A Comparative Study of GaAsO$_4$ Polymorphs: *ab initio* Calculations on High-pressure Forms

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Dedicated to Professor Gérard Demazeau on the occasion of his 65th birthday

First-principles calculations were performed to compare the relative stability and high-pressure behavior of four different GaAsO$_4$ polymorphs: the ordinary-pressure phase (berlinite, α-quartz-like) and three high-pressure phases: the β-VCrO$_4$-like, the rutile-like and a new hexagonal form, recently discovered and related to rutile.

Key words: Gallium Arsenate, High-pressure Polymorphs, *ab initio* Calculations

Introduction

Ternary oxides of formula ABO_4 adopt various crystal structures depending on the relative size of the A and B cations. For some $A^{III}B^{V}O_4$ compounds it is reasonable to expect pressure-induced transformations resembling those of dioxides provided that the A and B cationic sizes are similar [1]. For instance, in the case of A = Al, or if A and B are disordered Ga, and B = P, As, these compounds crystallize at ordinary pressure in the berlinite structure (α-quartz-like), or in a 2-fold superstructure of it if A and B are ordered along the c axis [2]. Other related compounds, such as boron phosphate or arsenate, prefer the cristobalite structure which, under high-pressure / high-temperature conditions, transform into the α-quartz modification [3].

On the other hand, it is well known that silica transforms under very high pressures (approx. 10 GPa) into stishovite, the rutile form of silica where the coordination number of Si changes from 4 (tetrahedra) to six (octahedra) and, associated with this, the density increases dramatically [4]. Therefore, by analogy to the rich phase diagram of silicon dioxide, one would expect that the above mentioned ternary oxides will finally transform into rutiles upon sufficiently increasing the pressure and temperature applied, but that other intermediate high-pressure phases would also be possible. In this paper we focus on the different reported polymorphs of GaAsO$_4$ where some controversy exists, probably related to different experimental conditions and procedures.

Some authors have reported that the quartz-type GaAsO$_4$ transforms – at 6 GPa and 900 °C – into a dirutile polymorph where As and Ga are ordered, but two additional new phases, not fully characterized, appear in the 4 – 7 GPa pressure range. One of these phases, of orthorhombic symmetry showing the β-VCrO$_4$ structure, is also known as the InPO$_4$ type [5]. It is worth mentioning that, in this last phase, tetrahedra and octahedra are coexisting and interconnected. Its intermediate character between α-quartz (only tetrahedra) and rutile (only octahedra) is evident. Recent reports deal with the synthesis at 6 GPa and 1000 °C in a "Belt" set-up [6] and the structural characterization of a new high-pressure phase of GaAsO$_4$ of hexagonal symmetry (a = 8.2051, c = 4.3946 Å, space group $P321$) which has some features in common with rutile (c. n. = 6, average distances, hexagonal close packing of anions, edge-sharing between octahedra, *etc.*) but also important differences (there are no octahedral chains as in rutile); in what follows we call this phase the Vegas polymorph, after the name of one of the authors [7]. To our knowledge, there only exists one more example of this structure although with different stoichiometry, the ternary oxide of formula β-MnSb$_2$O$_6$ reported by Vincent *et al.* [8]. Probably, more compounds with this new structure remain to be discovered.
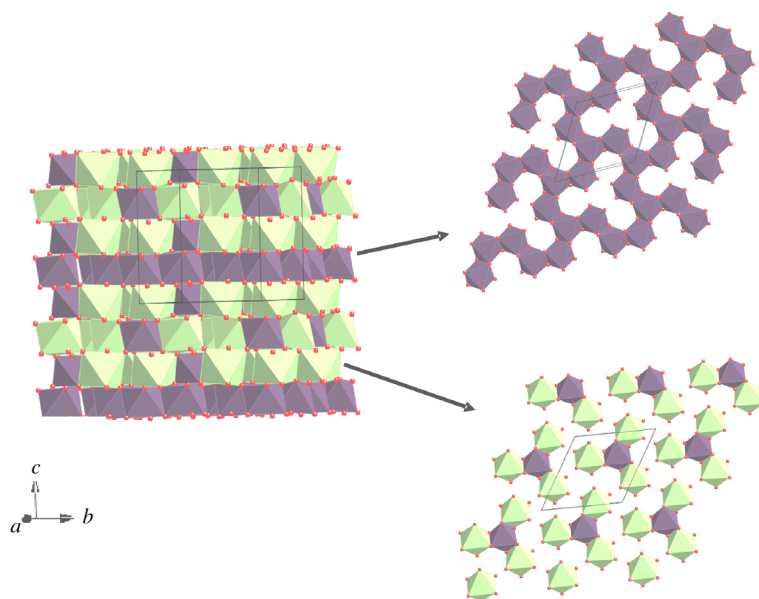
Fig. 1. Schematic representation of the superstructure of the GaAsO$_4$ Vegas polymorph (model 1 in the text). Green denotes gallium and purple arsenic (color online). Complementary layers are made up of 12-membered rings of $[XO_6]$ octahedra. Because of the atomic order imposed, one layer consists of groups of four $[XO_6]$ octahedra (X = As, Ga) in which a central $[AsO_6]$ octahedron shares three edges with three adjacent $[GaO_6]$ octahedra (bottom panel) while the next layer consists solely of $[AsO_6]$ octahedra (upper panel).

