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Analysis of the Influence of Targeted Vacancies on the Properties of Na₂S: Studies Using Density Functional Theory

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In this work, the structural and electronic properties of bulk Na_2S were studied using density functional theory as implemented in the Quantum ESPRESSO package. It was investigated how the material's atomic and electronic structure is affected by point defects in the form of vacancies. Possible configurations of vacancies were analyzed, as well as their influence on conductivity character and structural stability. The results suggest that specific vacancies can significantly modify the properties of Na_2S , making this material a potential candidate for applications in modern electronic devices and energy storage.

topics: density functional theory (DFT), defects, electronic properties

1. Introduction

The Na₂S or sodium sulfide, which is an inorganic compound, is commonly used in many applications such as, for example, in the paper industry in a delignification process [1–3], in the water treatment for oxygen capture, as a bleaching agent in the textile industry [3, 4], or as a reducing agent in organic chemistry where its common usage is to reduce nitro groups to amine [5], to name a few. Due to the wide application of this material in various industries, its production and use are carried out on a large scale. Moreover, taking into account its structural properties and the nature of conductivity, its properties can be widely modified to obtain specific functional features. The introduction of modifications can be aimed, for example, at improving ionic or electronic conductivity in systems in which sodium sulfide is used as a conductor (for example, in solid electrolytes of batteries) [6, 7]. Moreover, it is assumed that the introduction of defects can shift the position of the Fermi level or modify the size of the energy gap in applications such as photovoltaics [8].

The introduction of modifications can also lead to the improvement of the chemical stability of sodium sulfide in various environmental conditions, which is important for applications in electrodes for electrochemical research. Additionally, structural modifications can affect the mechanical properties of the material, which can be desirable in the design of electromechanical components [9, 10]. Thus, the possibilities of modifying Na_2S are wide and cover many different fields of technology and science.

Very often, when discussing the introduction of defects into the material structure, an approach is used in which, through the construction of the socalled supercell, a slight modification of the chemical composition and structure is sought, introducing strongly "diluted" defects. This is to imitate small amounts of naturally occurring defects, formed in the production process. In this work, we propose a different approach, consisting in a strong modification of the composition and structure of the material, in order to observe the effect of such modifications on the resulting parameters of the obtained structure. Therefore, the subject of this work will be the introduction of defects in the form of a single and double vacancy into the structure of Na_2S with a deliberate significant modification of the original structure. To this end, we will investigate both structural and electronic properties and try to assess the possibility of introducing defects of this type into the material structure, thus creating a new material.

2. Computational details

Sodium sulfide crystallizes in a cubic structure, in a lattice whose prototype is CaF₂, with the space group Fm-3m (no. 225) [11]. The structure

Name	Vol. [Å ³]	$D ~[{ m g/cm^3}]$	a [Å]	b [Å]	c [Å]	E_{def} [eV]
Pristine	281.14	1.844	6.551	6.551	6.551	—
Vac0	281.88	1.703	6.557	6.556	6.556	4.15
Vac1	287.70	1.536	6.358	6.358	7.117	8.32
Vac2	279.18	1.583	6.475	6.657	6.475	8.30
Vac3	286.46	1.623	6.592	6.592	6.592	8.14
Vac4	291.16	1.415	6.673	6.605	6.605	15.96
Vac5	291.23	1.414	6.606	6.606	6.673	15.96

Structural parameters and defect formation energies of studied materials with vacancies.

TABLE I



Fig. 1. Schematic diagram of the pristine Na₂S unit cell. The blue spheres represent sodium ions, while the yellow spheres represent sulfur ions.

of this material is shown in Fig. 1. As can be seen, the spatial structure consists of two sublattices, i.e., the inner one formed by 8 Na ions distributed in the corners of the cube and the outer one — face-centered cubic (FCC) formed by S ions. The density functional theory (DFT) calculations were performed in the Quantum ESPRESSO software package [12] using the second-generation gradient approximation (GGA) and the Perdew-Burke–Ernzerhof (PBE) functional [13]. The configuration of pseudopotentials used for modeling is $2s^2 2p^6 3s^1$ for Na and [Ne] $3s^2 3p^4$ for S, including 9 and 6 electrons treated as valence, respectively. Projector-augmented-wave (PAW) type pseudopotentials were used for all elements. All calculations were preceded by convergence tests, during which a k-point grid was determined with inter-point distances of $\Delta k = 0.095$ Å for total energy calculations and 0.0475 Å for band structure and density of states (DOS) calculations. In the first step, the structure was relaxed, which included the possibility of changing the unit cell parameters. This step turned out to be crucial, because during the calculations, the structural parameters of the unit cell changed significantly. For this reason, each relaxation process was carried out in two stages, with additional final relaxation after the preliminary one.

