

Structural characterization of a new high-pressure phase of GaAsO₄David Santamaría-Pérez,^a Julien Haines,^b Ulises Amador,^c Emilio Morán^d and Angel Vegas^{a*}^aInstituto de Química-Física 'Rocasolano', CSIC, C/Serrano 119, 28006 Madrid, Spain,^bLaboratoire de Physico-chimie de la matière condensée, UMR CNRS 5617, Université de Montpellier II, cc 003, place E. Bataillon, 34095 Montpellier CEDEX 5, France, ^cDepartamento de Química, Universidad San Pablo-CEU, Urb. Montepríncipe, 28668 Boadilla del Monte, Madrid, Spain, and ^dLaboratorio Complutense de Altas Presiones, Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

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As in SiO₂ which, at high pressures, undergoes the α -quartz \rightarrow stishovite transition, GaAsO₄ transforms into a dirutile structure at 9 GPa and 1173 K. In 2002, a new GaAsO₄ polymorph was found by quenching the compound from 6 GPa and 1273 K to ambient conditions. The powder diagram was indexed on the basis of a hexagonal cell ($a = 8.2033$, $c = 4.3941$ Å, $V = 256.08$ Å³), but the structure did not correspond to any known structure of other AXO₄ compounds. We report here the *ab initio* crystal structure determination of this hexagonal polymorph from powder data. The new phase is isostructural to β -MnSb₂O₆ and it can be described as a lacunary derivative of NiAs with half the octahedral sites being vacant, but it also contains fragments of the rutile-like structure.

1. Introduction

$A^{\text{III}}B^{\text{V}}O_4$ ($A^{\text{III}} = \text{Al, Ga}$; $B^{\text{V}} = \text{P, As}$) ternary oxides under normal conditions adopt either the α -quartz structure or a superstructure derived from it, in which the c axis becomes doubled as a consequence of the ordering of the A and B cations. A list of all these α -quartz homeotypes can be found in Haines & Cambon (2004). Other related compounds such as BPO₄, BAsO₄ and PON which, under normal conditions are cristobalite-like, undergo phase transitions towards the α -quartz-type at high temperatures and pressures (Haines, Chateau, Leger & Marchand, 2001; Leger *et al.*, 1999; Haines *et al.*, 2004).

As with SiO₂, which, at high pressures, undergoes the α -quartz \rightarrow stishovite transition, several of these compounds can be transformed into a rutile-like structure by increasing the pressure. This is the case for GaAsO₄, which transforms into a dirutile structure at 9 GPa and 1173 K, as reported by Matar *et al.* (1990). In this study, two additional phases were identified in the range $4 \leq P \leq 7$ GPa. One, for which the structure was not determined, was indexed on the basis of a monoclinic cell, and a second was indexed as orthorhombic; a structure of the CrVO₄ type was proposed. It should be outlined that the structures of these three phases have not been confirmed by Rietveld refinements.

Later, in a high-pressure study, in which the synthesis of pure rutile-like GaAsO₄ was attempted, Gallardo-Amores *et al.* (2002) found a new polymorph at 6 GPa and 1273 K, using a belt-type apparatus. The powder diagram was indexed on the basis of a hexagonal cell, but the structure did not correspond to any known structure of other AXO₄ compounds.

We report here the *ab initio* crystal structure determination of this hexagonal polymorph from powder data. It represents a

Table 1
Experimental details.

