

Supporting Information for

New Diluted Magnetic Semiconductor Based on the Expanded Phase of ZnS: Surmounting the Random Distribution of Magnetic Impurities

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I. Structure and equation of state of the sodalite phase of ZnS

Based on our previous report of the polymorphs built from $Zn_{12}O_{12}$,¹ we believe that the sodalite phase of ZnS (SOD-ZnS) can also be constructed from the stable cage cluster $Zn_{12}S_{12}$ (a truncated octahedron structure, see Fig.S1-a) which has been experimentally and theoretically characterized.^{2, 3} If every $Zn_{12}S_{12}$ is linked by twelve neighbouring $Zn_{12}S_{12}$ cages with edge-to-edge (square link, S, see Fig.S1-b) intercluster interactions *i.e.* $12 \times S$ links (Fig.S1-c), we can obtain the SOD-ZnS phase (Fig.S1-d) through periodic translation in keeping such way. After the full GGA-PBE optimizations without any symmetry constraint, all the building blocks can be well preserved in the assembled phase, which makes the framework of SOD-ZnS hold the symmetry of $Pm-3n$ (223). Several essential parameters of this phase are summarized in Table S1. The corresponding results of the traditional ZnS phases are also presented for comparing. Notably, the agreements between our results and the earlier data suggest that the computational scheme we chose is reasonable for describing the structures and properties of the cluster-assembled phase SOD-ZnS.

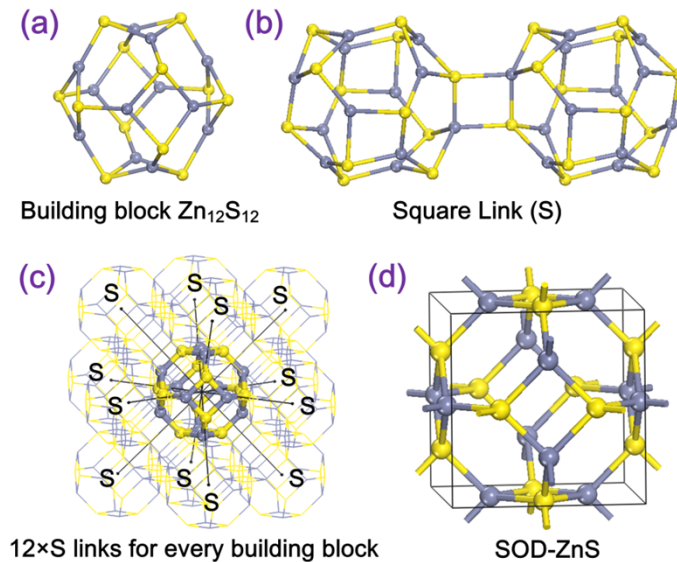


Fig. S1 The structure of the individual building block $Zn_{12}S_{12}$ (a), cluster-cluster interaction by using the square link, Zn-S edge facing Zn-S edge (b), coordination of every $Zn_{12}S_{12}$ cage in the SOD-ZnS phase (c), the primitive cell of SOD-ZnS (d).

Table S1. Unit cell parameters (a and c, in Å), mass density (ρ , in g cm⁻³), energies with respect to the ground state ZB (ΔE_0 , in eV/ZnS), volume per ZnS unit (V_0 , Å³), bulk modulus (B_0 , GPa) and Derivative B' for the considered ZnS phase of SOD, RS, WZ, and ZB. Experimental data are given in bold type.

Phase	a	c	ρ	ΔE_0	V_0	B_0	B'
SOD	6.71		3.21	0.209	50.37	54.1	4.39
				0.22 ^a	50.28 ^a	54.6 ^a	4.39 ^a
RS	5.094		4.85	0.629	33.34	85.5	4.50
	5.06^b, 5.13^c			0.63 ^a	33.33 ^a	86.1 ^a , 85^c	4.55 ^a , 4^b
WZ	3.884	6.345	3.99	0.006	40.55	68.5	4.43
				0 ^a	40.46 ^a	69.4 ^a	4.40 ^a
ZB	5.442		4.00	0	40.51	68.8	4.42
	5.410^d			0 ^a	40.40 ^a	69.7 ^a , 76.9^d	4.48 ^a , 4^b, 4.9^d

