



A new polymorph of GaAsO₄

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ABSTRACT

At room temperature, the compound GaAsO₄ (gallium arsenate) has a berlinite type structure (AlPO₄, *P3₁21*) and it is the only normal pressure polymorph reported as occurring at all temperatures. By means of a gaseous phase route, GaAsO₄ was obtained in a structure homeotypic with α -cristobalite and was retained at room temperature. Structural Rietveld refinement of this new GaAsO₄ polymorph was performed based on space group *C222₁* and refined lattice parameters are $a = 7.0592 \text{ \AA}$, $b = 7.0893 \text{ \AA}$, $c = 7.0977 \text{ \AA}$. Heating up to 1000 °C the α -cristobalite homeotype transforms to the stable berlinite type structure and it would invert to the β -cristobalite homeotype at about 530 °C.

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1. Introduction

At atmospheric pressure, the compound GaAsO₄ (gallium arsenate) has a berlinite type structure (AlPO₄, *P3₁21*). Berlinite structure is a homeotype of α -quartz (low temperature SiO₂, *P3₁21*) and it is adopted by several ternary oxides A³⁺B⁵⁺O₄. Normally for this structure, a cationic order is adopted. Therefore, space groups compared to SiO₂ could be different.

These compounds may also exhibit SiO₂ polymorphism including the occurrence of high pressure phases. The well known structural transitions in SiO₂ at atmospheric pressure [1] are briefly schematized in Fig. 1. Starting from α -quartz and upon heating, the sequence of phases horizontally indicated is obtained. Usually, β -tridymite is “skipped” and by quenching it is possible to retain high temperature phases at room temperature. By rapid cooling from β -tridymite or β -cristobalite, the corresponding α -phases could be obtained as indicated vertically in Fig. 1. All α - β transformations (inversions) are displacive, while the other ones are reconstructive.

In the case of GaAsO₄, the berlinite type structure is maintained up to 1030 °C, which is the temperature of decomposition of the compound in As₂O₅ and Ga₂O₃ [2]. Therefore, the berlinite structure is the

only GaAsO₄ polymorph reported at normal pressure as occurring at all temperatures.

2. Experimental

2.1. Synthesis of the new GaAsO₄ polymorph

An unknown phase of GaAsO₄ was reported in a previous article as occurring at room temperature [3]. In the present work, the structure of this polymorph is resolved and refined.

As previously reported [3], reaction of GaAs with a Cl₂(g)-O₂(g) mixture at 500 °C allowed to obtain a crystalline phase of GaAsO₄ composition which cannot be identified as the stable berlinite type structure from X-ray diffraction analysis. Experimental procedure was not able to yield a total mass of product greater than 5–8 mg and controlling of secondary phase presence is not easily reproducible. Other synthesis routes are currently considered in order to obtain a single phase sample. These ones include the design of a set up to achieve adequate controlled vapor pressure (CVP) conditions.

2.2. X-ray diffraction measurement

X-ray powder diffraction pattern was obtained in a Rigaku diffractometer, model D-Max III C, equipped with Ni filtered CuK α radiation and scintillation detector. Sample was mounted in a glass holder, 2 θ range was 10–90°, step size and counting time were fixed to 0.02° and 6 s, respectively.

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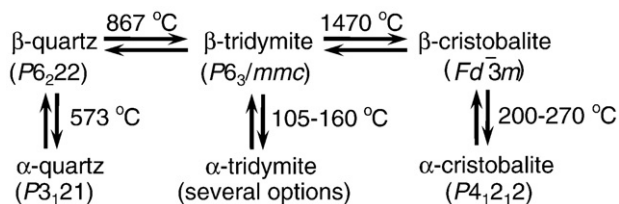


Fig. 1. SiO₂ polymorphism at 1 atm (space groups are indicated in parenthesis).

2.3. Thermal analysis

DTA measurements were performed on ~5 mg of sample, in a Shimadzu DTA-50 (Pt cells and Al₂O₃ as a reference) in N₂ flux (50 mL/min) and a heating rate of 10 °C/min from room temperature up to 1000 °C.

3. Results and discussion

From the X-ray diffractogram (see Fig. 2 below), the presence of weak reflections of GaAsO₄-berlinite (*P*3₁21, *a* = 5.059 Å, *c* = 11.424 Å, PDF No. 89-4432) and precursor GaAs (*F*4̄3*m*, *a* = 5.654 Å, PDF No. 32-0389) is observed. The main XRD reflections correspond to the new GaAsO₄ phase which can be indexed according to the α-cristobalite homeotype structure (space group *C*222₁). Structural Rietveld refinement was performed with Fullprof 2000 software [4] upon the X-ray diffractogram after subtraction of amorphous-like background which, considering the low sample amount, corresponds to glass holder signal. Profile function was pseudo-Voigt type. Due to the scattering factors for As⁵⁺ not being tabulated, Ge⁴⁺ scattering factor was used.