It seems, therefore, that the phase diagram of GaAsO$_4$ can be almost as rich as that of SiO$_2$ and is worth to be explored. To do this, *ab initio* methods can be very helpful as a guide for experimental work. In a very interesting previous paper, Duan *et al.* [9] have performed a first-principles search for six high-pressure phases of GaAsO$_4$ (three of them are real and the remaining three are model candidates), but their methodology was different, and the new hexagonal form was not included since it has been discovered later. Thus, the aim of this work is to compare, on the basis of energy *vs.* volume calculations, the relative stability of four, experimentally reported, ABO_4 structures: α-quartz, β-VCrO$_4$, rutile and the hexagonal new polymorph (Vegas).

Methodology

The total energy of GaAsO$_4$ polymorphs and of Ge, As, O$_2$, and Ga, was calculated using the Vienna *ab initio* Simulation Package (VASP) [10]. The exchange-correlation energy was approximated in the Generalized Gradient Approximation (GGA), using for the exchange and correlation functional a form suggested by Perdew, Burke, and Ernzerhof (PBE) [11]. A plane wave basis set with a kinetic energy cut-off of 550 eV was used. The reciprocal-space sampling was done with k-point grids of $6 \times 6 \times 6$ for the rutile, CrVO$_4$ and ambient pressure GaAsO$_4$ polymorphs, and of $4 \times 4 \times 4$, or $4 \times 4 \times 8$ for the Vegas polymorph. As a first step,

the LiFeSiO$_4$ structures were fully relaxed (cell parameters and atomic positions); the final energies of the optimized geometries were recalculated so as to correct for the changes in the basis set of the wave functions during relaxation. Secondly, relaxed structure calculations were performed at various constant volumes, and the energy-volume data was fitted to the Murnagham equation of state:

$$E(V) = B_0 V_0 \left[\frac{1}{b'(B'-1)} \left(\frac{V_0}{V} \right)^{B'-1} + \frac{V}{B'V_0} - \frac{1}{(B'-1)} \right] + E_0$$

where B_0 is the bulk modulus at zero pressure, B' its first derivative with respect to pressure, E_0 the minimum energy, and V_0 the volume at the minimum of energy. Preparation and analysis of VASP files were done primarily with the CONVASP code [12]. An analysis of the crystal symmetry was performed using the program PLATON [13].