^aRef[4], ^bRef[5], ^cRef[6], ^dRef[7]

In order to compare the stability of SOD-ZnS phase with that of the traditional ZnS phases, we calculated total energy *versus* volume for all the considered phases. The results are presented in Fig.S2-a, in which the solid curves derive from third-order Birch-Murnaghan EOS fitting⁸:

$$E_t(V) = E_0 + \frac{9}{16}B_0V_0 \left[(B' - 4) \left(\frac{V_0}{V} \right)^{\frac{2}{3}} - B' + 6 \right] \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2$$

On the basis of these fitted curves, the equilibrium values of the total energy (E_0), volume (V_0), bulk modulus (B_0) and derivative B' are obtained (see Table S1). As is shown in the figure and table, one can note that ZB-ZnS occupies the lowest equilibrium energy, indicating that it is the most energetically stable phase amongst all the considered phases. This is in accordance with the experimental fact that ZB is the ground state of ZnS. RS-ZnS is the metastable phase with larger equilibrium energy of 0.629 eV/ZnS than ZB, matching with the previous theoretical results (0.63 eV). Compared with this experimentally obtainable high pressure phase RS-ZnS, SOD-ZnS (just with larger equilibrium energy of 0.209 eV/ZnS than ZB) seems to have no energetic limitations in

experimental synthesis. From this point of view, it is reasonable to believe that this cluster-assembled phase would be an attractive synthesis target. Moreover, such belief is also based on the fact that its distinguished nanoporous structure can provide opportunities for doping in endohedral sites by atom or cluster.

To further understand the phase stability under different pressures, we derived the corresponding expression of enthalpy from the fitted EOS plots in Fig.S2-a, which can be used to confirm the range of pressures where the SOD-ZnS phase may possibly be stabilized. Since the DFT calculations are performed at zero temperature, the Gibbs free energies, $G = E_{total} + PV - TS$, should be equal to the enthalpy, $H = E_{total} + PV$. Consequently, the most stable phase at a given pressure has the lowest enthalpy value, and phase transition from one to another is given by a pressure at which the enthalpies for the two phases are equal. As is shown in Fig.2S-b, the lowest enthalpy passes through transitions of SOD→ZB→RS with the increase of pressure. In the range of high pressure, the transition of ZB→RS has been observed in experiment at the pressure of 14.7-18.1 GPa⁹. Our calculated result of 18.43 GPa is a little higher than these experimental values due to the overvaluation of GGA,¹⁰ while it falls within the previous theoretical value of 14.35-19.5 GPa (Ref[11] and references therein).¹¹ As for the region of negative pressure $P < -2.99$ GPa, the SOD phase is more stable than both ZB and RS, implying that if one except to stabilize the lower density SOD phase from the ground state ZB-ZnS, triaxial tensile stresses (negative pressure) should be applied to it.

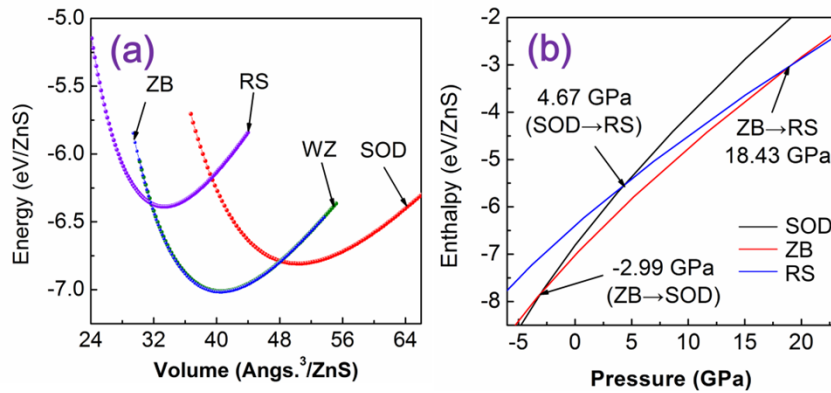


Fig.S2 (a) Total energy (eV/ZnS) versus volume ($\text{\AA}^3/\text{ZnS}$) for the considered phases of ZnO, (b)

Enthalpy versus pressure curves $H(P)$ for ZB, RS and SOD phases of ZnS

From experimental point of view, it is important to scrutinize whether the synthesis of the SOD-ZnS material in thin-film form is possible. In order to explore this aspect, we also carried out a calculation for the enthalpy of SOD-ZnS under bi-axial tensile stresses, namely, in-plane tensile strain in a thin-film form. As shown in Fig. S3, the difference of the enthalpy of the SOD phase between the case for tri-axial and bi-axial tensile stresses is negligibly small compared with that between the SOD and the ZB phases. This means that the SOD phase can also be stabilized with respect to the ZB phase under bi-axial tensile stresses.