	GaAsO ₄	As ₂ O ₃
Crystal data		
Chemical formula	GaAsO ₄	As ₂ O ₃
M_r	208.64	197.84
Cell setting, space group	Hexagonal, $P3$	Cubic, $Fd\bar{3}m$
Temperature (K)	273	273
a, b, c (Å)	8.203320 (1), 8.203320 (1), 4.394109 (1)	11.0771 (5), 11.0771 (5), 11.0771 (5)
α, β, γ (°)	90, 90, 120	90, 90, 90
V (Å ³)	256.08 (1)	1359.20 (10)
Z	4.5	16
D_x (Mg m ⁻³)	6.087	3.867
Radiation type	Cu $K\alpha$	Cu $K\alpha$
μ (mm ⁻¹)	33.6	21.3
Specimen form, colour	Cylinder (particle morphology: plate like), white	Cylinder, white
Specimen size (mm)	30 × 0.5 × 0.5	30 × 0.5 × 0.5
Specimen preparation cooling rate (K min ⁻¹)	5	5
Specimen preparation pressure (kPa)	6	6
Specimen preparation temperature (K)	1273	1273
Data collection		
Diffractometer	Bruker D8	Bruker D8
Data collection method	Specimen mounting: 60 rpm rotating glass capillaries of 0.5 mm diameter; mode: transmission; scan method: step	Specimen mounting: 60 rpm rotating glass capillaries of 0.5 mm diameter; mode: transmission; scan method: step
Absorption correction	None	None
2θ (°)	$2\theta_{\min} = 9.8416$, $2\theta_{\max} =$ 150.2341 , increment = 0.014643	$2\theta_{\min} = 9.8416$, $2\theta_{\max} =$ 150.2341 , increment = 0.014643
Refinement		
Refinement on	Raw data	Raw data
R factors and goodness of fit	$R_p = 0.0885$, $R_{wp} = 0.1294$, R_{exp} $= 0.0396$, $R_B = 0.0472$, $S =$ 10.7	$R_p = 0.0885$, $R_{wp} = 0.1294$, R_{exp} $= 0.0396$, $R_B = 0.1301$, $S =$ 10.7
Wavelength of incident radi- ation (Å)	1.540590	1.540590
Excluded region(s)	0–10, 150–180	0–10, 150–180
Profile function	Pseudo-Voigt	Pseudo-Voigt
No. of parameters	48	48
H-atom treatment	No H atoms present	No H atoms present
Weighting scheme	1/ σ	1/ σ
$(\Delta/\sigma)_{\max}$	<0.0001	<0.0001

Computer programs used: Bruker AXS software, *Endeavour* (Putz *et al.*, 1999; Crystal Impact, 2004), *FULLPROF* (Rodríguez-Carvajal, 1993), *DIAMOND* (Crystal Impact, 1988).

new structural type which will be compared with the rutile-type structure.

2. Experimental

The material was obtained from a mixture of the corresponding simple oxides (As₂O₅ and Ga₂O₃, analytical grade reagents as supplied by Sigma-Aldrich) stored and handled in an Ar-filled glove-box. A slight excess of arsenic oxide (5%) was used in order to avoid arsenic losses by volatilization. The high-pressure/high-temperature treatment was carried out

using gold capsules in a belt-type apparatus at 6 GPa and 1273 K for 30 min.

Besides the new GaAsO₄ polymorph, a small amount of arsenolite (As₂O₃) was also detected (estimated proportion from the Rietveld analysis: 1.4%) by the presence of two weak reflections at 2θ values of 13.83 and 27.85°. This was obviously because of the decomposition of excess arsenic pentoxide which was used as a reactant, providing gas oxygen pressure which seems to be needed for the synthesis in order to keep the high oxidation state of arsenic (5+); interestingly enough, other authors (Matar *et al.*, 1990) have also reported that high pressures of oxygen gas are necessary for the synthesis of gallium and aluminium arsenates.

A preliminary characterization of the parent and high-pressure products was performed by X-ray powder diffraction (XRD) on a Philips X'Pert diffractometer equipped with Cu ($K\alpha_1 + \alpha_2$) radiation ($\lambda = 1.5418$ Å) and a nickel filter.

The XRD pattern of the high-pressure polymorph of GaAsO₄ used for structure determination was obtained on a Bruker D8 diffractometer of Bragg–Brentano geometry, equipped with a primary germanium monochromator, giving a beam of pure Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å) using a MBraun PSD-50M position-sensitive detector (PSD). This pattern was recorded at room temperature in the transmission mode using glass capillaries of 0.5 mm diameter filled with the sample to overcome a severe preferred orientation

effect. The measured angular range (from $2\theta = 10$ to 150°), step size (0.015°) and counting times were selected to ensure a high enough resolution and accurate statistics.