Results and Discussion

Computing the energy of a periodic electronic structure requires that an atomic ordering scheme is imposed on the simulated unit cell. The unit cell of the Vegas polymorph of GaAsO$_4$ possesses a formula Ga$_{4.5}$As$_{4.5}$O$_{18}$ and shows hexagonal symmetry (space group $P3$) with lattice parameters a = 8.203 and c =
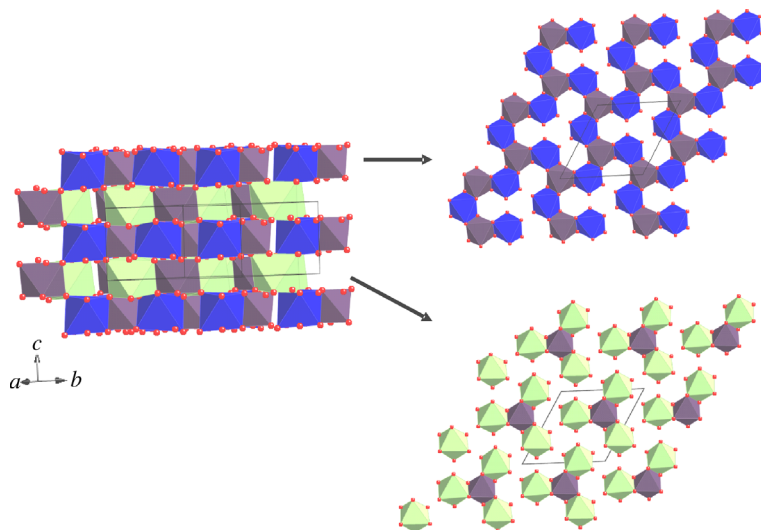
Fig. 2. Schematic representation of the structure considered for the Vegas polymorph Ga$_3$(Ga/As)$_3$As$_3$O$_{18}$ (model 2 in the text). Green denotes gallium, purple arsenic and blue refers to the shared position (color online).
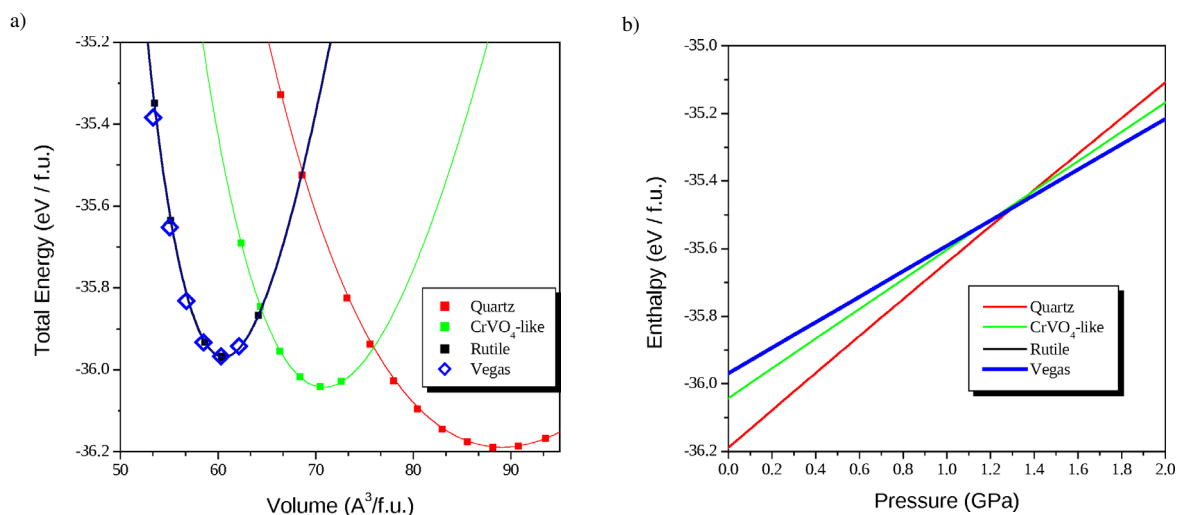
a)

b)

Fig. 3. a) Calculated total energy difference between the quartz-, CrVO$_4$-, rutile-, and Vegas-GaAsO$_4$ polymorphs *vs.* the equilibrium volume. b) Relative stability of possible GaAsO$_4$ forms as a function of pressure.

4.394 Å. The 3d position is shared between As and Ga. As this position is randomly occupied by two atoms it can only be studied by first-principles calculations establishing an ordered model. Two structural models were used for Ga$_{4.5}$As$_{4.5}$O$_{18}$. The first model is a super-cell of composition Ga$_9$As$_9$O$_{36}$ where As and Ga atoms are ordered as shown in Fig. 1. The second model is the compound Ga$_3$Ge$_3$As$_3$O$_{18}$ where the shared 3d site is occupied by Ge atoms (see Fig. 2). These two models will be denoted as model 1 and model 2, respectively.

Table 1 compares the calculated lattice parameters for the fully relaxed structures of the GaAsO$_4$ poly-

Table 1. Cell parameters (in Å) for the experimental and calculated structures of the GaAsO$_4$ polymorphs.

