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The Influence of Potassium Substitution on the Structural and Electronic Properties of Na₂S: *Ab Initio* Analysis

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This paper presents the study of the influence of potassium substitution on the structural and electronic properties of Na_2S using the density functional theory methodology implemented in the Quantum ESPRESSO package. The focus is on the analysis of the structural stability and changes in the density of electronic states distribution due to the introduction of potassium. The results indicate that the presence of potassium in the Na_2S lattice can lead to significant changes in both the structural and electronic properties of the material, affecting its conductivity and potential applications in energy storage devices.

topics: density functional theory (DFT), electronic structure, substitution defect

1. Introduction

The pristine Na₂S material is known to have a semiconductor nature [1, 2], and due to the abundance of both sodium and sulphur in Earth's crust, it is also cost-effective to produce. This makes Na₂S a promising candidate for use in various electronic applications [3, 4] and batteries [5, 6]. However, the parameters of pure sodium sulphide are not always suitable for all uses, so modifications may be necessary. For example, substitution with different elements can improve the conductivity and stability of the material, change its properties, and enhance its performance under specific conditions. Adjustments to the chemical composition can also help tailor the material for particular use cases, such as catalysts [7]. In addition, the introduction of substitutions may be dictated by the desire to change the spatial structure of the material, leading to different physical and chemical properties. In general, by making modifications to pure sodium sulphide, one could create custom materials that meet the specific requirements of different electronic applications, making it a versatile option for a wide range of uses in the industry. One way to achieve these goals is to perform element substitutions. The introduction of potassium into the Na_2S structure is of great importance due to its potential to improve the material's properties for various applications. For example, increasing its conductivity for use in high-performance batteries or enhancing its catalytic activity in fuel cells is highly desirable [8, 9]. Understanding the impact of this replacement on the electronic structure of Na_2S is crucial for optimizing its performance not only in batteries and energy storage devices but also in its wide applications in industry [10, 11]. By manipulating the density of states (DOS) distribution by introducing potassium, the material parameters can be tailored to meet specific requirements in different fields. The aim of this paper is to provide information on how potassium atom substitution affects the atomic structure, band structure, and density of states in highly changed Na₂S using DFT methodology, providing an understanding of the mechanisms behind these improvements.

2. Computational details

Density functional theory (DFT) calculations for Na₂S were performed using the Quantum ESPRESSO package to investigate its structural and electronic properties [12]. A k-point sampling grid of $10 \times 10 \times 10$ was employed for the structural relaxations, ensuring adequate sampling of the Brillouin zone. A two-stage "vc-relax" approach was utilized, with the first stage achieving structural optimization under the constraint of high-precision parameters, including the total energy convergence threshold of 10^{-6} Ry and the force convergence threshold of 10^{-4} a.u., alongside a pressure convergence threshold of 0.1 kbar. The plane-wave basis set was defined by ecutwfc = 320 Ry and ecutrho = 80 Ry, ensuring convergence of the total energy and stress tensors. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation



Fig. 1. Schematic diagram of the pristine Na_2S structure. Blue spheres represent sodium sites, while yellow spheres represent sulphur sites.

(GGA) was used, while projector augmented-wave (PAW) pseudopotentials for Na₂S and K atoms accurately described the core–valence interactions.

For electronic structure calculations, such as density of states (DOS) and band structure, a finer k-points sampling grid of $20 \times 20 \times 20$ was used to enhance the accuracy in electronic property predictions. Where required, a "cold" smearing scheme with a degauss value of 0.005 Ry was used to facilitate convergence, particularly in metallic or nearmetallic cases; otherwise, no smearing was applied. The ion dynamics during relaxations were handled using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm, ensuring a robust optimization of the ionic positions. These computational parameters collectively provided reliable and high-accuracy results, suitable for detailed analysis of the structural and electronic properties of Na₂S.

