the change in the polarization of a material under deformation. Together the piezoelectric coefficients, strain and spontaneous polarization define the total polarization of a material.\textsuperscript{50,53,54} Figure 6 shows the relevant piezoelectric coefficients of Zn(Sn, Ge)N\textsubscript{2}: $e_{31}$, $e_{32}$, and $e_{33}$ with the different order parameters represented in the structural dataset. $e_{33}$ is plotted separately because of its different range and sign from the other coefficients as well as to give an example of the trend in piezoelectric coefficients with composition. Sn\textsuperscript{4+} and Ge\textsuperscript{4+} behave similarly chemically in ceramic materials due to their common Group IV characteristics. However, even the small change in the ionic radius (69 pm for Sn\textsuperscript{4+} and 53 pm for Ge\textsuperscript{4+})\textsuperscript{55} plays a significant role in the piezoelectric coefficients as seen by the wide spread of coefficients in Fig. 6. $e_{33}$ in particular exhibits a wide range from 0.37 C/m\textsuperscript{2} to 0.68 C/m\textsuperscript{2}. Higher Sn contents yield higher piezoelectric coefficients though not necessarily a monotonic trend as seen for $e_{33}$ at the lowest order parameter screened.

Important to the comparison between composition and ordering, we can identify whether each property is more sensitive to one characteristic or the other. Table I compares the maximum range in the property values with changes in either the composition or order. This allows us to compare the relative sensitivity of each property. These sensitivities compare compositions from 0% to 12.5% Sn and parameters for $0.125 \leq S \leq 1$. Ranges are taken as the maximum
CONCLUSION

cation order plays a strong role in the properties of multinary semiconductors. By calculating properties of Zn(Sn, Ge)N₂ simulated with varied composition and order, we are able to deconvolve some of the relationships between these characteristics. In this material system, the composition dictates clear trends in the lattice parameters and thermodynamics of the system. Increased Sn content and elastic modulus and polarization constants are not all monotonic, varying depending on specific proportions of group IV cations.

The property values calculated exhibit similar characteristics to each other with respect to order parameter. These properties display local extrema at $S = 0.2$ and $S = 0.3$. This finding is consistent with our prior study of formation enthalpy as a function of order in ZnGeN₄. Formation enthalpy and lattice parameters exhibit clear trends in this work with respect to both composition and order as shown in Figs. 2 and 3. Similarly to trends in properties for composition, the trends in properties with ordering are the strongest for formation enthalpy and lattice parameters. Unlike for composition, however, the extrema in properties with order remain fairly consistent in elastic moduli and polarization quantities. Comparing the sensitivity of the different properties to composition and ordering, we find that $c$, $e_{33}$, $C_{12}$, $C_{13}$, and $C_{23}$ are most sensitive to the composition, while $dH$, $a$, $b$, the majority of the piezoelectric coefficients and the diagonal elastic moduli, $C_{ii}$ through $C_{66}$ change most with the degree of cation order for the ranges of composition and order represented.

SUPPLEMENTARY MATERIAL

The supplementary material contains datasets necessary for reproducing the study and figures in this manuscript. The datasets include structure files (POSCARs) for materials simulated in this study, a spreadsheet (.csv) including the tabulated properties of these structures plotted in Figs. 2–6, and a README file containing instructions to interpret file and variable names in the supplementary material.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Jacob J. Cordell: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Resources (supporting); Validation (lead); Visualization (lead); Writing – original draft (lead); Writing – review & editing (equal). Stephen Lany: Conceptualization (supporting); Funding acquisition (supporting); Methodology (supporting); Resources (lead); Supervision (equal); Validation (supporting); Writing – review & editing (equal). M. Brooks Tellekamp: Conceptualization

Table I. Percent change in calculated variables with order parameter and composition. Numerical values indicate the change in each parameter with respect to the range in order parameter ($S$) or composition (comp) as a percent. The sensitivity rows indicate whether a parameter is more influenced by order or composition.

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