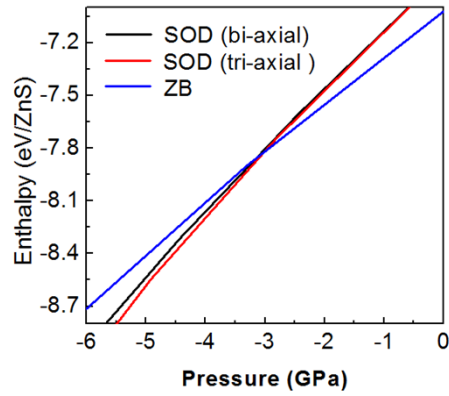


Fig. S3 Enthalpy versus pressure curves for ZB-ZnS and SOD-ZnS phases under tri-axial tensile stresses and bi-axial tensile stresses.

II. Dynamic and thermal stability of the SOD-ZnS phase

To examine whether the SOD-ZnS phase is dynamically stable, we carried out the calculation of its phonon dispersion curves by using the supercell method as implemented in the PHONOPY code¹². In Fig. S4, the phonon dispersion curves and density of phonon state of SOD-ZnS phase are displayed. Clearly, there are no imaginary phonon modes in the whole Brillouin zone. Thus the SOD phase is dynamically stable.

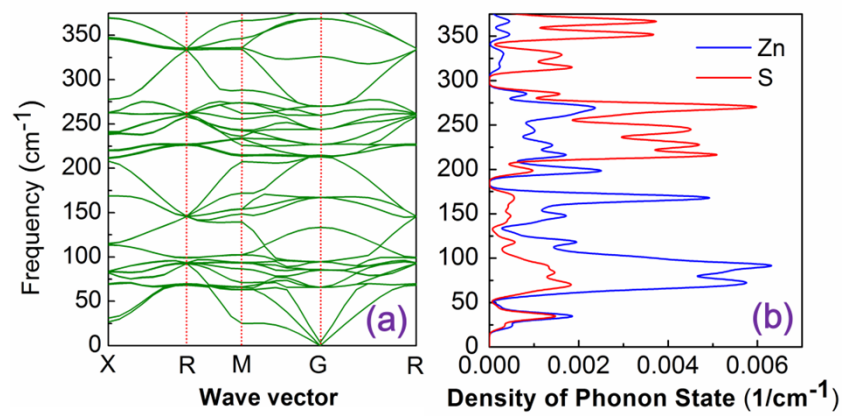


Fig. S4 (a) phonon dispersion curves and (b) partial phonon total density of states of SOD-ZnS phase

The first-principles molecular dynamic simulations for a large supercell ($2 \times 2 \times 3$) containing 144 atoms with a Nosé-Hoover thermostat at 500 K were performed to test the thermodynamic stability of SOD-ZnS phase. Figs.S5-a and b present the fluctuations in temperature and potential energy, respectively, as a function of the simulation time at 500 K. After 10ps, we found no structure destruction of the SOD-ZnS phase (see the snapshot of the simulated structure in Fig.S5-c), except for some thermal fluctuations, which suggests that the SOD-ZnS phase is thermally stable up to at least 500 K.

