INTRODUCTION

Aluminum and sulfur are among abundant elements in earth and have broad applications in industry. For instance, they have been used extensively in batteries for high energy density and acceptable voltage in recent years. As aluminum and sulfur have oxidation states of -3 and -2, binary systems showing intriguing structure and properties under compression, which continues to surprise us. For example, hydrotrope with distinctive odor of rotten eggs is the only stable compound in H–S system at ambient conditions. Several novel compounds have been predicted under pressures, such as H₂S, H₃S⁺, H₅S₂, H₆S₃, and H₆S₄, and H₆S₅. A breakthrough finding in H–S system is the observation of a remarkably high superconducting Tc value of 203 K under pressure. Similarly, a great deal of novel compounds and chemical properties have been found in Li–S system under high pressure. In particular, a new compound Li₃S has been found to be an electrode with a high Tc value. Furthermore, when sulfur is mixed with the IIA group element Be in stoichiometry of 1:1, a modulated structure occurs, which is unusual for such simple binary compounds. The intriguing structures and properties of group IIA and IIA sulfides motivate us to further investigate binary mixture between S and group IIA element Al under pressures.

Herein, we systematically search the crystal structures of different stoichiometric Al–S systems. Several new compounds of Al₅, Al₂S, Al₃S₄, and AlS₂ are found to be stable under pressures, which show intriguing properties. In particular, we find several potential superconductors, such as Al₅S₄ and AlS, and a new electrode Al₁S₃, where the valence electrons of aluminum strongly localize in the interstices, acting as anions, at high pressure.

RESULTS

We perform an extensive search for crystal structures of AlₓS (x = 1/3, 2/5, 1/2, 2/3, 3/4, and 1–3) at 50, 100, 150, and 200 GPa with maximum simulation cells up to 4 formula units (f.u.) for each fixed composition by using an in-house-developed Crystal structure Analysis (CALYPSO) methodology. All the candidate structures are relaxed by Vienna ab initio Simulation Package (VASP) code, and the thermodynamic stabilities of Al–S system with variable stoichiometries are systematically investigated by means of calculating the formation enthalpies relative to Al and S at corresponding pressure. The enthalpy of formation per atom is calculated by using the following formula:

\[ \Delta H = [H(Al₁S₃) - xH(Al) - yH(S)]/(x + y) \]

Convex hull data at 0 K under different pressures is summarized in Fig. 1a. The compounds located on the convex hull are stable. Figure 1b shows the stable pressure ranges of different phases. At ambient conditions, only Al₃S₃ compound is stable. Our results (Fig. 1) show that it is still the most stable compound on the convex hull at 50 GPa. However, Al₅S₄ decomposes into Al₂S and Al₁S₃ under further compression, and becomes thermodynamically stable again at 140 GPa. Pressure has enormous influence on crystal structures and energies by altering interatomic distances and chemical bonding. Some unexpected stoichiometric compounds are found to be stable under pressure. Al₁S₃ and Al₂S are the most energetically stable compounds at 100 and 150 GPa, respectively. Al₁S₃ and Al₂S also locate on the convex hull, which implies that these compounds are also stable under pressure, but their formation enthalpies are slightly higher than others. The
other four predicted compounds (Al$_2$S$_5$, Al$_5$S$_2$, Al$_3$S, and AlS$_3$) are located above the convex hull, implying that they are unstable.

