

Pressure dependent phase stability transformations of GaS: A first principles study

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ABSTRACT

First principle calculations are used to determine the pressure dependent phase stability transformations for GaS polytypes at pressures up to 1000 GPa. Our results indicate that the relative stability sequence changes with the increase in pressure. With the increase in pressure, the phase stability sequence is β -GaS, GaS-II, rocksalt GaS, CsCl structure of GaS and β -GaS, and the corresponding transformation pressures are 2, 19, 75 and 680 GPa. Finally, we discuss the influence of pressure dependence of these GaS polytypes on their electronic properties.

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1. Introduction

As a typical III–VI semiconductor compound, gallium sulfide (GaS) and other sulfide-based nanomaterials and nanostructures have been receiving considerable attention due to its unique optical, semiconducting, photoconducting and luminescent properties [1–8]. GaS is known to exist in a very stable layered phase with D_{6h} hexagonal symmetry. Its crystal structure consists of plane hexagonal lattices that are associated in pairs [9]. Intralayer bonding is strongly covalent with some ionic contribution and its interlayer forces are mainly of the van der Waals type. Depending on the growth conditions, the members of GaS semiconductors can adopt different stacking sequences of the layers, resulting in different three-dimensional polytypes of different symmetries. Besides such layered GaS polytypes as β -GaS [9] and GaS-II [10], GaS can also exist in other metastable cubic forms, including rocksalt (B1 structure) GaS [11–14], zinc-blend GaS [15], etc.

At ambient conditions, β -GaS is a stable phase, while GaS-II, rocksalt and zinc-blend GaS are metastable phases [16]. However, the phase stability sequence changes with increase in pressure. The pressure dependent phase transformation among GaS polytypes has been investigated by both experimental and computational means. For example, the phase transformation from β -GaS to GaS-II has been investigated by a laboratory diffractometer [10] and pressure dependent dielectric constant measurement experiments [17]. These results indicated that this phase transition occurs at around 1.5 GPa. Previous optical absorption measurement experiments by Polian et al. [1] showed that an additional GaS phase transition takes place at 19 GPa. Recently, single crystal diffraction experiments and first principle calculations by Pellier-Porres et al. [18] indicated that the phase transformation from β -GaS to GaS-II takes place at 2.7 GPa. However, up till now there have been no structural characterizations of GaS at pressures above 40 GPa. Note also that a high pressure stable phase structure for a two element compound is usually a CsCl structure [19,20]. Nevertheless, to the best of our knowledge, there have been no CsCl structures studied for GaS. This is done in the present paper. Furthermore, in this paper, the pressure

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dependent phase stability transformation of different GaS polytypes at pressures up to 1000 GPa is analyzed in detail with first-principles methods.

2. Computational methods

Five kinds of GaS polytypes (namely, β -GaS, GaS-II, rocksalt GaS, zinc-blend GaS and CsCl structure of GaS) have been considered in this paper. The crystal lattices parameters and atom positions of different GaS polytypes under pressure have been optimized using density functional theory (DFT) based on a planewave pseudopotential technique implemented in the CASTEP package [21], and the corresponding enthalpies have been obtained. In this work, the interactions between the valence electrons and the ion-cores have been modeled by ultrasoft pseudo-potentials [22]. Within this CASTEP computational scheme, the generalized gradient approximation (GGA), with the Perdew–Burke–Ernzerhot (PBE) exchange–correlation functional, [23] has been employed. The k point separation in the Brillouin zone of the reciprocal space was taken to be 0.05 nm^{-1} , i.e. $6 \times 6 \times 2$ k point mesh for β -GaS, $6 \times 6 \times 2$ for GaS-II, $7 \times 7 \times 7$ for rocksalt GaS, $6 \times 6 \times 6$ for zinc-blend GaS and $6 \times 6 \times 6$ for CsCl structure of GaS. A high cutoff energy of 400 eV has been selected for the planewave basis. Trial calculations have been performed for stress-free β -GaS, rocksalt GaS and zinc-blend GaS lattice. The calculated Ga–S and Ga–Ga bond lengths in β -GaS are 0.2361 and 0.2477 nm, respectively, and they are compare well with the corresponding experimental data of 0.2301 and 0.2281 nm [2]. The calculated lattice parameters for stress-free rocksalt GaS and zinc-blend GaS, $a=0.52912$ and 0.5912 nm, are also in close agreement with experimental values $a=0.537$ and 0.55 nm, respectively [12].

