Pressure-induced elemental dissociation in zinc chalcogenides

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Abstract. We have extensively explored the high-pressure structures of zinc chalcogenides (ZnX, X = S, Se and Te) by using first-principles calculations. The previously assumed high-pressure CsCl phase was ruled out and an intriguing dissociation into Zn + X at strong compressions was predicted. We find that before the dissociation, a tetragonal P4/nmm phase (4 f.u. cell⁻¹) forms in ZnS and ZnSe driven by the soft phonon mode of the lower-pressure Cmcm phase. A metastable phase with CsCl-like arrangement was proposed for ZnTe as its post-Cmcm structure and was found to match the experimental data concerning both x-ray diffraction patterns and transition pressure. The pressure-induced dissociation for ZnX discovered here has important implications for the behavior of other compounds at high pressure and also for the physics in the Earth’s interior.

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1. Introduction

Materials under high pressure exhibit rich transition behavior, which gives us broadened views into the essence of atomic binding in solids [1–4] while greatly challenging our instinctive understanding [5]. High pressure is hence a powerful tool probing into the fundamental physics and synthesis of novel materials [6]. The high-pressure structural transition of $A^N B^{8-N}$ octet semiconductors has been a widely focused topic in the high-pressure research community [3]. Based on the notion of competition among the covalent, ionic and metallic bonding mechanisms, the transition sequence of zinc-blende (ZB) or wurtzite (WZ) → NaCl → Cmcm can be generally expected in such compounds. The ZB (or WZ) and NaCl phases have been known to sit at two extremes, i.e. strong covalence and strong ionicity. Structural characterization of the base-centered-orthorhombic Cmcm phase was an important contribution from sophisticated x-ray diffraction measurements and data analysis upon correction of the previously assigned $\beta$-Sn phase [7]. The formation of the metallic Cmcm phase can actually be attributed to a distortion of the NaCl phase that involves shuffle movement of adjacent (001) planes along the [010] direction driven by the soft transverse acoustic (TA) phonon mode at the $X$ point [8, 9].

Zinc chalcogenides (denoted as Zn$X$, $X =$ S, Se and Te), as representative in the $A^N B^{8-N}$ compounds family, are wide-gap semiconductors at ambient conditions and have many important technological applications [10, 11]. Obeying the general transition sequence, occurrence of the Cmcm phase has been well confirmed in Zn$X$; however, like in other compounds, little is known about phase transitions at higher pressures [3]. Sign of further transformation was indeed experimentally detected in ZnTe at $\sim 85$ GPa, but the new phase remains unresolved [12]. There exists an empirical guess on the CsCl phase as the candidate structure at very high pressures on account of its low Madelung energy, which becomes dominant in determining structures at small volumes [13]. However, the question is still open until convincing proof is provided. In this work, we have extensively carried out theoretical exploration on the high-pressure structures of Zn$X$ beyond the Cmcm phase in the hope of clarifying and extending their structural modifications at large compressions. Our results have denied the previous proposition on the CsCl phase and surprisingly uncovered a dissociation tendency toward elemental solids Zn + $X$ at high pressures. This dissociation behavior contributes an interesting complement to our knowledge of high pressure, which plays an active role in binding different constituents into a compound [6, 14].

2. Method

Ab initio evolutionary simulation was performed to search for the structure possessing the lowest free energy [15, 16]. This methodology is featured by its capability of predicting the stable structure at given pressure and temperature conditions by knowing just the chemical compositions [5, 17, 18]. The structural optimizations were carried out using density functional theory (DFT) [19, 20] within the Perdew–Burke–Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) [21, 22], as implemented in the VASP code [23]. The electron and core interactions are included by using the frozen-core all-electron projector-augmented wave (PAW) method [24], with Zn 3d$^{10}$4s$^2$, S 3s$^2$3p$^4$, Se 4s$^2$4p$^4$, and Te 5s$^2$5p$^4$ treated as the valence electrons. The convergence test used a kinetic energy cutoff of 400 eV for the calculation of these three compounds. Dense Monkhorst–Pack $k$-point meshes [25] with
3. Results and discussions