The substitutions in Na₂S were performed in reference to Fig. 1. The process involved both singleatom and double-atom substitutions, with potassium (K) being selected as the substituent due to its chemical similarity to sodium (Na). Initially, two independent single-atom substitutions were carried out. In the first case, one Na atom at the site Na(1) was replaced by K, referred to as SUB0. In the second case, one sulphur atom at the site S(1) was replaced by K, referred to as SUB3. Subsequently, simultaneous double-atom substitutions were performed, yielding four distinct configurations. In SUB1, two Na atoms, specifically Na(1)and Na(4), were substituted with K. Similarly, in SUB2, the substituted sites were Na(1) and Na(7). For sulphur substitutions, in SUB4, S(1) and S(3)were replaced by K, while in SUB5, S(1) and S(4)were substituted. These substitutions were always followed by relaxation of the structure and allowed us to systematically investigate the structural and electronic effects of replacing Na and S atoms with K in the Na₂S lattice.

3. Results and discussion

3.1. Structural properties

Na₂S generally exhibits a cubic antifluorite structure (space group $Fm\bar{3}m$) under standard conditions. The sulphide ions create a face-centred cubic (fcc) lattice, whereas the sodium ions occupy tetrahedral interstitial positions. This structure resembles fluorite (CaF₂), but with the roles of the cations and anions reversed. In Fig. 1, the structure of pristine Na₂S is presented. Upon implementing substitutions and allowing the resulting structures to undergo another full structural relaxation using the variable cell method, we observed changes in crystallographic symmetry depending on the substitution pattern. These results provide insight into the structural impact of introducing potassium (K) atoms into the Na₂S lattice.

For SUB0 and SUB3, i.e., the cases where only one Na or S ion was replaced, the space group remained unchanged compared to the pristine Na₂S structure, indicating that the single-atom substitutions of Na(1) or S(1) by K did not significantly perturb the overall symmetry of the lattice. In contrast, the double-atom substitutions led to notable symmetry changes. For SUB1 and SUB2, where two Na atoms (Na(1) and Na(4), and Na(1) andNa(7), respectively) were replaced by K, the resulting space group was identified as $P4_2/mcm$ (space group number 132). Similarly, for SUB4 and SUB5, where two sulphur atoms (S(1) and S(3), and S(1))and S(4), respectively) were substituted with K, the space group changed to P4/mmm (space group number 123). These results highlight the dependence of structural symmetry on substitution pattern and provide a systematic framework to understand structural distortions induced by specific atomic replacements in Na_2S .

The structural changes observed after substitutions can be attributed to the significant difference in empirical atomic radii between potassium (K) and the substituted atoms — sodium (Na) and sulphur (S). Potassium, with an atomic radius of ≈ 2.20 Å, is notably larger than sodium (1.80 Å) and sulphur (1.05 Å). This size mismatch leads to lattice distortions and symmetry changes, especially in the cases of double-atom replacement. The afterrelaxation cell parameters are presented in Table I.

For single exchange, such as in SUB0 and SUB3, where either one Na atom or one S atom was replaced by K, the overall impact on the lattice symmetry and unit cell parameters was minimal. As a result, the space group remained unchanged in these cases compared to the pristine Na₂S structure. However, in the cases of double substitutions (SUB1, SUB2, SUB4, and SUB5), the introduction of two large K atoms into the lattice caused significant perturbations. These substitutions disrupted the original balance of the lattice, leading to The Influence of Potassium Substitution on the Structural and...