3. Results and discussions

Based on our first principle calculations, stress-free lattice parameters for different GaS polytypes are obtained and listed in Table 1. As can be seen from Table 1, at ambient conditions, β -GaS is the stable phase. It is slightly more stable than GaS-II by 0.0028 eV per GaS unit, and it is more stable than rocksalt GaS, zinc-blend GaS and CsCl structure of GaS by 0.58275, 0.88354 and 1.35641 eV per GaS unit, respectively. Although this energy difference is probably slightly underestimated because of the well known problems of DFT in dealing with layered systems where the van der Waals force plays a role [8,24,25], our calculated results agree well with the experimental results [18].

Table 1
Experimental and optimized crystallographic data and total energy of different GaS polytypes.

Phase	Space group	Lattice parameters		Total energy (eV per GaS unit)	Reference
		<i>a</i> (nm)	<i>c</i> (nm)		
β -GaS	P63/MMC	0.36336	1.67931	0	This work
GaS-II	P63/MMC	0.3592	1.5465	0.00281	[2]
	P63/MMC	0.36341	1.6472		This work
	P63/MMC	0.3547	1.474		[10]
Rocksalt	FM-3M	0.52912		0.58275	This work
	FM-3M	0.537			[11]
CsCl structure	PM-3M	0.32873		1.35641	This work
Zinc-blend	PM-3M	0.5912		0.88354	This work
		0.55			

Since no temperature effects are considered in this work, the pressure dependent phase stability of GaS polytypes can be determined by comparing the enthalpies [26]. In particular, the geometries of these GaS polytypes under pressure have been optimized here using the DFT, and the enthalpies for these optimized GaS polytypes under pressure up to 1000 GPa have been obtained. The relationship between the enthalpies and pressure for various GaS polytypes are plotted in Fig. 1. As can be seen from Fig. 1, when the pressure is below 2 GPa, the layered β -GaS is the most energetically stable GaS phase. When the pressure is above

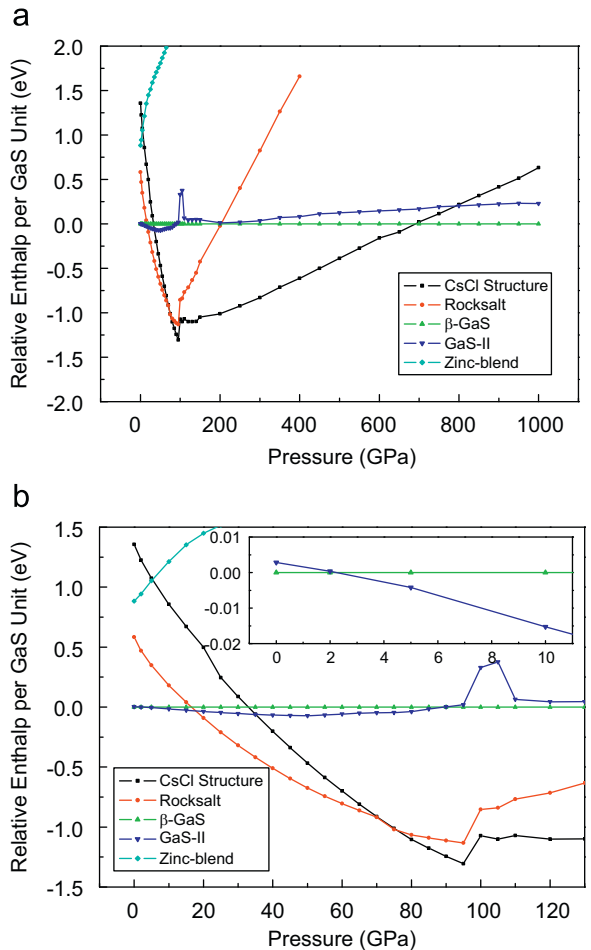


Fig. 1. Relative enthalpy for β -GaS, GaS-II, CsCl structure GaS, rocksalt GaS and zinc-blend GaS polytypes under pressure. (b) is a partial enlargement of (a).