We carried out evolutionary simulations for ZnS at 140 and 180 GPa using two, four and six formula units per cell. We predicted a tetragonal $P4/\text{mmm}$ phase ($4 \text{ f.u. cell}^{-1}$, denoted as ZnS-IV) to be most stable. This structure becomes energetically more favorable than the Cmcm phase above 120 GPa, as deduced from the calculated enthalpy curves (figure 1(a)). Existence of this phase was also revealed in ZnSe (denoted as ZnSe-IV) by evolutionary simulations at 150 GPa using two, four and six formula units per cell. Figure 1(b) gives the thermodynamically stable region of this phase in ZnSe and suggests a stability region of above 110 GPa. We have included the earlier proposed CsCl phase and the PbO phase, being a distorted form of the CsCl phase predicted in ZnO by the lattice-dynamics study [8], in the enthalpy calculation (figures 1(a) and 1(b)). Yet their apparent high energy compared to that of the predicted tetragonal phase enables us to fairly exclude their occurrences in ZnS and ZnSe.

The predicted ZnS-IV phase in fact has a close connection with the low-pressure Cmcm phase, as demonstrated by our subsequent lattice-dynamics study. In figure 1(c), we plot the

![Figure 1. Enthalpy curves of CsCl (open circle), PbO (open square), ZnS-IV (solid square), ZnTe-IV (open down triangle), sandwich-like (solid up triangle) structures and decomposition into Zn + X (solid circle, dash line) relative to the Cmcm phase for ZnS (a) and ZnSe (b). Phonon dispersion curves for Cmcm (c) and ZnS-IV (d) phases of ZnS at 150 GPa calculated by using $4 \times 4 \times 4 \kappa$-meshes within a $2 \times 2 \times 2$ supercell.](http://www.njp.org/)

resolutions better than 0.1 Å$^{-1}$ were used to ensure the overall energy convergence within $\sim 1 \text{ meV atom}^{-1}$ in calculations of enthalpy difference. Phonon calculations were performed using the supercell method, where the dynamical matrix is generated by the Hellmann–Feynman forces calculated in the supercell with proper atomic displacements [26].
Figure 2. (a) Conventional cell of the Cmcm phase with the eigenvector of the TA($Y$) mode indicated by arrows. The vibration amplitudes for Zn and S atoms are slightly different, but we neglect the difference to have a clear view of the shuffle movement of the (001) planes. The origin of the cell has been shifted to have a direct comparison with the ZnS-IV structure (b). In (a) and (b), small and large balls are S and Zn atoms, respectively. (c) CsCl-like ZnTe-IV phase (group symmetry: $P4/nmm$) in ZnTe at 100 GPa. Its lattice parameters are $a = b = 3.0765$ Å, $c = 5.6503$ Å with atomic positions of Zn: $2c$ (0.5, 0, 0.6023) and Te: $2c$ (0.5, 0, 0.16334). The origin of the cell has also been shifted for a convenient comparison with the CsCl structure. (d) CsCl-like structure predicted with 3 f.u. cell$^{-1}$ at 100 GPa for ZnTe. It has a space group of $P4/mmm$ with lattice parameters $a = b = 2.9494$ Å, $c = 9.2204$ Å and atomic positions of Zn: $1c$ (0.5, 0.5, 0.0) and $2g$ (0, 0, 0.876 38); Te: $1b$ (0, 0, 0.5) and $2h$ (0.5, 0.5, 0.286 47). In (c) and (d), small and large balls are Te and Zn atoms, respectively.