Name	Vol [Å ³]	$D ~[{ m g/cm^3}]$	a [Å]	<i>b</i> [Å]	c [Å]	E_{def} [eV]	E_{coh} [eV]
Pristine	281.14	1.844	6.551	6.551	6.551	_	3.16
SUB0	298.391	1.826	6.682	6.682	6.682	0.71	3.10
SUB1	312.43	1.830	6.791	6.791	6.774	1.23	3.05
SUB2	314.31	1.819	6.799	6.780	6.7989	1.33	3.04
SUB3	349.55	1.516	7.044	7.044	7.044	9.73	2.34
SUB4	463.08	1.170	10.281	6.711	6.711	15.09	1.90
SUB5	423.38	1.279	6.749	6.749	9.295	15.45	1.87

Structural parameters and cohesive and defect formation energies of studied materials with substitutions.

substantial changes in symmetry and unit cell geometry. Specifically, replacing two Na atoms with K (SUB1 and SUB2) resulted in a reduction in symmetry to the $P4_2/mcm$ space group (number 132). Similarly, the substitution of two S atoms with K (SUB4 and SUB5) caused a symmetry change to the P4/mmm space group (number 123). In general, it can be concluded that the Na₂S lattice is sensitive to the size and nature of substituent atoms, where the larger atomic radius of K induces structural distortions that significantly affect symmetry and lattice parameters in cases of multiple substitutions.

Knowing the values of cohesive energy, we evaluate the structural stability of the substituted configurations. The cohesive energy was calculated using

$$E_{coh} = \frac{\sum_{i=1}^{n} E_{\text{atom},i} - E_{tot}}{N_{\text{atom}}},\tag{1}$$

where E_{coh} is the cohesive energy (per atom), $E_{\text{atom},i}$ — the energy of the *i*-th atom in an isolated state, E_{tot} — the total energy of the whole system, N_{atom} — the number of atoms in the unit cell.

This energy provides a measure of the energetic stability of the pristine (for comparison) and substituted Na₂S structures. The cohesive energies, summarized in Table I, are positive for all cases, indicating that the materials are energetically stable. The pristine Na₂S exhibits the highest cohesive energy of 3.16 eV, reflecting the inherent stability of the unmodified structure. Substituted configurations show reduced cohesive energies, with values of 3.10 eV, 3.05 eV, and 3.05 eV for SUB0, SUB1, and SUB2, respectively, indicating moderate stability reductions due to sodium substitutions. For sulphur substitutions, the cohesive energies are lower, with 2.34 eV for SUB3 and 1.89871 eV and 1.87 eV for SUB4 and SUB5, respectively, highlighting a greater structural impact from sulphur replacements.

Defect formation (substitution) energies E_{def} are calculated using

$$E_{\text{defect}} = E_{def} - E_{\text{pristine}} + \sum_{i} n_{i} \mu_{in,i} - \sum_{j} m_{j} \mu_{out,j},$$
(2)

where n_i is the number of atoms of the given element *i* that were introduced into the system, m_i — the number of atoms of the given element j that were removed from the system, $\mu_{in,i}$ — chemical potential of the introduced atom i, $\mu_{out,j}$ — chemical potential of the removed atom j. The E_{def} results, summarized in Table I, quantify the energy cost of introducing potassium atoms into the Na₂S lattice. The single substitutions (SUB0 and SUB3) have defect formation energies of 0.71 eV and 9.73 eV, respectively, with the much higher energy for SUB3 reflecting the larger disruption caused by replacing sulphur with potassium. For double substitutions, E_{def} increases further, with values of 1.23 eV for SUB1, 1.33 eV for SUB2, 15.09 eV for SUB4, and 15.45 eV for SUB5. The higher defect formation energies for double substitutions compared to single substitutions and for sulphur ions compared to sodium ions can be attributed to the significant difference in atomic radii between the substituted atom and the potassium atom, which causes greater lattice distortions and a higher energetic penalty.

TABLE I

3.2. Electronic properties

The band diagrams for the unsubstituted reference (Fig. 2) and for the materials with sodium substituted by potassium (SUB0, SUB1, and SUB2) and sulphur substituted by potassium (SUB3, SUB4, and SUB5) are presented in Figs. 3 and 4, respectively, with the corresponding data summarized in Table II. The pristine Na₂S structure exhibits a direct semiconducting band gap of 2.47 eV. with the HOMO and LUMO bands both located at the Γ point (where HOMO and LUMO mean the highest occupied and lowest unoccupied molecular orbital, respectively). Substitutions in the Na₂S lattice result in modifications of the electronic structure, changing band gap type to indirect $(\Gamma - X)$, as reflected in the band diagrams and associated energies.