3. Structure solution and refinement

All the experimental details are given in Table 1. The unit-cell dimensions of the new hexagonal phase are $a = 8.2033$ (1) and $c = 4.3941$ (1) Å with $V = 256.08$ (1) Å³. Assuming that the dirutile unit cell ($V_R = 107.56$ Å³) contains two GaAsO₄ formula units (Matar *et al.*, 1990), the calculated Z value for the new phase would be $Z = 4.5$. This fractional number could indicate either the existence of a superstructure with some

Table 2
Ga/As—O bond lengths (Å) in the different (Ga/As)O₆ octahedra.

As1O ₆ octahedron	
As1—O	3 × 1.67 (1)
	3 × 2.03 (1)
As2O ₆ octahedron	
As2—O	3 × 1.85 (1)
	3 × 1.84 (1)
As3O ₆ octahedron	
As3—O	3 × 1.75 (1)
	3 × 1.99 (1)
(As,Ga)O ₆ octahedron	
(As,Ga)—O	1 × 1.83 (1)
	1 × 1.84 (1)
	1 × 1.89 (1)
	1 × 1.95 (1)
	1 × 1.97 (1)
	1 × 2.02 (1)
GaO ₆ octahedron	
Ga—O	1 × 1.74 (1)
	1 × 1.88 (1)
	1 × 1.98 (1)
	1 × 2.13 (1)
	1 × 2.16 (1)
	1 × 2.21 (1)

doubled axis (*c*, for example) or the existence of some type of positional disorder between Ga and As in such a way that the cell would contain $Z = 9$ XO_2 ($X = \text{Ga, As}$) units.

The possibility of a doubled unit cell was discarded because the doubling of the *c* axis could not account for the existence of three insignificant peaks ($2\theta = 18.24, 26.26$ and 28.30°). Moreover, when these extremely weak reflections were added in the indexation process, no reliable solution was obtained. In

view of this, the structure solution was attempted based on the assumption of cation positional disorder, with 9 formula units of the isoelectronic compound GeO₂ in the unit cell. The diagram showed no systematic absences, leading to 16 possible space groups with hexagonal and trigonal symmetry. The space group of the lowest symmetry (*P3*) was assumed for the structure solution.

The structure was solved *ab initio* using the program *Endeavour* (Putz *et al.*, 1999; Crystal Impact, 2004). The unit-cell dimensions and contents as well as a list of 2θ values and integrated intensities of the peaks were used to solve the structure. Convergence was achieved giving an *R* factor of 0.10. At this point, the symmetry checking facility (Symmetry Finder; Hannemann *et al.*, 1998; Hundt *et al.*, 1999) was used to detect the possible space groups of higher symmetry which were consistent with the structure. The unique alternative solution was the space group *P321*. A new structure solution using this space group led to a similar *R* factor (around 0.10). The structure was then refined by means of the program *FULLPROF* (Rodríguez-Carvajal, 1993). The initial refinement was carried out in *P3* using the GeO₂ model with an R_{Bragg} value of 0.085. From the Ge—O distances, it was seen that some were shorter and more consistent with octahedral As—O distances (around 1.80 Å), whereas others were more similar to octahedral Ga—O distances (around 2.0 Å). This led us to locate three As atoms at the positions 1(*a*), 1(*b*) and 1(*c*) and three Ga atoms at the site 3(*d*). The three remaining cations (Ga, As) could not be separated and was assumed to be disordered at the 3(*d*) site with an occupancy factor of 0.5. A new profile refinement was carried out with this model in

