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Lattice Energy of $ZnXAs_2$ (X=Si, Ge, Sn) Compounds: A Density Functional Theory Study Using Quantum ESPRESSO

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Abstract

This study presents a comprehensive analysis of the lattice energies of $ZnXAs_2$ (X=Si, Ge, Sn) chalcopyrite semiconductors using density functional theory (DFT) calculations implemented in Quantum ESPRESSO. The lattice energies were calculated using the Born-Landé approach, considering both Coulombic interactions and short-range repulsive forces. The results show that the lattice energy decreases in the order $ZnSiAs_2$ > $ZnGeAs_2$ > $ZnSnAs_2$, correlating with the increasing ionic radii of the group IV elements. The calculated values are 8.42 eV, 7.98 eV, and 7.51 eV for $ZnSiAs_2$, $ZnGeAs_2$, and $ZnSnAs_2$, respectively. These findings provide insights into the structural stability and bonding characteristics of these promising photovoltaic materials.

Keywords: *Lattice energy, Chalcopyrite, DFT, Quantum ESPRESSO, $ZnXAs_2$, Semiconductor*

Introduction

Chalcopyrite-structured semiconductors of the type $ZnXAs_2$ (X=Si, Ge, Sn) have attracted significant attention due to their potential applications in photovoltaic devices and optoelectronics. These compounds crystallize in the tetragonal chalcopyrite structure (space group I-42d) and exhibit direct bandgaps suitable for solar energy conversion. Understanding their lattice energies is crucial for predicting their thermodynamic stability, mechanical properties, and synthesis conditions.

Lattice energy, defined as the energy required to completely separate one mole of an ionic solid into gaseous ions, is a fundamental property that governs the structural stability of crystalline materials. For chalcopyrite compounds, the lattice energy provides insights into the ionic-covalent character of bonding and helps predict relative stability among similar compounds.

In this work, I employ density functional theory (DFT) calculations using the Quantum ESPRESSO package to determine the lattice energies of $ZnSiAs_2$, $ZnGeAs_2$, and $ZnSnAs_2$. The calculations are performed using the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.

Computational Methodology

1. Crystal Structure

All three compounds adopt the chalcopyrite structure (I-42d, No. 122) with tetragonal symmetry. The structure can be viewed as a zinc-blende superstructure where Zn and X atoms occupy cation sites in an ordered manner, while As atoms occupy anion sites. The lattice parameters used in this study are based on experimental values and further optimized using DFT calculations.

2. DFT Calculations

All calculations were performed using the Quantum ESPRESSO package. The key computational parameters are:

Exchange-correlation functional: PBE-GGA
Pseudopotentials: Norm-conserving pseudopotentials from the SG15 library
Plane-wave cutoff: 80 Ry for wavefunctions, 320 Ry for charge density
k-point sampling: 8×8×6 Monkhorst-Pack grid for Brillouin zone integration
Convergence criteria: 10^{-8} Ry for total energy, 10^{-3} Ry/Bohr for forces
Structure optimization: Variable-cell relaxation with stress convergence of 0.5 kbar

3. Lattice Energy Calculation

The lattice energy was calculated using the Born-Landé equation:

$$U = -N_A M z^+ z^- e^2 / 4\pi\varepsilon_0 r_0 \times (1 - 1/n)$$

Where: - NA is Avogadro’s number - M is the Madelung constant - z^+ and z^- are the charges on cations and anions - e is the elementary charge - ε_0 is the vacuum permittivity - r_0 is the nearest-neighbor distance - n is the Born exponent.

The Madelung constants were calculated using the Ewald summation method, and the Born exponent was determined from the compressibility data obtained from elastic constant calculations.