For substitutions involving Na (SUB0, SUB1, and SUB2), the materials retain their semiconducting nature, with direct band gaps at the Γ point.



Fig. 2. Band structure and corresponding partial density of states (pDOS) along special k vector for pristine Na₂S structure.



Fig. 3. Electronic band diagram for cases where K substituted Na.

The nature of the materials' conductivity with asso-
ciated calculated corresponding energies. For metallic
character, Fermi energy is presented, while for semi-
conducting, the gap width is presented.

Name	номо	LUMO	GAP/Fermi	Type	
rame	[eV]	[eV]	[eV]		
$\mathbf{Pristine}$	1.8270	4.2955	2.47	semicond.	
SUB0	1.9018	4.3192	2.42	semicond.	
SUB1	2.1161	4.4398	2.28	semicond.	
SUB2	1.9989	4.3530	2.35	semicond.	
SUB3	—	_	3.8892	metal	
SUB4	_	_	2.5297	metal	
SUB5	_	_	2.9370	metal	

TABLE II

The band gap slightly decreases from 2.47 eV in the pristine structure to 2.42 eV, 2.28 eV, and 2.35 eV for SUB0, SUB1, and SUB2, respectively. These changes indicate a minor impact on the electronic properties due to Na substitutions. The Fermi level for SUB0 lies near the conduction band, while for SUB1 and SUB2 cases, it shifts closer to the valence band, reflecting hole carrier characteristics, like in p-type semiconductors.

In contrast, substitutions involving sulphur (SUB3, SUB4, and SUB5) introduce the metallic character as the Fermi level crosses the bands, leading to zero band gap values. The Fermi energies for these metallic structures are 3.8892 eV, 2.5297 eV, and 2.9370 eV for SUB3, SUB4, and SUB5, respectively, as reported in Table II along with the



Fig. 4. Electronic band diagram for cases where K substituted S.



Fig. 5. Total density of states and pDOS projected on Na, S, and K atoms for cases where K substituted Na.



Fig. 6. Total density of states and pDOS projected on Na, S, and K atoms for cases where K substituted S.

band gap parameters and conductivity type. This transition from semiconducting to metallic behaviour arises from significant lattice and electronic distortions caused by the replacement of smaller sulphur atoms with larger potassium atoms, which disrupts the band structure. These results highlight that Na substitutions primarily modify the band gap width while maintaining semiconducting behaviour, whereas S substitutions induce metallic characteristics as a result of the overlap of the Fermi level with the conduction and valence bands.

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Bader analysis results for pristine Na_2S and substituted variants for all studied cases. In each case, only a valence charge is presented. Results in bold indicate K substitution.										
Id.		Pristine	SUB0	SUB1	SUB2	SUB3	SUB4	SUB5		

Id.		Pristine	SUB0	SUB1	SUB2	SUB3	SUB4	SUB5
1	Na	8.196	8.280	8.266	8.284	8.264	8.439	8.428
2	Na	8.196	8.199	8.192	8.192	8.265	9.054	8.428
3	S	7.609	7.593	7.583	7.574	9.447	8.589	9.515
4	Na	8.196	8.193	8.192	8.188	8.266	8.691	8.428
5	Na	8.196	8.190	8.266	8.188	8.265	8.458	8.428
6	S	7.609	7.593	7.585	7.574	7.810	7.772	9.517
7	Na	8.196	8.193	8.187	8.284	8.266	8.458	8.428
8	Na	8.196	8.190	8.187	8.192	8.265	8.691	8.428
9	S	7.609	7.593	7.585	7.576	7.810	7.772	7.773
10	Na	8.196	8.193	8.187	8.188	8.266	9.054	8.428
11	Na	8.196	8.190	8.187	8.188	8.266	8.439	8.428
12	S	7.609	7.593	7.583	7.574	7.810	8.581	7.773