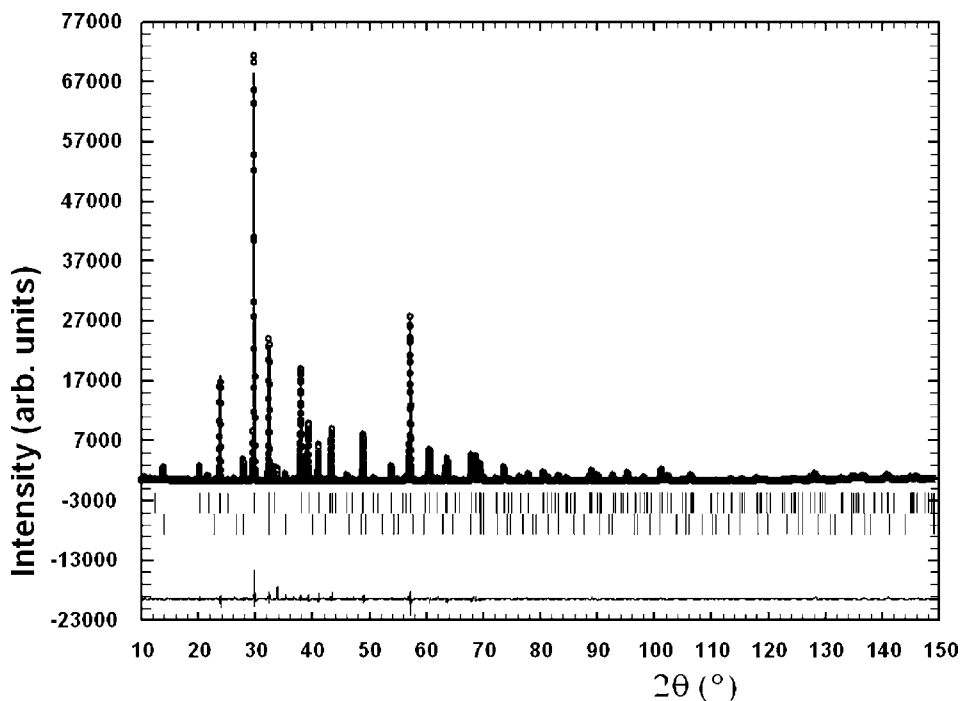


Figure 1
Observed, calculated and difference X-ray diffraction patterns (all in the same scale) for the new high-pressure high-temperature *P3* GaAsO₄ phase. Vertical marks indicate Bragg reflections. In addition to the GaAsO₄ structure, As₂O₃ (arsenolite) was included in the refinement.

which symmetry- and *hkl*-dependent anisotropic microstrain parameters were included (Stephens, 1999). This was necessary as the observed diffraction lines with $l > h$ were preferentially broadened. This may be related to static Ga/As disorder. The resulting agreement factors improved as follows: $R_p = 0.144$, $R_{\text{wp}} = 0.179$, $R_{\text{Bragg}} = 0.047$ and $\chi^2 = 10.7$. Agreement parameters slightly higher than usual were due to the presence of some weak peaks, which were most likely due to small amounts of unknown impurities. It is worth noting that in samples prepared at high-pressure/high-temperature side phases were often formed.

Finally, a refinement was made in the space group *P321*. Although the agreement factors were similar to those attained in *P3*, greater dispersion in the As—O and Ga—O distances was obtained. For this reason *P3* was selected as the most probable space group for the