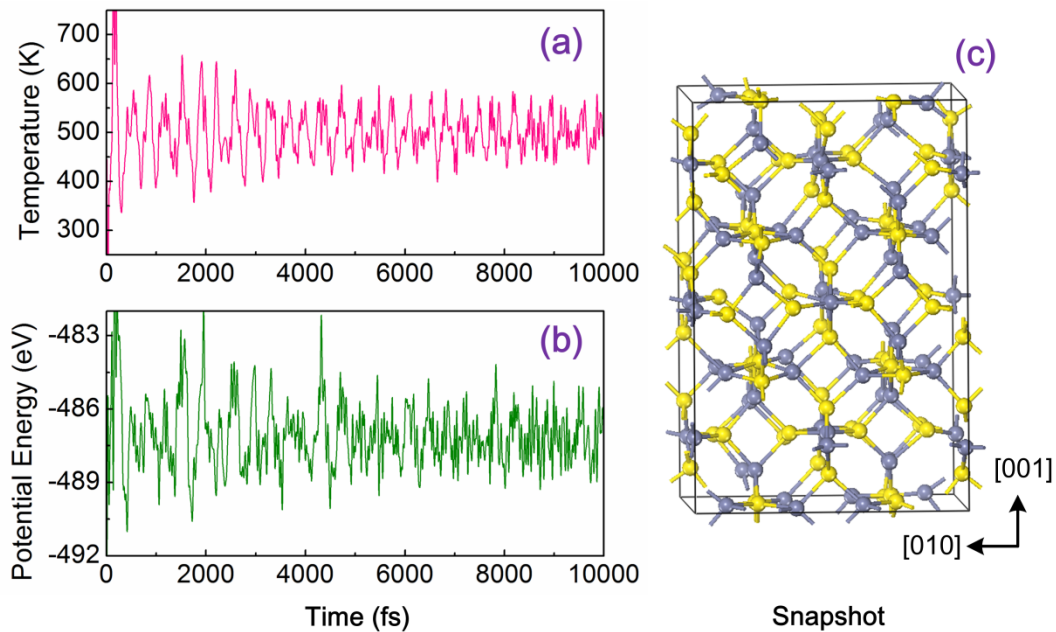


Fig. S5 The fluctuations of temperature (a) and potential energy PE (b) as a function of the molecular dynamic simulation step at 500 K. A snapshot of the simulated system is also shown (c).

III. Energy barrier surmounting the clustering between Mn atoms

To examine the hypothesis that the cage-like building blocks of SOD-ZnS can provide potential wells to trap the foreign atoms surmounting their clustering for strong $d-d$ interaction, we calculated the relative energy with respect to the equilibrium state for the central Mn atom diffusing along two different crystal orientations, *i.e.*, [001] and [111]. As is shown in Fig.S6, the encapsulated Mn atom should cross an energy barrier of 25.95 eV to cluster with Mn atom in the neighboring $Zn_{12}S_{12}$ clusters in the crystal orientation [001], and an energy barrier of 3.85 eV in the [111] direction. Since the [111] direction holds the smallest energy barrier, it is reasonable to believe that the 3.85 eV is large enough to surmount the clustering between the doped Mn atoms (the binding energy of Mn_2 molecular is just 0.44 ± 0.30 eV^{13,14}).

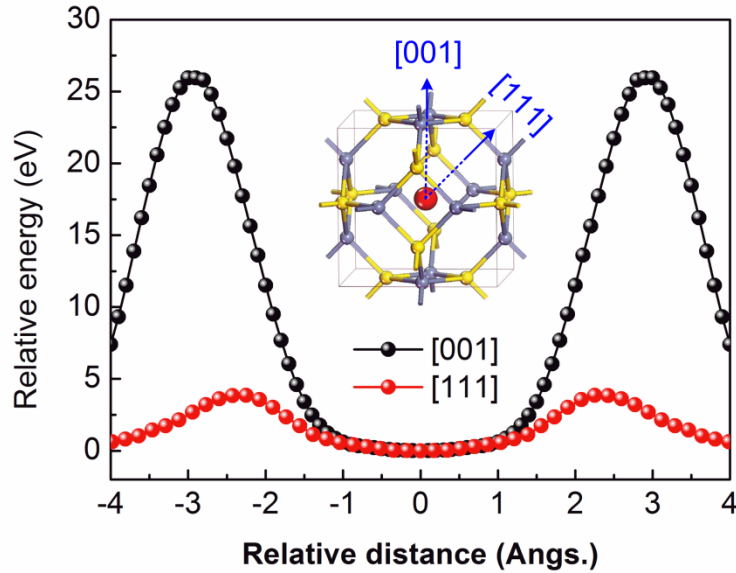


Fig.S6 The relative energy with respect to the equilibrium state for the central Mn atom diffusing along different crystal orientations.

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