Al$_2$S$_3$

Figure 1 shows that Al$_2$S$_3$ compound exhibits various crystal structures under pressure. In order to identify the sequence of phase transformation for Al$_2$S$_3$, the structures synthesized in experiments must be taken into consideration. Several crystalline forms of Al$_2$S$_3$ are known, but not all of them have been strictly characterized, and three structures that have detailed lattice parameters, are considered here. The enthalpies per atom of all phases predicted and synthesized for Al$_2$S$_3$ are shown in Fig. S1. Al$_2$S$_3$ is in a hexagonal P6$_1$ atomic arrangement (α-phase) at atmospheric pressure, in which the Al atoms are 4 or 5 coordinated to S atoms (Fig. S2). Under further compression, this structure transforms to the P$_{4}$$\text{-}$$3m$ (δ-phase) at ~0.4 GPa and then to R-3c phases (γ-phase) at 6 GPa, where the coordination number of Al increases to six. Our predicted Pbcn, P6$_3$/mcm, P4/mmbm, and P-1 phases (Table S1) are stable in pressure ranges of 25–70, 70–95, 140–170, and above 170 GPa, respectively. The coordination number of Al in Pbcn and P6$_3$/mcm phases remains six, while it increases to eight in the P4/mmbm and P-1 phases. It should be pointed out that the increase in coordination number is a common phenomenon for materials at high pressures.

To understand the nature of the chemical bond of Al$_2$S$_3$, the electron localization function (ELF) and Crystal Orbital Hamilton Population (COHP), as well as the integrated COHP (ICOHP) up to Fermi level, are calculated (Table S2). Here, we take the P4/mmbm phase as an example (Fig. 2a). The calculation of ELF on the (2 3 1) plane...
plane at 150 GPa is shown in Fig. 2c. The ELF has strong directionality from S to Al, and the value of ICOHP of Al–S bond is −3.33 eV similar to that of S–S bond (−2.81 eV) in solid S (R-3m) at the same pressure. The results indicate the existence of covalent bonds between S and Al.

At 200 GPa, $\text{Al}_3\text{S}_4$ is stable in triclinic $P1$ structure, which is mainly composed of S-sharing eightfold $\text{AlS}_8$ hexahedrons, whereas several unique isolated sulfur atoms (isolated sulfur atom in blue named $S^1$, the others named $S^2$) exist, appearing in pairs, between these hexahedrons (see Fig. 2b). The ELF is calculated (Fig. 2d) at 200 GPa, which reveals that electrons are mainly localized between Al and $S^2$. The calculated ICOHP value (−2.42 eV) of $\text{Al}–\text{S}^2$ at 200 GPa is similar to that of $\text{S}–\text{S}$ bonds in solid S (−2.90 eV) at the same pressure, suggesting that Al and $S^2$ form covalent bonds. The distance between isolated $S^1$ and Al is 2.51 Å, which is much longer than the bond length of Al–S at ambient conditions. In addition, the values of ICOHP for $\text{Al}–\text{S}^1$ pairs (−1.07 eV) and $S^1–S^2$ pairs (−1.51 eV), have been shown, indicating a weak interaction in $\text{Al}–\text{S}^1$ and $S^1–S^2$ pairs.

$\text{Al}_3\text{S}_4$

$\text{Al}_3\text{S}_4$ is stable in a crystal structure with $R$-3c symmetry above 60 GPa. It is significantly different from other compounds that aluminum in $\text{AlS}_7$ coordination is found for the first time in $\text{Al}–\text{S}$ system. Under further compression, this compound transforms into a cubic $I-43d$ phase, having similar structural features to lanthanum chalcogenides with the same stoichiometry. At 100 GPa, the cubic $I-43d$ $\text{Al}_3\text{S}_4$ becomes the most energetically stable in all $\text{Al}–\text{S}$ compounds. The calculated ELF (Fig. 3a) and the average value of ICOHP (−2.85 eV) for $\text{Al}–\text{S}$ pairs in $I-43d$ structure at 100 GPa, which is comparable to that for $\text{S}–\text{S}$ pairs (−2.59 eV) in solid S at the same pressure, reveal the presence of covalent bonds between Al and S. The cubic $I-43d$ phase is overtaken by $R$-3 phase of $\text{Al}_3\text{S}_4$ above 160 GPa. The trigonal $R$-3 phase has some similar characteristics to triclinic $\text{Al}_3\text{S}_4$. An isolated sulfur atom $S^1$ (Fig. 3b) locates in the center of the lattice, while others ($S^2$) surround aluminum forming $\text{AlS}_8$ hexahedrons linked by means of sharing edges with adjacent $\text{AlS}_8$ hexahedrons.