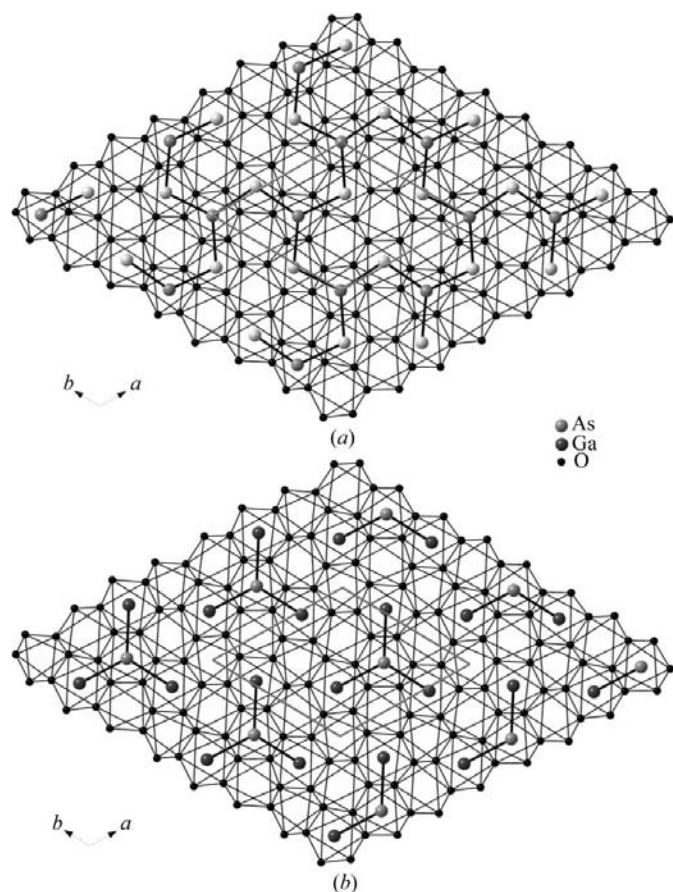


Figure 2
Complementary octahedral layers present in the $P3$ GaAsO_4 structure. (a) This layer corresponds to the cations at $z \approx 0.5$ and is made up of 12-membered rings of $[\text{XO}_6]$ octahedra ($X = \text{As}, \text{Ga}$) sharing edges. (b) The cations of this layer are situated at $z \approx 0$. The layer consists of groups of four $[\text{XO}_6]$ octahedra ($X = \text{As}, \text{Ga}$) in which a central $[\text{AsO}_6]$ octahedron shares edges with three adjacent $[\text{GaO}_6]$ octahedra.

structure. Fig. 1 shows the graphic result of the fitting of the X-ray diffraction data to the structural model presented in the supplementary material.¹ The interatomic distances which define the cation-centered octahedra are given in Table 2.

4. Results and discussion

The structure of this new high-pressure high-temperature phase of GaAsO_4 was formed by a slightly distorted hexagonal close packing of O atoms, whose layers ...*ABAB*... were arranged perpendicularly to the c axis of the hexagonal $P3$ cell. Cations, *i.e.* both Ga and As atoms, occupy half the octahedral positions. In GaAsO_4 , Ga and As atoms underwent an increase in their coordination numbers as a consequence of the application of pressure. Thus, in the ambient-pressure GaAsO_4 quartz-type structure, both atoms presented a tetrahedral coordination. In the high pressure ($4 < P < 7$ GPa)

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV5074). Services for accessing these data are described at the back of the journal.