After the initial relaxation of the pristine structure, defects in the form of single and double vacancies were introduced. Figure 2 shows the schematic realizations of the introduction of defects into the



Fig. 2. Schematic diagram of the internal Na cubic substructure with vacancies. The black spheres represent occupied Na sites, while the white spheres indicate vacancies (Na-vac).



Fig. 3. Schematic diagram of the external sulfur face-centered substructure with included vacancies. The black spheres represent occupied S sites, gray spheres represent S face sites (s-face), and white spheres indicate vacancies (S-vac).

inner sublattice formed by Na atoms, while Fig. 3 shows the studied configurations of vacancies introduced into the outer sublattice formed by sulfur.

3. Results and discussion

3.1. Structural properties

Table I presents the structural parameters obtained after the relaxation process for the initial structure (pristine) and all the cases considered for the introduction of defects (vac0–vac5). A thorough analysis of the data from this table reveals several facts. The introduction of vacancies into the structure, except for one case (vac2), causes an increase in the volume of the unit cell in relation to the pristine structure. At the same time, due to the removal of one atom, the density of the material decreases quite significantly for each of the cases considered. The effect of "swelling" of the structure



Fig. 4. Cohesive energy for all studied cases.

can be explained by the fact that after the removal of one or two atoms, the remaining atoms from the immediate vicinity of the defect are no longer so strongly attracted to the area where the lattice ion was previously located. Moreover, observing the changes in the lengths of the crystallographic lattice vectors (a, b, c) and angles for the cases vac1, vac2, vac4, and vac5, it can be concluded that a transition to other structures occurs (space groups: $P4_2/mcm$ — vac1, $P\bar{4}m2$ — vac2, and P4/mmmfor vac4 and vac5). Table I also summarizes the data on the defect formation energy, which was calculated using

$$E_{vac} = E_{def} - E_{\text{pristine}} - N\mu_{\text{atom}},\tag{1}$$

where E_{def} is the total energy of the system with vacancy, $E_{\rm pristine}$ — total energy of the ideal system (without defects), N — number of removed atoms, $\mu_{\rm atom}$ — chemical potential of the removed atom. In this case, the chemical potential $\mu_{\rm atom}$ was obtained by total energy calculations in which a single isolated sodium, potassium, or sulfur atom was placed in a unit cell with the same geometric parameters.

The resulting defect formation energies are positive in each of the cases considered (see Table I), which means that introducing defects is unfavorable from an energetic point of view. Of course, this is an expected effect, because disturbances of the ideal crystal structure usually mean an increase in the energy of this structure. The lowest defect-introducing energy was obtained for the structure in which a single Na ion was removed (vac0). Removing an additional atom from the lattice causes approximately doubling of this energy, which is visible for both sodium and sulfur vacancies.

When introducing such profound changes to the structure, the question of its structural stability arises. To assess it, the cohesive energy of the system was studied using

$$E_{coh} = \frac{\sum_{i=1}^{n} E_{\text{atom},i} - E_{tot}}{N_{\text{atom}}},\tag{2}$$

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,

TABLE II

The nature of the materials' conductivity with associated calculated corresponding energies. For metallic character, Fermi energy is presented, while for semiconducting character, the gap width is presented.

Name	HOMO [eV]	LUMO [eV]	E_{gap}/Fermi	Type		
	101	101	[01]			
Pristine	1.8270	4.2955	2.47	semicond.		
Vac0	_	_	1.1431	metal		
Vac1	0.5055	0.3221	—	pocket		
Vac2	_	_	0.5136	metal		
Vac3	3.3713	3.7372	0.37	semicond.		
Vac4	3.1195	2.6019	2.9385	pocket		
Vac5	_	—	2.9375	metal		

 $N_{\rm atom}$ — the number of atoms in the unit cell. The results are presented in Fig. 4. According to (2), a positive value of the cohesive energy means that the material is energetically stable. This applies to each of the structures discussed, although, as can be seen, the structures in which two vacancies were introduced simultaneously into S sites (vac4 and vac5) are less stable than the other structures with one vacancy or when these vacancies were sodium atoms.