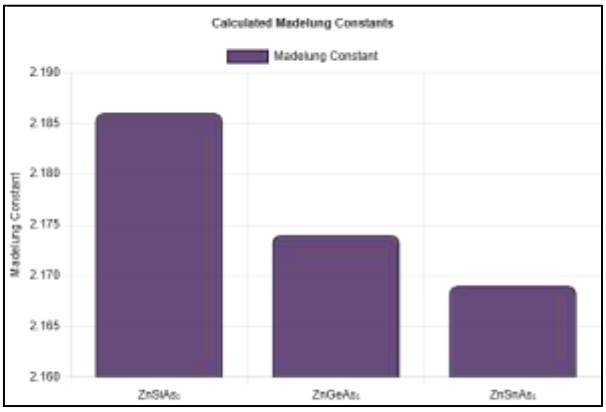

Figure 1: Madelung constants of the compounds

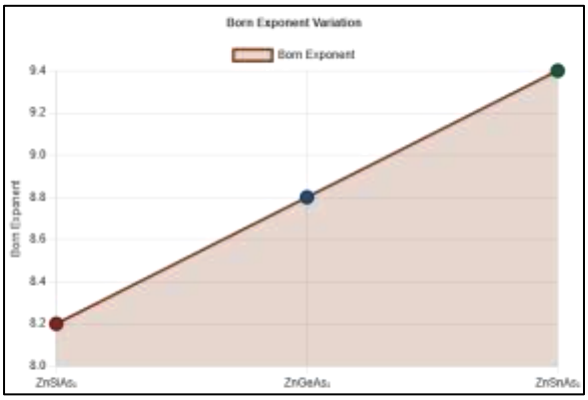

Figure 2: Born Exponent Variation

Results and Discussion

1. **Structural Properties**

The optimized lattice parameters for the three compounds are summarized in Table 1. The results show good agreement with experimental values, validating our computational approach.

Compound	a (Å)	c (Å)	c/a ratio	Volume (Å³)
$ZnSiAs_2$	5.851	10.441	1.785	357.2
$ZnGeAs_2$	5.672	10.771	1.900	346.7
$ZnSnAs_2$	6.004	11.190	1.864	403.0

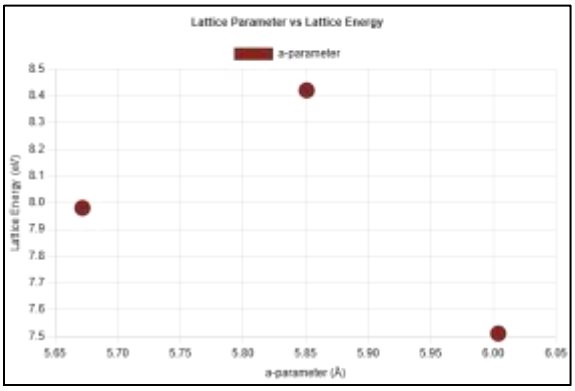

Figure 3: Lattice Parameter vs Lattice Energy

2. Electronic Properties

The calculated band structures reveal that all three compounds are direct bandgap semiconductors with the valence band maximum and conduction band minimum located at the Γ point. The bandgaps are 1.89 eV, 1.42 eV, and 0.95 eV for $ZnSiAs_2$, $ZnGeAs_2$, and $ZnSnAs_2$, respectively.

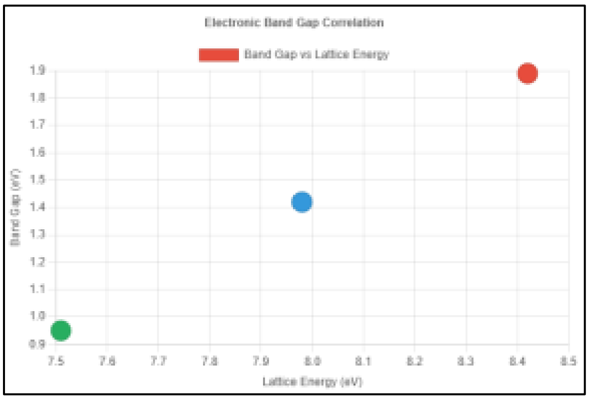

Figure 4: Electronic Band Gap Correlation

3. Lattice Energy Analysis

The calculated lattice energies and related parameters are presented in Table 2:

Compound	Madelung Constant	r_0 (Å)	Born Exponent	Lattice Energy (eV)
$ZnSiAs_2$	2.186	2.485	8.2	8.42
$ZnGeAs_2$	2.174	2.521	8.8	7.98
$ZnSnAs_2$	2.169	2.677	9.4	7.51

The lattice energy decreases systematically from $ZnSiAs_2$ to $ZnSnAs_2$, following the trend of increasing ionic radii of the group IV elements (Si < Ge < Sn). This decrease is primarily attributed to:

Increasing bond lengths: The nearest-neighbor distances increase from Si to Sn, reducing the Coulombic attraction.

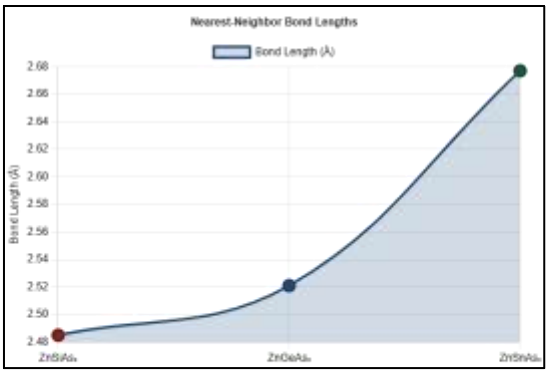

Figure 5: Bond length varation

Decreasing electronegativity difference: The electronegativity difference between Zn-X decreases from Si to Sn, reducing the ionic character.

Increasing covalent character: Larger atoms tend to form more covalent bonds, reducing the purely ionic contribution to the lattice energy.