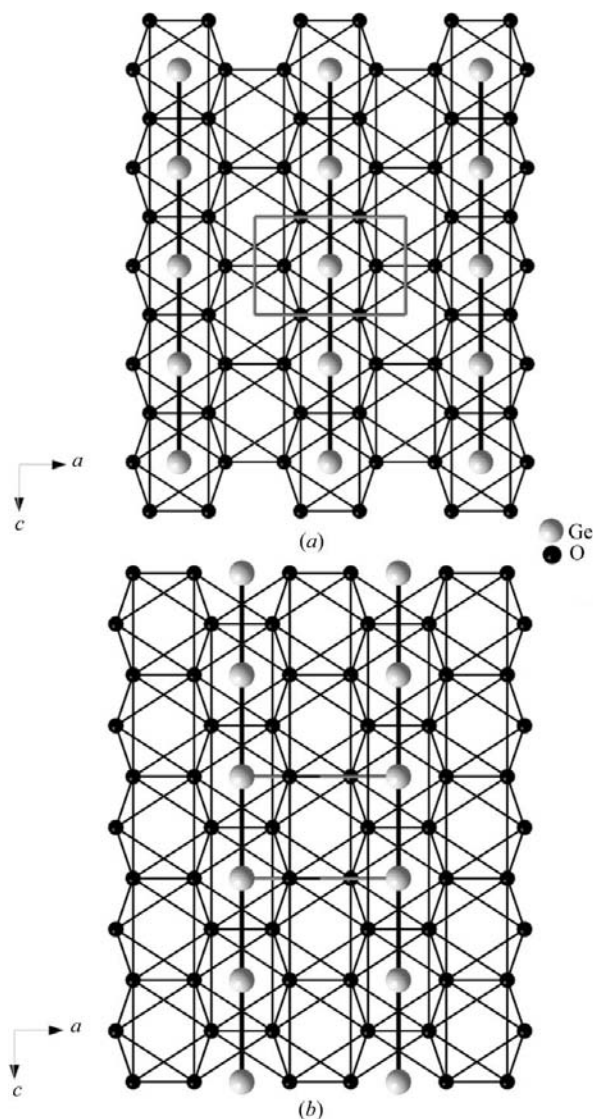


Figure 3
(a) and (b) Complementary octahedral layers present in the GeO_2 rutile-like structure, to be compared with those of the $P3$ GaAsO_4 structure represented in Figs. 2(a) and (b).

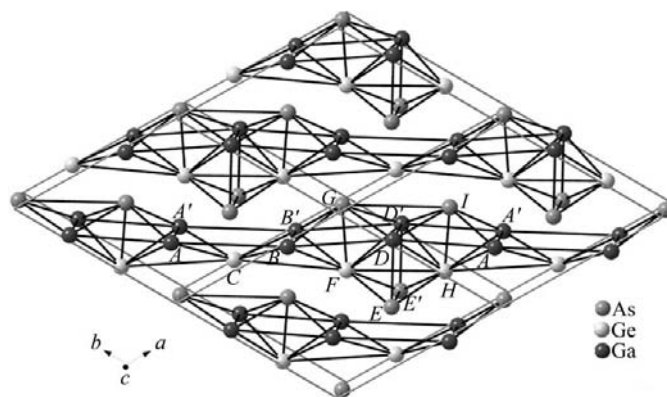


Figure 4
Four unit cells of the $P3$ GaAsO_4 structure in which the infinite two-dimensional blocks running parallel to $[110]$ are depicted. In these blocks, the topology and the distances are comparable with those of the GeO_2 rutile structure.

Table 3

Unit-cell parameters (*a* and *c*) of the three incomplete and the complete rutile-like fragments, to be compared with those of the GeO₂ unit cell.

Distances between the vertices of these 'rutile-like unit cells' and their centers (*d*) are also included.

