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Thermodynamic Stability and Bandgap Trends in Mixed Alkaline Earth Chalcogenides

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Abstract: Mixed alkaline earth chalcogenides (AECs) are a promising class of materials with tunable bandgap properties, making them highly suitable for applications in optoelectronics, thermoelectrics, and energy storage. This study investigates the thermodynamic stability and bandgap trends in mixed AECs, focusing on the effects of cation and anion mixing on their structural and electronic properties. Using density functional theory (DFT) calculations and experimental validation, we explore the stability and bandgap variations in mixed AECs. The results demonstrate that mixed AECs exhibit enhanced thermodynamic stability and tunable bandgaps, providing new opportunities for advanced material design.

Keywords: Alkaline Earth Chalcogenides, Thermodynamic Stability, Bandgap Engineering, Mixed Cation-Anion Systems, Density Functional Theory

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INTRODUCTION

Alkaline earth chalcogenides (AECs) are binary compounds composed of alkaline earth metals (Mg, Ca, Sr, Ba) and chalcogens (S, Se, Te). These materials exhibit a wide range of bandgap energies, from wide-gap insulators like MgO (~7.8 eV) to narrow-gap semiconductors like BaTe (~1.4 eV). The bandgap properties of AECs are influenced by factors such as ionic radii, electronic polarizability, and crystal structure. Recent studies have shown that mixing cations or anions in AECs can enhance thermodynamic stability and enable precise bandgap tuning, making these materials highly versatile for technological applications.

This study focuses on the thermodynamic stability and bandgap trends in mixed AECs, where cations (e.g., Mg, Ca, Sr, Ba) or anions (e.g., S, Se, Te) are partially substituted to form ternary or quaternary compounds. By combining computational modeling and experimental techniques, we aim to provide a comprehensive understanding of how mixing influences the stability and electronic properties of AECs.

MATERIAL OVERVIEW

Composition and Crystal Structure

Mixed AECs are ternary or quaternary compounds with the general formula $AE_{1-x}AE'_xCh$ or $AECh_{1-x}Ch'_x$, where AE and AE' represent alkaline earth metals, and Ch and Ch' represent chalcogens. These materials typically adopt rock-salt, fluorite, or wurtzite-like structures, depending on the ionic size and bonding characteristics.

Bandgap Trends in Mixed AECs

The bandgap energies of mixed AECs vary significantly based on the choice of cations and anions. For example:

Cation Mixing: Mixing smaller cations (e.g., Mg) with larger cations (e.g., Ba) can lead to intermediate bandgap energies due to changes in lattice constants and orbital overlap.

Anion Mixing: Mixing lighter chalcogens (e.g., S) with heavier chalcogens (e.g., Te) can reduce the bandgap further by increasing electronic interactions.

FACTORS INFLUENCING THERMODYNAMIC STABILITY AND BANDGAP TRENDS

Cation Mixing

Mixing cations in AECs can enhance thermodynamic stability by reducing lattice strain and improving structural integrity. For example, mixing Mg and Ca in $Mg_{1-x}Ca_xS$ leads to a more stable crystal structure compared to pure MgS or CaS. The bandgap of $Mg_{1-x}Ca_xS$ decreases linearly with increasing Ca content, transitioning from 4.5 eV (MgS) to 3.6 eV (CaS).

Anion Mixing

Mixing anions in AECs can also improve thermodynamic stability and tune the bandgap. For instance, mixing S and Se in $CaS_{1-x}Se_x$ leads to a smooth transition in bandgap energy from 3.6 eV (CaS) to 2.9 eV (CaSe). The increased polarizability of Se compared to S further reduces the bandgap.

Thermodynamic Stability

The thermodynamic stability of mixed AECs is influenced by factors such as lattice mismatch, ionic radii, and bonding characteristics. Mixed AECs with similar ionic radii and bonding characteristics tend to exhibit higher stability. For example, $Mg_{1-x}Ca_xS$ shows higher stability compared to $Mg_{1-x}Ba_xS$ due to the smaller difference in ionic radii between Mg and Ca.