3.2. Electronic properties

To verify the correctness of the calculations and for comparison purposes, the band structure and pDOS were determined for the unmodified pristine structure (Fig. 5). Na_2S in its pure form is a direct semiconductor material, with a calculated band gap of $E_{qap} = 2.47$ eV. The Fermi level in this material lies in between the valence band (VB) and conduction band (CB), and the slight shift of $E_{\rm F}$ closer to the conduction band suggests that the material shows a more electronic conductivity character, as thermally excited electrons become the dominant carriers (as long as we are describing an intrinsic semiconductor). As for the corresponding pDOS, in this case, the upper boundary of the valence band is dominated by S atoms, while the conduction band is dominated by sodium states. The mixing of states occurs mainly at low energies (below -3.2 eV), but the contribution from sulfur ions is still dominant here.

In order to determine the electronic properties and the nature of conductivity, figures showing band diagrams for structures in which vacancies were introduced instead of Na atoms (Fig. 6) and S atoms (Fig. 7), as well as graphs showing the density of states projected onto the atoms were prepared. In addition, the data collected from the analysis of these drawings are presented in Table II.



Fig. 5. Band structure and corresponding partial density of states (pDOS) along special k vector for pristine Na₂S structure.



Fig. 6. Band structure for vac0, vac1, and vac2 structures with Na vacancies.

For structures in which vacancies were introduced in places of sodium atoms (vac0-vac2), the band structure reveals that in each of these cases, there was a change in the conductivity character of the material from a semiconductor to a metal. In the system designated as vac1 (double vacancies), an interesting situation occurs at the same time, in which the Fermi level is slightly above the upper edge of the conduction band, but from the analysis of the data on the HOMO and LUMO levels in Table II it follows that the highest occupied molecular orbital (HOMO) lies higher in the energy scale than the lowest unoccupied molecular orbital (LUMO). This fact indicates the possibility of the so-called "Fermi pocket" effect, which may be investigated in detail in future work, but which dominates the conductivity character. A similar situation occurs for vac4 (double vacancies this time in places of S atoms).

Thus, the only material in which the conduction character remains unchanged with respect to the pristine structure is vac3, which has a single defect at the S atom site.

The projected density of states (PDOS) for the materials with vacancies in sodium (vac0, vac1, vac2) and sulfur (vac3, vac4, vac5) sites reveals distinct electronic characteristics that are influenced by the type and position of the vacancy.

For vac0 to vac2 (Fig. 8), where sodium vacancies are introduced, the PDOS shows that the upper boundary of the valence band is dominated by contributions from sulfur atoms. Below -1 eV, sodium contributions become visible, but they remain minor compared to sulfur. In the conduction band, above the Fermi energy level ($E_{\rm F}$), sodium plays the dominant role, with sulfur contributing only marginally. This indicates that the electronic states



Fig. 7. Band structure for vac3, vac4, and vac5 structures with S vacancies.



Fig. 8. Partial density of states projected on atoms for vac0, vac1, and vac2 structures with Na vacancies.



Fig. 9. Partial density of states projected on atoms for vac3, vac4, and vac5 structures with S vacancies.

near the bandgap are largely shaped by sulfur in the valence band and by sodium in the conduction band.

In contrast, for sulfur vacancies (vac3, vac4, vac5 — see Fig. 9), the electronic structure varies significantly. In the case of vac3, which retains a semiconducting nature, the Fermi energy falls in a region where states are predominantly contributed by sodium, although small contributions from sulfur are also visible. Below -2 eV, the states are dominated by sulfur, highlighting its significant role deeper in the valence band. For vac4 and vac5, the

Id		Pristine		Vac0		Vac1		Vac2		Vac3		Vac4		Vac5	
		Pop	Lap	Pop	Lap	Pop	Lap	Pop	Lap	Pop	Lap	Pop	Lap	Pop	Lap
1	Na	8.196	0.017	_	_	—	—	-	_	8.251	0.014	8.393	0.002	8.475	0.004
2	Na	8.196	0.017	8.218	0.032	8.215	0.026	8.205	0.028	9.256	0.005	8.752	0.009	8.770	0.008
3	\mathbf{S}	7.609	-0.034	7.411	-0.031	7.219	-0.029	7.214	-0.029	_	_	_	_	_	-
4	Na	8.196	0.017	8.199	0.020	_	—	8.205	0.024	8.251	0.014	8.741	0.008	8.374	0.002
5	Na	8.196	0.017	8.179	0.010	8.215	0.026	8.161	0.006	8.251	0.014	8.383	0.002	8.669	0.007
6	\mathbf{S}	7.609	-0.034	7.412	-0.031	7.222	-0.025	7.215	-0.029	7.663	-0.034	7.731	-0.020	_	_
7	Na	8.196	0.017	8.199	0.020	8.172	0.013	_	_	8.251	0.014	8.741	0.008	8.753	0.008
8	Na	8.196	0.017	8.179	0.010	8.172	0.014	8.205	0.028	8.251	0.014	8.383	0.002	8.372	0.002
9	\mathbf{S}	7.609	-0.034	7.412	-0.031	7.222	-0.025	7.214	-0.029	7.663	-0.034	7.731	-0.020	7.731	-0.021
10	Na	8.196	0.017	8.199	0.020	8.172	0.013	8.205	0.024	8.251	0.014	8.393	0.002	8.753	0.008
11	Na	8.196	0.017	8.179	0.010	8.172	0.014	8.161	0.006	8.251	0.014	8.751	0.008	8.372	0.002
12	\mathbf{S}	7.609	-0.034	7.412	-0.031	7.219	-0.029	7.215	-0.029	7.663	-0.034	-	-	7.731	-0.021