phonon bands of the Cmcm phase at 150 GPa for ZnS, and it is found that the TA phonon modes become notably softened at the $Y$ point of the Brillouin zone boundary. It is known that a soft mode is intimately associated with symmetry-broken transformation of the structure and, as a consequence, a lower-symmetry child structure having a group–subgroup relation with the parent structure will be energetically favored [8, 27]. A reasonable way to unveil the transformed phase is by a twofold procedure, i.e. freezing atoms along the eigenvector of the soft mode and then performing structural relaxations to release its internal stress. This technique has been successfully applied to predictions of the high-pressure structures of MgTe, ZnO and MgH$_2$ [8, 27, 28]. In figure 2(a), we depict atomic vibrations along the eigenvector of the TA($Y$) mode, which are incorporated into a conventional cell of the Cmcm phase, noting that $Y$ corresponds
to $\tilde{q} = (2\pi/a, 0, 0)$. The softening of this mode causes shuffle movement of alternate (100) planes along the [010] direction and thus results in the formation of a simple-orthorhombic Pmmn phase [$Z = 4$; atomic positions: Zn at 2a (0, 0, z1) and 2b (0, 0.5, z2) and S at 2a (0, 0, z3) and 2b (0, 0.5, z4)]. Structural optimization of the resulting Pmmn phase ends in the high-symmetry ZnS-IV phase (figure 2(b)), which corroborates the prediction by evolutionary simulations. Accordingly, the Cmcm $\rightarrow$ ZnS-IV transition can be naturally explained as a result of soft-mode distortion and internal-stress release. We note that the ZnS-IV phase itself does not have a group–subgroup relation with Cmcm but is closely related to Cmcm structure via their common subgroup Pmmn. Both ZnS-IV and Cmcm phases can be represented by Pmmn symmetry under which, at 150 GPa, the Cmcm phase has lattice parameters $a = 4.2569$ Å, $b = 4.0774$ Å, $c = 4.4356$ Å with $z1 = 0.59336$, $z2 = 0.90664$, $z3 = 0.07711$ and $z4 = 0.42289$, while ZnS-IV adopts $a = b = 4.1479$ Å, $c = 4.4429$ Å with $z1 = 0.5$, $z2 = 0.85483$, $z3 = 0$ and $z4 = 0.37338$. Besides, extra constraints of $z1 + z2 = 1.5$; $z3 + z4 = 0.5$ for Cmcm and $a = b$; $z1 = 0.5$; $z3 = 0$ for ZnS-IV must necessarily be incorporated in such Pmmn representation. One unique feature of the ZnS-IV structure is its special occupation of the 2a positions, which can be illustrated by alternate Zn and S atomic planes perpendicular to the c-axis (figure 2(b)). Our phonon calculation (figure 1(d)) has confirmed that the ZnS-IV phase is dynamically stable with the absence of imaginary phonon frequency. It should be pointed out that interpretation of the mechanism of the Cmcm $\rightarrow$ ZnS-IV transition also applies to ZnSe in view of the identical TA(Y) phonon softening behavior.

Under the constraint of four formula units per cell, we performed evolutionary simulations for ZnS (ZnSe) at much higher pressure, 250 GPa (200 GPa). Surprisingly, we obtained a sandwich-like structure made up of alternate Zn and S (Se) atomic blocks. The peculiar sandwich arrangement suggests an interesting tendency toward decomposition into Zn + S (Se) at these strong compressions. To confirm this speculation, we carefully calculated the decomposition enthalpy by adopting hcp structure for Zn and $\beta$-Po structure for S [29, 30]. It is found that the decomposition indeed becomes favorable to any other proposed phase above 157 GPa in ZnS (figure 1(a)). Similar decomposition into Zn + Se was also found for ZnSe at above 113 GPa (figure 1(b)). With the decomposition knowledge in mind, we have extended the same study to ZnTe and discovered an amazingly low decomposition pressure (38 GPa) (figure 3(a)).

We note that the pressure-induced dissociation in ZnX is strongly supported by energy calculation (figures 1 and 3), yet is quite unexpected. The physical mechanism for this dissociation remains quite challenging. We here, however, provide one possible argument. At lower pressures, ZnX adopts covalent or ionic bonding, where the Zn and chalcogen atoms are alternately separated. When subjected to high pressures, inter-atomic distances shorten and electron bands are largely widened, thus resulting in a metallization (e.g. Cmcm phase) where the valence electrons are highly delocalized. This then hinders the formation of localized electron pairs for covalence or charge transfer for ionicity. As a result, the direct Zn–X bonding is significantly frustrated and dissociation into elemental substances is promoted. It is interesting to compare the studied heavy ZnX compounds with the light material, ZnO, which remains insulating up to very high pressure. We do not find any dissociation sign in ZnO up to at least 800 GPa with respect to the high-pressure CsCl structure. This sheds strong light on the correlation of metallization with dissociation in ZnX compounds. By all appearances, much theoretical effort is needed to quantitatively understand this intriguing phenomenon.