	<i>a</i> (Å)	<i>c</i> (Å)	<i>d</i> (Å)
First fragment	2 × 4.373 (<i>AA'</i>) (<i>BB'</i>) 2 × 5.109 (<i>AB</i>) (<i>A'B'</i>)		1 × 3.408 (<i>BC</i>) 1 × 3.502 (<i>AC</i>) 1 × 3.519 (<i>B'C</i>) 1 × 3.610 (<i>A'C</i>) Average value = 3.510
Second fragment	2 × 4.373 (<i>BB'</i>) (<i>DD'</i>) 2 × 4.648 (<i>BD</i>) (<i>B'D'</i>)	1 × 2.877 (<i>FG</i>) 2 × 2.952 (<i>DE</i>) (<i>D'E'</i>)	1 × 3.282 (<i>EF</i>) 1 × 3.328 (<i>EF</i>) 2 × 3.445 (<i>B'G</i>) (<i>D'G</i>) 1 × 3.472 (<i>BF</i>) 2 × 3.478 (<i>BG</i>) (<i>DG</i>) 1 × 3.502 (<i>DF</i>) 1 × 3.580 (<i>B'F</i>) 1 × 3.610 (<i>D'F</i>) Average value = 3.462
Third fragment	2 × 4.373 (<i>DD'</i>) (<i>AA'</i>) 2 × 4.457 (<i>DA</i>) (<i>D'A'</i>)	1 × 2.858 (<i>HI</i>) 2 × 2.952 (<i>DE</i>) (<i>D'E'</i>)	2 × 3.250 (<i>DI</i>) (<i>AI</i>) 1 × 3.282 (<i>EH</i>) 1 × 3.328 (<i>EH</i>) 1 × 3.408 (<i>DH</i>) 1 × 3.472 (<i>AH</i>) 2 × 3.510 (<i>D'I</i>) (<i>A'I</i>) 1 × 3.519 (<i>D'H</i>) 1 × 3.580 (<i>A'H</i>) Average value = 3.411
Complete rutile unit-cell fragment	2 × 4.292 (<i>FH</i>) (<i>F'H'</i>) 4 × 4.373 (<i>FF'</i>) (<i>GG'</i>) (<i>HH'</i>) (<i>II'</i>) 2 × 4.735 (<i>GI</i>) (<i>G'I'</i>)	2 × 2.858 (<i>HI</i>) (<i>HI'</i>) 2 × 2.877 (<i>FG</i>) (<i>F'G'</i>)	1 × 3.250 (<i>D'I</i>) 1 × 3.408 (<i>D'H'</i>) 1 × 3.445 (<i>D'G</i>) 1 × 3.478 (<i>D'G'</i>) 1 × 3.502 (<i>D'F</i>) 1 × 3.510 (<i>D'I</i>) 1 × 3.519 (<i>D'H</i>) 1 × 3.610 (<i>D'F</i>) Average value = 3.465
GeO ₂ unit cell	8 × 4.402	4 × 2.865	8 × 3.426

CrVO₄-type structure reported by Matar *et al.* (1990), the Ga atoms adopted an octahedral coordination, whereas the As atoms were tetrahedrally coordinated and, in this new high-pressure structure, as in the rutile-type structure, all cations were octahedrally coordinated.

As the unit cell contains nine Ga/As atoms, five of them were located in one octahedral layer whereas the four remaining atoms occupy the octahedra in the adjacent layer. These two octahedral layers, represented in Fig. 2(*a*) and (*b*), form a repetitive period along **c**. Both layers were complementary in such a way that the filled octahedra of one layer were located on the empty octahedra of the adjacent one. Thus, this occupancy shows strong differences with those present in other HP silica polymorphs, including the rutile-type GeO₂ (see Fig. 3). A comparison with those structures can be found in Haines (2004) and Teter *et al.* (1998).

A structural search of similar compounds has shown that this structure is identical to β-MnSb₂O₆ (Vincent *et al.*, 1987) and can be described as ordered lacunary NiAs. A comparison

of the differences in the octahedral filling can be found in Teter *et al.* (1998).

Although the differences between the structure of this new phase and that of rutile are evident, an analysis of the cation distribution allows us to recognize fragments of the structure of rutile in this high-pressure phase. These rutile-like fragments can be seen in Fig. 4 in which four unit cells of GaAsO₄ have been drawn. As can be seen, there are infinite two-dimensional blocks running parallel to [110]. These blocks contain As and Ga atoms which are linked by hypothetical bonds when distances similar to those shown by the Ge atoms in isoelectronic GeO₂ (rutile; Yamana *et al.*, 2000) are taken into account. These blocks are divided in three types of fragments which will be identified by the atoms labelled with letters in Fig. 4.

All these fragments contains at least one (100) plane of a rutile-like unit cell and additional atoms, which correspond to the atom that centers the tetragonal unit cell of the rutile structure. By comparing Table 3 and Fig. 4 it can be seen that the topology and the cation–cation distances compare well with the GeO₂ structure. The greatest deviation is shown by the Ga–Ga distance (5.109 Å), which deviates by ca 16% from the expected value of 4.402 Å in GeO₂. Moreover, the *F*, *G*, *H*, *I* and *D* atoms

(Fig. 4) form columns of complete rutile unit cells running parallel to the *c* axis of the *P3* structure. One of these complete rutile unit cells is represented in Fig. 5.