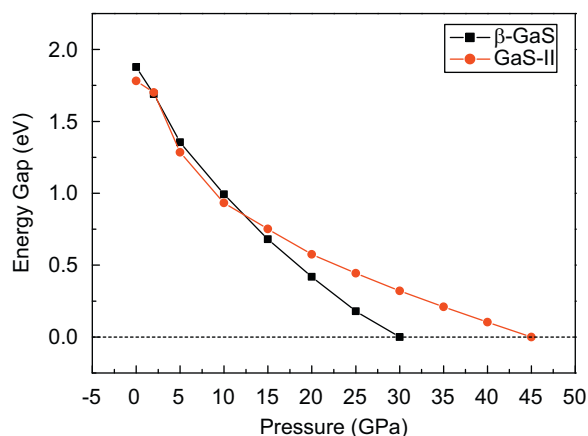


Fig. 2. Minimum energy gaps versus pressure for different GaS polytypes.

2 GPa, the layered GaS-II becomes the most stable phase with the increase in pressure. These results agree well with experimental results reported by d'Amour et al. [10] and Errandonea et al. [17]. When the pressure is above 19 GPa and below 75 GPa, cubic rocksalt GaS becomes the most stable phase, and these calculated results compare well with the optical absorption measurement experiment results by Polian et al. [1]. When the pressure is above 75 GPa and below 680 GPa, the cubic CsCl structure of GaS becomes the most stable phase. When the pressure is above 680 GPa, layered β -GaS becomes the most stable phase again with the increase in pressure, and zinc-blend GaS is not the stable phase with respect to other GaS polytypes at any given pressure range considered in this work.

In order to understand the electronic properties of these GaS polytypes under changing pressure conditions, pressure dependent energy gaps have been calculated and plotted in Fig. 2. It is known that the GGA approaches to the DFT often fail to describe systems with localized (strongly correlated) *d* and *f* electrons as a result of neglecting electron correlation [27]. This is especially true for GaS structures, where the experimental energy gap of β -GaS is 2.5 eV [6], whereas our calculated band gap is only 1.88 eV. It is worth mentioning that both β -GaS and GaS-II are direct semiconductors at zero pressure condition, and these results contradict with some experimental indirect semiconductors results [6]. Besides β -GaS and GaS-II, all other GaS polytypes are conductors at the pressure range considered in this work. For β -GaS and GaS-II, the relationship between energy gap and pressure is plotted in Fig. 2. With the increase in pressure, the energy gap decreases. When the pressure is below 12 GPa, the energy gap for GaS-II is lower than that of β -GaS. When the pressure is above 12 GPa, the energy gap for GaS-II is higher than that of β -GaS. However, when the pressures are above 30 and 45 GPa for β -GaS and GaS-II, respectively, they become conductors. In addition, with the increase in pressure, the conduction-band minimum locations change. For β -GaS, when the pressure is above 2 GPa and below 5 GPa, the conduction-band minimum is located at M point. However, when the pressure is above 10 GPa and below 25 GPa, the conduction-band minimum is located at K point. For GaS-II, the conduction-band minimum is still located at L point when the pressure ranges from 2 to 40 GPa.

4. Conclusion

In summary, in this work the pressure dependent phase stability transformations for GaS polytypes are determined using first principle calculations. We have also obtained the pressure dependence energy gaps for β -GaS and GaS-II. Our results indicate that the relative stability sequence changes with the increase in pressure. With the increase in pressure,

the relative stability sequence is β -GaS, GaS-II, rocksalt GaS, CsCl structure of GaS and β -GaS, and the corresponding transformation pressures are 2, 19, 75 and 680 GPa, respectively.

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