The projected density of states (pDOS) corresponding well to the band plots is presented in Fig. 5 for cases where potassium (K) substituted sodium (Na) and in Fig. 6 for cases where K substituted sulphur (S). In the cases where K substitutes Na (SUB0, SUB1, and SUB2), the pDOS below $E_{\rm F}$ is dominated by states originating from sulphur (S), with only marginal contributions from Na and K. Above $E_{\rm F}$, the situation reverses, and the DOS is contributed predominantly by K, with a slightly smaller contribution from Na states. This indicates that sulphur states play a crucial role in the valence band, while potassium states dominate the conduction band.

For K substituting S (SUB3, SUB4, and SUB5), the pDOS exhibits a different pattern, as shown in Fig. 6. In SUB3, the states above $E_{\rm F}$ are a mixture of contributions from Na and K, while directly at $E_{\rm F}$, the DOS is dominated by Na, with the contributions of Na and K being higher than that of S. In SUB4 and SUB5, the contributions from Na, S, and K are more evenly distributed near and above $E_{\rm F}$, although K slightly dominates. This reflects a more uniform mixing of atomic states in the electronic structure for these configurations.

Table III presents the results of Bader charge analysis for pristine Na_2S and its substituted variants. Table III lists the valence charges of the individual atoms, with the initial charges for Na = 9, for S = 6, and for K = 9. Substitution sites involving potassium (K) are highlighted in **bold**, distinguishing cases where K replaces Na (SUB0, SUB1, SUB2) and S (SUB3, SUB4, SUB5). The data are compared with respect to the pristine Na_2S structure, providing information on charge redistribution upon substitution.

In the pristine case, Na atoms have a mean Bader charge of ≈ 8.196 , indicating partial charge transfer to the more electronegative sulphur atoms, which exhibit a mean charge of 7.609, manifesting an ionic

bonding between Na and S. When K substitutes Na (SUB0, SUB1, SUB2), the substituted K atoms exhibit slightly higher charge (8.280, 8.266, and 8.284, respectively), reflecting the larger size and slightly lower electronegativity of K compared to Na. The remaining Na and S atoms show minimal deviations from their pristine values, indicating localized charge effects around the substitution site.

In the cases where K substitutes for S (SUB3, SUB4, SUB5), the charge redistribution is more pronounced. The substituted K atoms exhibit significantly higher charges (9.447, 8.589, and 9.515, respectively), reflecting their reduced ability to attract charge compared to sulphur. This change is accompanied by increased charges on neighbouring Na atoms, with values such as 8.439 and 8.691, compared to 8.196 in the pristine structure. The remaining S atoms also show slight charge increases in SUB4 and SUB5 (8.581 and 9.517, respectively), indicating complex charge redistribution in the lattice.

Overall, the Bader analysis reveals that K substitutions induce localized charge redistributions, with the extent and nature of these changes depending on whether K replaces Na or S. Substitutions on sulphur sites result in more significant deviations from pristine values, consistent with the larger electronegativity difference between S and K compared to Na and K.

4. Conclusions

In this paper, the results of an ab initio study on the influence of substitution on structural and electronic properties in Na_2S are presented. As it was shown, all studied configurations are feasible in terms of energetic stability, and the introduction of K in place of Na or S ions significantly changes the structural parameters of the unit cell, especially when two elements are substituted simultaneously. As a result of substituting S, the conduction character changes to metallic from a semiconducting state presented by the material in the pristine form. Furthermore, there is also a change in the semiconductor type from direct to indirect in the case of double Na ion substitutions. The Bader analysis of the charge distribution indicates that in the case of substitutions for sulphur, significantly greater changes in the electronic structure occur than in the case of substitutions for sodium.

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