For further information see Table 3. This complete unit cell bears a strong resemblance to that of the CaCl₂ form of GeO₂ observed at high pressure (Haines, Leger, Chateau & Pereira, 2000).

The average values of the distances defining this unit cell are 4.443 and 2.867 Å, *cf.* the unit-cell axis of the GeO₂ structure (*a* = 4.402 and *c* = 2.865 Å).

It should be noted that besides the cation–cation distances quoted in Table 3, other short contacts exist (around 2.90 Å). These additional contacts connect atoms belonging to two adjacent blocks. For example, the contacts between the *C* atom of the labelled block and both the *G* and *I* atoms of the lower block, or the contacts between the *A* and *B* atoms and the *E* atom of the upper block. Similar contacts can be found between parallel blocks in Fig. 4. These inter-block contacts have not been drawn in the figure because the arrangement of

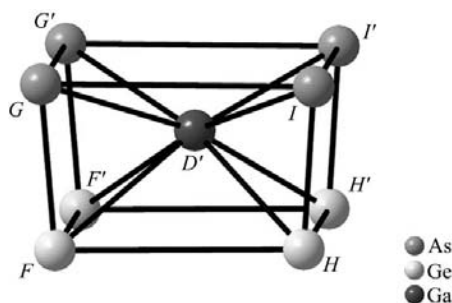


Figure 5
Complete rutile-like unit-cell fragment present in the $P3$ GaAsO_4 structure. The average values of the distances defining this ‘unit cell’ (4.443 and 2.867 Å) are similar to the unit-cell axis of GeO_2 ($a = 4.402$ and $c = 2.867$ Å).

the involved atoms does not correspond to the topology of the rutile structure. Moreover, the absence of lines connecting these atoms serves to separate the rutile-like blocks.

An interesting question is whether these blocks can be displaced with respect to each other by a simple mechanism (known as a crystallographic shear) leading to the reconstruction of the entire rutile structure, which is the final step in the phase transition under pressure. The answer to this question is that such a mechanism exists and that the rutile structure can be constructed by displacement of adjacent blocks by $\frac{1}{2}c$. This crystallographic shear is considered to involve only the cation substructure, because the oxygen substructure remains unaltered. This pure cation displacement mechanism may well require thermal activation. Recall that in both the rutile structure and the new phase described here, the O atoms form a hexagonal closed-packed arrangement. This is also the case for the high-pressure forms (monoclinic $P2_1/c$, orthorhombic CaCl_2 and $\alpha\text{-PbO}_2$ -type found for SiO_2 and GeO_2 at high pressure; Haines & Cambon, 2004; Stephens, 1999; Haines *et al.*, 2000; Kingma *et al.*, 1995; Haines, Leger, Gorelli & Hanfland, 2001; Haines, Leger & Chateau, 2000; Brazhkin *et al.*, 2000; Dubrovinsky *et al.*, 1997; Andrault *et al.*, 1998; Prakabanka *et al.*, 2003, 2004; Dubrovinsky *et al.*, 2004).

The proximity of this new structure to that of rutile is also justified by the values of their respective volumes per formula unit. Thus, this new high-pressure phase has a volume per formula unit of 56.94 \AA^3 , a value which is intermediate between two high-pressure varieties of this compound, the CrVO_4 (69.03 \AA^3) and rutile-type (53.78 \AA^3) structures, even though the value is closer to the latter. Consequently, this hexagonal phase could be considered as the preceding high-pressure step before obtaining the rutile-type structure. Therefore, according to the investigations of Matar *et al.* (1990), GaAsO_4 at high pressures would follow the sequence quartz \rightarrow monoclinic (structure unknown) \rightarrow $\text{CrVO}_4 \rightarrow P3 \text{ GaAsO}_4 \rightarrow$ rutile-type structure. The $P3$ structure type represents a new step in this high-pressure phase-transition

sequence. GaAsO_4 may thus provide a model for other ABO_4 compounds.

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