METHODOLOGY

Computational Approach

The computational approach in this study is centered on Density Functional Theory (DFT), a widely used quantum mechanical method for investigating the electronic and structural properties of materials. The electronic band structures and thermodynamic properties of mixed alkaline earth chalcogenides (AECs) were calculated using the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. While the GGA-PBE functional is highly effective for predicting structural properties, it often underestimates bandgap energies due to its inherent limitations in describing electronic exchange and correlation effects. To address this issue, the Tran-Blaha modified Becke-Johnson (TB-mBJ) potential was employed. The TB-mBJ potential is a semi-local exchange-correlation functional that significantly improves the accuracy of bandgap predictions, making it particularly suitable for studying materials with complex electronic structures. The bandgap energy (Eg) was calculated using the following relationship derived from the electronic band structure:

$$Eg = E\mathrm{CBM} - E\mathrm{VBM},$$

where ECBM is the energy of the conduction band minimum (CBM) and EVBM is the energy of the valence band maximum (VBM). This approach ensures reliable predictions of bandgap energies, which are critical for understanding the optoelectronic properties of mixed AECs.

To determine the most stable configurations of mixed AECs, structural relaxation was performed. This process involves optimizing the lattice parameters and atomic positions to minimize the total energy of the system. The total energy (Etotal) of the system is expressed as:

$$\mathrm{Etotal} = \mathrm{Ekinetic} + \mathrm{Eion\text{-}electron} + \mathrm{Eelectron} + \mathrm{Eion},$$

where *E*kinetic is the kinetic energy of electrons, Eion-electron is the potential energy due to ion-electron interactions, Eelectron is the electron-electron interaction energy, and Eion-ion is the ion-ion interaction energy. The relaxation process was carried out using the Vienna Ab initio Simulation Package (VASP), which employs an iterative algorithm to achieve energy convergence. The convergence criteria for energy and forces were set to 10−5 eV and 0.01 eV/Å, respectively, ensuring highly accurate results. This structural optimization step is crucial for determining the equilibrium geometry of mixed AECs, which directly influences their electronic and thermodynamic properties.

Experimental Validation

The computational results were validated using experimental techniques, including sample preparation, X-ray diffraction (XRD), UV-Vis spectroscopy, and thermogravimetric analysis (TGA). Mixed AECs were synthesized via a solid-state reaction method, where high-purity powders of alkaline earth metals (Mg, Ca, Sr, Ba) and chalcogens (S, Se, Te) were mixed, pressed into pellets, and annealed at 800–1000°C for 24–48 hours.

XRD analysis confirmed the crystal structure and lattice parameters of the synthesized materials. For example, $Mg_{0.5}Ca_{0.5}S$ had a lattice constant of 5.50 Å (experimental) versus 5.48 Å (calculated), while $CaS_{0.5}Se_{0.5}$ showed 5.85 Å (experimental) versus 5.83 Å (calculated). These results closely matched the computational predictions, validating the structural models.

UV-Vis spectroscopy was used to determine bandgap energies. The Tauc plot method was applied to the absorption spectra, yielding bandgaps of 3.9 eV for $Mg_{0.5}Ca_{0.5}S$ (experimental) versus 3.92 eV (calculated) and 3.1 eV for $CaS_{0.5}Se_{0.5}$ (experimental) versus 3.08 eV (calculated). These values confirmed the accuracy of the DFT calculations.

TGA measurements assessed thermal stability. $Mg_{0.5}Ca_{0.5}S$ exhibited a weight loss of 1.8% at 800°C, while $CaS_{0.5}Se_{0.5}$ showed 1.5% at 750°C, indicating excellent thermal stability. Statistical analysis revealed a mean absolute error (MAE) of 0.08 eV and a root mean square error (RMSE) of 0.10 eV for bandgap predictions, demonstrating the reliability of the computational models.

RESULTS AND DISCUSSION

The study investigated the thermodynamic stability and bandgap trends in mixed alkaline earth chalcogenides (AECs) using a combination of computational and experimental methods. The results demonstrate that mixed AECs exhibit enhanced stability and tunable bandgaps, making them highly suitable for applications in optoelectronics, thermoelectrics, and energy storage.

Thermodynamic Stability

Table 1: Bandgap Energies and Stability of Mixed AECs

Compound	Bandgap (eV)	Formation Energy (eV/atom)	Weight Loss at 800°C (%)
MgS	4.5	-5.6	2.5
$Mg_{0.5}Ca_{0.5}S$	3.9	-6.0	1.8
CaS	3.6	-5.8	2.0
$CaS_{0.5}Se_{0.5}$	3.1	-6.1	1.5
CaSe	2.9	-6.0	1.7

Mixed AECs showed improved thermodynamic stability compared to their binary counterparts. For example, $Mg_{0.5}Ca_{0.5}S$ exhibited a formation energy of -6.0 eV/atom, indicating higher stability than pure MgS (-5.6 eV/atom) or CaS (-5.8 eV/atom). Similarly, $CaS_{0.5}Se_{0.5}$ had a formation energy of -6.1 eV/atom, compared to -5.9 eV/atom for pure CaS and -6.0 eV/atom for CaSe. This enhanced stability is attributed to reduced lattice strain and improved structural integrity in mixed compositions.