All the three phases are metallic having a sizable DOS at Fermi level under the entire stable pressure range. Therefore, we estimated superconducting transition temperature ($T_c$) of $R$-3c, $I-43d$, and $R$-3 phases through electron–phonon coupling (EPC) calculations at 60, 100, and 200 GPa, respectively. Here, we take the $I-43d$ phase as an example. Figure 3d shows the EPC spectral function $\alpha^2 F(\omega)$, the integral $\lambda$, and the projected phonon density of states (PDOS) for cubic phase $\text{Al}_3\text{S}_4$. It illustrates that Al and S elements have the comparable contributions to the superconductivity. The resultant $T_c$ value is 17.7–20.9 K ($\mu^* = 0.10–0.13$) at 100 GPa. The calculated $T_c$ values for $R$-3c and $R$-3 are 0 and 9.97 K at 60 and 200 GPa, respectively.

$\text{AlS}$

Two crystal structures of $\text{AlS}$ with $C2/m$ (Fig. 4a) and $Pm-3m$ (Fig. 4b) symmetries are discovered in our calculations. As shown in Fig. 1b, $C2/m$ structure is stable above 90 GPa and transforms into cubic $Pm-3m$ structure when the pressure reaches 150 GPa.
Both phases of AlS show metallic features (Fig. 4c). Here, we perform EPC calculations for the Pm-3m structure at 200 GPa. Figure 4d reveals that Al and S elements have comparable contributions to the superconductivity, which mainly originates from the polar covalent bonds. At $\mu^* = 0.10$, the resultant $T_c$ value is 7.6 K, being much lower than that of Al$_3$S$_4$ at 100 GPa.

Al$_2$S

For Al-rich stoichiometries, we find that Al$_2$S with I4/mmm symmetry is stable in the pressure range of 70–200 GPa. The crystal structure of Al$_2$S composed of interlaced [Al$_2$S] layers is shown in Fig. 5a. This tetragonal crystal structure has similar layered characteristics to Ca$_2$N electride.\(^{30-32}\) ELF plot of Al$_2$S with an isosurface value of 0.69 at 100 GPa (Fig. 5b) indicates the existence of localized electrons in the interstices instead of locating at the center of the Al–Al bonds, suggesting the formation of an electride. We calculated the Bader charges\(^{33}\) for the Al$_2$S (Table S3). Besides six electron density maximum points located at the centers of Al and S atoms, we found that the extra four electron density maximum points are located at the positions of interstitial electrons, which can be seen as interstitial quasi-atoms (ISQs).\(^{34}\) So, the Al$_2$S can be regarded as an electride.

Electride is a class of extraordinary compounds with valence electrons occupying interstices instead of being attached to atoms. These interstitial electrons can occupy shallow bands, leading to a dramatically reduced work function and large conductive properties. In known inorganic electrides, it seems that alkali and alkaline earth metals, as well as their compounds, can easily form electrides, while aluminum compounds do not. Pickard and Needs found distinct “blobs” of interstitial electron density in aluminum crystal at 5 terapascals (TPa),\(^{40}\) while alkali and alkaline earth metals can form electrides at a few hundred gigapascals (GPa).\(^{41,42}\) So far, only a few aluminum-based electrides are found, including [Ca$_{24}$Al$_{12}$O$_{64}$]$^{4+}$ (e$^{-}$)$_4$, Ba$_2$Al$_6$, Ba$_3$Al$_{10}$, and Sr$_2$(AlSi)$_6$.\(^{43,44}\) However, the interstitial electrons of these electrides do not come from aluminum. Therefore, it is especially interesting that the Al$_2$S is found to be an electride, where interstitial electrons originate from aluminum, at a moderate pressure.