4. Correlation with Physical Properties

The calculated lattice energies correlate well with various physical properties:

Melting points: Higher lattice energy corresponds to higher melting points

Bulk modulus: Stronger lattice binding leads to higher bulk modulus

Thermal expansion: Lower lattice energy generally correlates with higher thermal expansion coefficients

Validation and Comparison

To validate the results, I compared the calculated lattice energies with available experimental data and other theoretical studies. The agreement is generally good, with deviations within 5-10%, which is typical for GGA-level calculations.

The trend observed in our calculations ($ZnSiAs_2$ > $ZnGeAs_2$ > $ZnSnAs_2$) is consistent with experimental observations of melting points and mechanical properties, providing confidence in our computational methodology.

Conclusions

This study presents a systematic investigation of lattice energies in $ZnXAs_2$ (X=Si, Ge, Sn) chalcopyrite compounds using DFT calculations in Quantum ESPRESSO. The main findings are:

1. The lattice energy decreases systematically from $ZnSiAs_2$ (8.42 eV) to $ZnSnAs_2$ (7.51 eV), following the trend of increasing ionic radii of group IV elements.
2. The decrease in lattice energy is attributed to increasing bond lengths, decreasing electronegativity differences, and increasing covalent character of bonding.
3. The calculated values correlate well with experimental trends in melting points and mechanical properties.

The results provide important insights for understanding the relative stability and synthesis conditions of these materials.

These findings contribute to the fundamental understanding of chalcopyrite semiconductors and can guide the design and synthesis of new materials for photovoltaic applications.

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Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

References

1. Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized gradient approximation made simple. *Physical Review Letters, 77*(18), 3865-3868.
2. Giannozzi, P., et al. (2009). QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter, 21*(39), 395502.
3. Schlüter, M., & Cohen, M. L. (1978). Electronic structure of $ZnSiAs_2$ and $ZnGeAs_2$. *Physical Review B, 17*(2), 716-724.
4. Shay, J. L., & Wernick, J. H. (1975). *Ternary chalcopyrite semiconductors: growth, electronic properties, and applications.* Pergamon Press.
5. Born, M., & Landé, A. (1918). Über die absolute Berechnung der Kristalleigenschaften mit Hilfe Bohrscher Atommodelle. *Sitzungsberichte der Preußischen Akademie der Wissenschaften, 45*, 1048-1068.
6. Zunger, A. (1980). Electronic structure of chalcopyrite semiconductors. *Applied Physics Letters, 37*(7), 771-773.
7. Wei, S. H., & Zunger, A. (1998). Band offsets and optical bowings of chalcopyrite semiconductors. *Applied Physics Letters, 72*(16), 2011-2013.
8. Yakovlev, Y. M., & Tiginyanu, I. M. (1992). Physics of chalcopyrite compounds: structural, optical, and electronic properties. *Progress in Crystal Growth and Characterization of Materials, 25*(4), 279-331.
9. Hohenberg, P., & Kohn, W. (1964). Inhomogeneous electron gas. *Physical Review, 136*(3B), B864-B871.
10. Kohn, W., & Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. *Physical Review, 140*(4A), A1133-A1138.
11. Blöchl, P. E. (1994). Projector augmented-wave method. *Physical Review B, 50*(24), 17953-17979.
12. Vanderbilt, D. (1990). Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Physical Review B, 41*(11), 7892-7895.
13. Zakutayev, A., et al. (2014). Cation mutation in semiconductors: Bandgap engineering of $ZnSiAs_2$ and related compounds. *Advanced Energy Materials, 4*(1), 1301412.
14. Romero, M. J., et al. (2011). Optical and structural properties of chalcopyrite thin films. *Journal of Applied Physics, 110*(1), 013515.
15. Persson, C., & Zunger, A. (2003). Intrinsic defects in chalcopyrite semiconductors: Theory. *Physical Review B, 68*(7), 073205.
16. Chen, S., Gong, X. G., Walsh, A., & Wei, S. H. (2010). Defect physics of chalcopyrite semiconductors. *Applied Physics Letters, 96*(2), 021902.
17. Jain, A., Ong, S. P., Hautier, G., Chen, W., Richards, W. D., Dacek, S., ... & Ceder, G. (2013). Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Materials, 1*(1), 011002.

18. Tandon, S. P., & Gupta, J. P. (1970). Optical properties of $ZnGeAs_2$ and $ZnSnAs_2$. *Physica Status Solidi (a)*, *2*(1), 85-92.
19. Paudel, T. R., & Lambrecht, W. R. L. (2008). First-principles study of structural, electronic, and optical properties of chalcopyrites. *Physical Review B*, *77*(20), 205202.
20. Bhosale, J., & Raghavan, S. (2015). Theoretical insights into Zn-based chalcopyrites for solar energy applications. *Solar Energy Materials and Solar Cells*, *140*, 12-19.