GaAsO$_4$ polymorph	Experimental [5, 6]	Calculated	Error (%)
Quartz	81.79	87.91	7
CrVO$_4$	69.03	70.47	2
Rutile	53.78	60.38	11
Vegas	56.3	59.23	5

morphs with the reported experimental values. The GGA method allows a correct reproduction of the cell parameters, with an over-predictive trend which is typical for DFT methods within the GGA approximation.
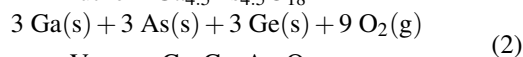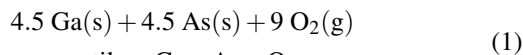
Fig. 3a shows the relative energies of the GaAsO$_4$ polymorphs *vs.* their corresponding equilibrium vol-

umes, (model 1 for the Vegas polymorph) together with the corresponding fit of the DFT data to the Murnagham equation of state. The ambient pressure polymorph (quartz) is the global minimum of energy. The rutile form is 0.215 eV / f. u. less stable than the quartz form. $CrVO_4$ appears as an intermediate phase between the quartz and the rutile polymorphs, being 0.139 eV less stable than the quartz form. The Vegas polymorph (model 1) is energetically as stable as the rutile form.

Fig. 3b shows the calculated enthalpy-pressure variation for the $GaAsO_4$ polymorphs. It can be observed that the quartz polymorph is effectively predicted as the thermodynamically stable phase below 1.4 GPa. Noteworthy, the $CrVO_4$ type is not stable at any pressure, as was found in a previous DFT investigation [8], though some experimental works reported the preparation of this form at $4 \sim 7$ GPa [5]. At higher pressures the rutile and/or the Vegas forms are stable, the enthalpy lines being indistinguishable in Fig. 3b. Because, at 0 K, there is no thermodynamic preference for either the rutile or the Vegas structure (model 1) it is plausible that HP experiments could lead to the Vegas polymorph. One should bear in mind that in the crystal structure calculations we have imposed an order of atoms. While Ga and As might disorder or not in the rutile structure, it is for sure that a disordering of Ga/As occurs in the shared $3d$ position of the Vegas structure. Thus, one can expect a greater gain of mixing entropy in the Vegas structure than in the rutile form, lowering the free energy of the computed model 1 with respect to that of rutile. This reasoning leaves us to conclude that the Vegas polymorph might be entropically favored over the rutile form at high temperatures commonly used in HP experiments.

From all the above, utilizing the structural model 1 for the Vegas polymorph does not allow to conclude whether the rutile or the Vegas polymorph is thermodynamically favored under high pressures. Next, we investigate the Vegas polymorph using the structural model 2, where a Ge atom is taken to represent the disordered Ga+As shared occupation ($Ga_3Ge_3As_3O_{18}$). The calculated total energy of $Ga_3Ge_3As_3O_{18}$ can not be directly compared to that of the $GaAsO_4$ compositions, but we can still confront the values of the formation energies according to the reactions:

$$4.5\,Ga(s) + 4.5\,As(s) + 9\,O_2(g) \tag{1}$$
$$\rightarrow rutile - Ga_{4.5}As_{4.5}O_{18}$$
$$3\,Ga(s) + 3\,As(s) + 3\,Ge(s) + 9\,O_2(g) \tag{2}$$
$$\rightarrow Vegas - Ga_3Ge_3As_3O_{18}$$

Calculated energies are 8.678 eV / M_2O_4 and 9.1 eV / M_2O_4 for reactions (1) and (2), respectively. This supports the idea that the Vegas polymorph might be more stable than the rutile form.

Conclusions

For a long time, rutile-like $GaAsO_4$ was considered the high-pressure polymorph of quartz-$GaAsO_4$. Recently, a new HP polymorph of $GaAsO_4$ has been prepared, its crystal structure being closely related to that of rutile. In this work we investigated by DFT calculations the relative stability of possible $GaAsO_4$ polymorphs: quartz, rutile, and $CrVO_4$-like, including the newly proposed structure (Vegas structure). We found that the ambient pressure form, quartz-$GaAsO_4$, will transform under pressure to either the rutile or the Vegas structure, both being energetically comparable. Other quartz-ABO_4 compounds could also transform to the Vegas-like structure under pressure.

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