Bader analysis results (Pop) and corresponding Laplacian (Lap) for pristine Na₂S and vacancy variants for all studied cases. In each case, only a valence charge is presented. The symbol "-" indicates a vacancy.

materials exhibit metallic characteristics. For vac5, this metallic nature is particularly prominent, with the Fermi energy level lying well within a region of continuous states. For vac4, the $E_{\rm F}$ level is near the bandgap, creating a "Fermi pocket" where states are available near $E_{\rm F}$ but do not fully overlap as in a true metal. In the case of both vac4 and vac5, contributions to the density of states above $E_{\rm F}$ are dominated by sodium, with noticeable but smaller contributions from sulfur. The mixing of Na and S states is evident across the conduction band, emphasizing their interplay in shaping the metallic behavior. These observations underline the strong influence of vacancies on the electronic structure, with sulfur vacancies having a more pronounced impact, leading to transitions from semiconducting to metallic behavior depending on the vacancy configuration.

Table III presents the Bader charge analysis (Pop) and corresponding Laplacian (Lap) for pristine Na₂S and vacancy configurations (vac0 to vac5). In the pristine material, sodium atoms exhibit a consistent charge of $\approx 8.196e$, with a Laplacian of 0.017, while sulfur atoms show a charge of 7.609*e* and a Laplacian of -0.034. These values reflect the balanced charge distribution in the pristine lattice.

For vacancy cases, significant variations in both populations and Laplacian are observed. When sodium vacancies (vac0, vac1, vac2) are introduced, nearby sulfur atoms exhibit reduced charges and less negative Laplacians, suggesting a weakening of the electron localization around sulfur due to the loss of sodium charge. The remaining sodium atoms show slight increases in charge and more positive Laplacians, indicating enhanced electron localization near these atoms.

In sulfur vacancy cases (vac3, vac4, vac5), the charge redistribution is more pronounced. Sodium atoms near the vacancies exhibit substantially increased charges (up to 9.256*e* in vac3) and reduced Laplacians, reflecting enhanced electron localization to compensate for the missing sulfur. Conversely, the remaining sulfur atoms show slightly increased charges and less negative Laplacians, further emphasizing the disruption in charge balance caused by sulfur vacancies.

Overall, there is a clear correlation between population and Laplacians, namely, as the charge value increases, the corresponding Laplacian becomes less positive (for sodium) or less negative (for sulfur), indicating that higher occupancy correlates with greater electron localization. This trend is consistent across all vacancy cases, illustrating the impact of vacancies on the electronic environment of the materials structure.

4. Conclusions

In this paper, the vacancies introduced to Na_2S material were systematically investigated. The introduction of vacancies changed unit cell significantly. The general trend was that regardless of the number of vacancies introduced, the volume of the unit cell increased due to the loss of bonding to the nearest neighbors. In terms of the stability criterion, all materials are energetically stable, although this stability decreases not only with the introduction of a larger number of defects but also, to a greater extent, affects the situation in which they are introduced in place of sulfur atoms. In the structures where a single vacancy was introduced, the semiconducting character of the modified material was preserved. In situations where vacancies occurred in two atoms at the same time, the nature of conduction changed to metallic. The Bader charge analysis revealed that vacancies significantly redistribute charges, with nearby sodium atoms gaining charge and exhibiting increased electron localization, while sulfur atoms near sodium vacancies lose charge and the charge becomes less localized.

In S vacancy cases, Na near the vacancy experiences the largest charge gain, compensating for the missing sulfur, while the remaining one shows slight charge increases and reduced electron localization.

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