One question is naturally raised associated with the too low dissociation pressure (38 GPa) in ZnTe, which contradicts the experimentally reported stability of Cmcm up to $\sim$85 GPa [12].
Two points need to be addressed. Firstly, we did not include the temperature effect in the calculation, but experience tells us that room temperature is not too high to significantly revise the dissociation pressure. Secondly, we suspect that there exists a large kinetic energy barrier for dissociation, and extra pressure is needed to overcome this barrier. This resembles the high-pressure synthesis of transition metal nitrides from the elemental constituents [31]–[34], where much higher pressures are necessary to promote the reaction. We also note that application of high temperature could be helpful in lowering the energy barrier for the realization of dissociation. The lesson learnt from the knowledge on ZnTe suggests that the experimental observation of the dissociation in ZnS and ZnSe could be at pressures higher than we predicted through the static enthalpy calculation (figures 1(a) and (b)).

We focus here on the experimentally observed unknown phase above 85 GPa in ZnTe, although it is metastable relative to the decomposition. Evolutionary simulations at the pressure of 100 GPa with two, three and four formula units per cell were performed. Interestingly, each of these variable-cell simulations generated a different CsCl-like structure that can be artificially transformed to the CsCl structure by Zn–Te atomic exchange on a body-centered cubic (bcc) lattice. The CsCl-like crystal structures predicted with 2 and 3 f.u. cell$^{-1}$ are depicted in figure 2(c) and (d), respectively. The structure evolution from figures 2(c) to (d) is quite straightforward and can be characterized by the layer-by-layer expansion of Zn or Te atomic blocks along the c-axis. We find a monotonic enthalpy decrease with increasing unit cell size (figure 3(a)). This actually reflects the energetic priority of the decomposition into Zn + Te, an ultimate case of the CsCl-like structure. This implies that the dissociation may be accomplished via a gradual Zn–X atomic exchange on the basis of a bcc lattice. We have simulated the x-ray diffraction patterns for predicted CsCl-like phases to compare with the experimental data for the unresolved phase above 85 GPa. We found that basically the structure with 2 f.u. cell$^{-1}$ (denoted as ZnTe-IV) can explain the major features of the experimental data (see figures 3(b) and (c)), while the x-ray results on structures with 3, 4, . . . f.u. cell$^{-1}$ deviate significantly from the experimental data [12]. As another argument for the validity of this predicted ZnTe-IV structure, enthalpy calculation gives the Cmcm → ZnTe-IV transition at 83 GPa (figure 3(a)),

**Figure 3.** (a) Enthalpy curves of CsCl (solid square), PbO (open square), ZnS-IV (open circle) structures, decomposition into Zn + Te (solid circle, dash line), and three CsCl-like phases for ZnTe predicted with constraints of two (ZnTe-IV, open down triangle), three (solid diamond) and four (open up triangle) formula units per cell relative to the Cmcm phase. The simulated x-ray diffraction patterns for the CsCl-like ZnTe-VI structure (c) are compared with the experimental data for the unresolved phase at 93 GPa (b).
in excellent agreement with the experimental value of 85 GPa [12]. Phonon calculation has further confirmed the dynamical stability of the ZnTe-IV phase.

In conclusion, we predicted a tetragonal ZnS-IV (ZnSe-IV) phase as the post-Cmcm phase for ZnS (ZnSe) using evolutionary simulations on the crystal structural prediction. This tetragonal phase is corroborated by our soft-mode analysis of the Cmcm phase and accordingly a transition path through Pnnm symmetry is revealed. A CsCl-like ZnTe-IV phase was proposed in ZnTe with the transition pressure and x-ray diffraction patterns in good agreement with experiment. The two predicted phases do not have any known analogy yet and can be used as structural prototypes. In addition, we have ruled out the CsCl phase as the high-pressure structure.

We have discovered an intriguing phenomenon of pressure-induced decomposition into Zn + X, which originates from the metallization of these compounds at large compression. We also propose that a large kinetic barrier for the dissociation likely exists and can explain the predicted very low dissociation pressure in ZnTe; however, this makes the accurate prediction of dissociation pressure challenging. We suggested that the dissociation process for ZnTe may be accomplished via atomic exchanges on a bcc lattice. The uncovered high-pressure dissociation of ZnX in this study has important implications for other binary compounds. Moreover, since strong compression and high temperature are prerequisite conditions for materials existing in the interior of the earth, the dissociation into elemental substances can be generally expected there.

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