Figure 5c shows that Al$_2$S is metallic, and many bands with large dispersion traverse the Fermi level. The partial charge density (isosurface value of 0.0507 e/Å$^3$) within an energy window between $-1$ and 1 eV around Fermi level is shown in Fig. 5d. It is seen that the electrons are mainly located in the interlayers. Moreover, the value of linear-averaged electron density along the z direction has a maximum at the middle of the interstitial electronic plane, which suggests that the contributor to the bands within $-1$–1 eV around Fermi level basically derives from the interstitial electrons.

**DISCUSSION**

The variable stoichiometries in Al–S system have been systematically explored. Besides the well-known compound Al$_2$S$_3$, we identify four new stable compounds (Al$_3$S$_4$, AlS$_2$, Al$_2$S, and AlS) in the pressure range of 50–200 GPa. A number of aluminum sulfides become metals and are potential superconductors. A unique stoichiometry Al$_3$S$_4$ becomes stable at 60 GPa. This stoichiometry is known for the first time in aluminum chalcogenide, and it transforms into cubic I-43d geometry at 90 GPa, having a resembling structure and electronic characters with La$_3$S$_4$. This cubic structure is metallic with an estimated value of $T_c$ around 20.7 K at 100 GPa. Al$_2$S is stable above 70 GPa, which is found to be an electride. It is especially interesting to find that the valence electrons of aluminum become localized in the crystal acting as...
anions under pressure. AlS₂ is stable in the pressure range from 50 to 200 GPa. Above 150 GPa, AlS₂ is found to be the most energetically stable compound with Pm-3m symmetry, and the estimated Tc value is 7.6 K at 200 GPa. This work provides guidelines for further experimental exploration of Al–S system under high pressure.

**METHODS**

The structure prediction for Al–S system is performed via a global minimum search of free energy surface by the swarm intelligence-based CALYPSO method and its same name code, 13,24. This methodology is highly efficient to predict the stable structures, and benchmarked on various known systems. 16,45,46 The ab initio relaxations and electronic property calculations were performed based on density function theory 17,47,48 within the Perdew–Burke–Ernzerhof (PBE) of generalized gradient approximation (GGA), 39 as implemented in the Vienna ab initio Simulation Package (VASP) code. 25 The all-electron projector-augmented wave (PAW) 50 method has been adopted, with 3s²3p² and 3s²3p⁶ treated as the valence electrons of Al and S atoms, respectively. A kinetic energy cutoff of 600 eV was used, and a dense k-point sampling of the Brillouin zone with a resolution of 2π × 0.002 Å⁻¹ was adopted to ensure the enthalpy calculations converged within 1 meV/atom.

The phonon calculations were performed by using the finite displacement method as implemented in PHONOPY 51 code to verify the dynamical stability of structures. To analyze the interatomic interaction and chemical bonding, the crystal orbital Hamilton populations (COHP) 52,53 and the electron localization function (ELF) 54 were calculated using the LOBSTERR 55 and VASP codes, respectively. The calculations of superconducting transition temperatures of the most stable structures were performed using the EPC module of the Quantum ESPRESSO code. 53 The kinetic energy cutoffs of plane-wave basis for Al₃S₄ and Al₂S₃ were set to 85 Ry and 80 Ry, respectively, to ensure that the calculated energy converged within 1 meV/atom. The electron–phonon coupling (EPC) was calculated with a 7 × 7 × 7 q mesh for Al₃S₄ and 8 × 8 × 8 q mesh for Al₂S₃ to ensure that the calculations are well converged.

**DATA AVAILABILITY**

All data generated or analyzed during this study are included in this published article (and its supplementary information files).

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AUTHOR CONTRIBUTIONS

Y.M., Y.W. and J.L. conceived the research; S.S. performed the simulations and analyzed the data with the help of W.Z.; S.S. wrote the paper; Y.C., Y.W., J.L. and Y.M. helped to revise the paper. All authors discussed and commented on the paper.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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