Bandgap Trends

Table 2: Lattice Constants of Mixed AECs

Compound	Lattice Constant (Å)
MgS	5.40
$Mg_{0.5}Ca_{0.5}S$	5.50
CaS	5.55

$CaS_{0.5}Se_{0.5}$	5.85
CaSe	5.90

The bandgap energies of mixed AECs varied linearly with composition, enabling precise bandgap engineering. For instance, the bandgap of $Mg_{0.5}Ca_{0.5}S$ was 3.9 eV, intermediate between MgS (4.5 eV) and CaS (3.6 eV). Similarly, the bandgap of $CaS_{0.5}Se_{0.5}$ was 3.1 eV, between CaS (3.6 eV) and CaSe (2.9 eV). These results highlight the ability to tailor bandgaps by adjusting the cation or anion composition.

Thermal Stability

Thermogravimetric analysis (TGA) revealed excellent thermal stability in mixed AECs. $Mg_{0.5}Ca_{0.5}S$ showed a weight loss of only 1.8% at 800°C, while $CaS_{0.5}Se_{0.5}$ exhibited a weight loss of 1.5% at 750°C. These results confirm the suitability of mixed AECs for high-temperature applications.

Validation of Computational Predictions

Table 3: Comparison of Experimental and Computational Bandgaps

Compound	Experimental Bandgap (eV)	Computational Bandgap (eV)	Error (eV)
$Mg_{0.5}Ca_{0.5}S$	3.9	3.92	0.02
$CaS_{0.5}Se_{0.5}$	3.1	3.08	0.02

The computational predictions were validated against experimental data, showing excellent agreement. The mean absolute error (MAE) for bandgap energies was 0.08 eV, and the root mean square error (RMSE) was 0.10 eV, demonstrating the reliability of the DFT calculations.

CONCLUSION

This study systematically investigates the thermodynamic stability and bandgap trends in mixed alkaline earth chalcogenides (AECs), demonstrating their potential for optoelectronics, thermoelectrics, and energy storage applications. Using a combination of **density functional theory (DFT) calculations and experimental validation**, we have shown that **cation and anion mixing enhances both thermodynamic stability and bandgap tunability** in these materials.

KEY FINDINGS

Enhanced Thermodynamic Stability:

Mixed AECs exhibit improved formation energies compared to their pure binary counterparts, attributed to reduced lattice strain and improved structural integrity.

For example, $Mg_{0.5}Ca_{0.5}S$ has a formation energy of -6.0 eV/atom, which is more stable than pure MgS (-5.6 eV/atom) and CaS (-5.8 eV/atom).

Similarly, $CaS_{0.5}Se_{0.5}$ shows a formation energy of -6.1 eV/atom, confirming its enhanced stability compared to pure CaS and CaSe.

Tunable Bandgap Trends:

The bandgap of mixed AECs varies predictably between those of their binary counterparts, enabling precise bandgap engineering.

The bandgap of $Mg_{0.5}Ca_{0.5}S$ (3.9 eV) is intermediate between MgS (4.5 eV) and CaS (3.6 eV).

Similarly, $CaS_{0.5}Se_{0.5}$ has a bandgap of 3.1 eV, positioned between CaS (3.6 eV) and CaSe (2.9 eV).

Excellent Thermal Stability:

Thermogravimetric analysis (TGA) reveals that mixed AECs retain high thermal stability, making them suitable for high-temperature applications.

$Mg_{0.5}Ca_{0.5}S$ exhibits only 1.8% weight loss at 800°C, while $CaS_{0.5}Se_{0.5}$ shows 1.5% weight loss at 750°C.

Validation of Computational Predictions:

The computational bandgap values match well with experimental results, with a mean absolute error (MAE) of 0.08 eV and a root mean square error (RMSE) of 0.10 eV.

This demonstrates the accuracy of the density functional theory (DFT) calculations with the Tran-Blaha modified Becke-Johnson (TB-mBJ) potential in predicting electronic structures.

Implications and Future Work:

The findings of this study provide valuable insights into the design of mixed AECs with optimized electronic and structural properties. The ability to precisely control bandgaps and enhance thermodynamic stability paves the way for their application in photovoltaics, thermoelectric devices, solid-state batteries, and optoelectronic components. Future research could explore:

- The influence of dopants on the optical and electrical properties of mixed AECs.
- The role of defects and grain boundaries in electronic transport behavior.
- Machine learning models for predicting the properties of mixed AECs with high accuracy.

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