Fig. 2 shows the Rietveld refinement and Table 1 summarizes the crystallographic parameters [5].

In spite of berlinite-ABO₄ oxides resembling the polymorphism of silica including high pressure behavior, high pressure structures were not taken into account as candidates for Rietveld analysis of the new room pressure phase of GaAsO₄. Although the possibility of retaining a high pressure phase at room pressure cannot be discarded a priori, other orthorhombic- *C* structures like CrVO₄-type (*Cmcm*), which was reported for high pressure GaAsO₄ [6] was not retained at a normal pressure. This behavior seems to be that of the other silica like-ABO₄ structures. For example, GaPO₄ transforms with applied pressure from α-cristobalite homeotype (*C*222₁) to CrVO₄-type (*Cmcm*) by a displacive mechanism [7]. Therefore, reversibility would be favored. This was confirmed by more recent studies [8] because CrVO₄-type for GaPO₄ is

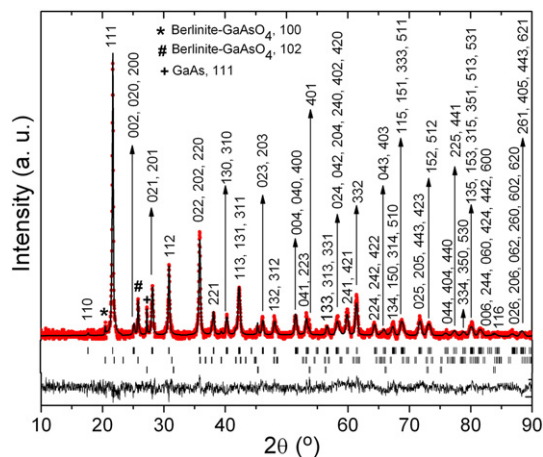


Fig. 2. Observed (points), calculated (line) and difference XRD patterns. Vertical marks show Bragg reflections for (from top to bottom): new GaAsO₄ phase, berlinite-GaAsO₄ and GaAs.

Table 1
Refined parameters for the new GaAsO₄ phase (α-cristobalite homeotype).

Crystal System	Orthorhombic
Space group	<i>C</i> 222 ₁ (No. 20)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.0592 (11), 7.0893 (2), 7.0977 (2)
<i>V</i> (Å ³)	355.20 (6)
<i>Z</i>	4
Density (g cm ⁻³)	3.90023 (6)
As: 4 <i>a</i> (<i>x</i> , 0, 0), <i>x</i>	0.3232 (12)
Ga: 4 <i>b</i> (0, <i>y</i> , ¼), <i>y</i>	0.1787 (12)
O1: 8 <i>c</i> (<i>x</i> , <i>y</i> , <i>z</i>)	0.1780 (6), 0.0030 (7), 0.2087 (8)
O2: 8 <i>c</i> (<i>x</i> , <i>y</i> , <i>z</i>)	0.4573 (6), 0.2126 (5), 0.9963 (8)
<i>R</i> _{exp}	24.1%
<i>R</i> _{wp}	27.6%
χ ²	1.31
Typical average bond lengths (Å)	Ga–O = 1.864 (7) As–O = 1.790 (6)
Additional phases amounts (wt.%)	GaAsO ₄ (berlinite type): 9 GaAs: 3

not retained at a normal pressure. The structures involved on the GaPO₄ (*C*222₁) D = GaPO₄ (*Cmcm*) transformation are easily taken apart by X-ray powder diffraction [8] because the X-ray diffractograms of both phases are different. Even though the X-ray of GaAsO₄ (*Cmcm*) was not reported at reference [6], the same difference with that of GaAsO₄ (*C*222₁) should be expected. However, a direct proof was made and it was verified that *Cmcm* space group does not fit the experimental X-ray diffractogram. Therefore the new GaAsO₄ polymorph is well described by *C*222₁ space group.

It has been pointed out that Ga–O and As–O bond lengths in gallium arsenate were inaccurately determined by X-ray diffraction [9]. It is due to the fact that Ga³⁺ and As⁵⁺ are isoelectronic species. Therefore, both the X-ray scattering factors are very similar [9]. Then, Ga³⁺ and As⁵⁺ are not distinguishable by X-ray diffraction techniques (laboratory and synchrotron modalities). Such is the case of the values determined here, which are greater than those predicted from Shannon and Prewitt's ionic radii [10] (Ga–O = 1.82 Å, As–O = 1.68 Å).

Among A³⁺B⁵⁺O₄ oxides such as AlPO₄ and GaPO₄, the α-quartz homeotype (berlinite type) is the stable structure. For these systems, the α-cristobalite homeotype can be obtained and retained as a metastable phase at room temperature by means of high temperature annealing (1300 °C [11]) and subsequent quenching. This thermal treatment allows obtaining the β-cristobalite homeotype as a precursor before cooling, according to the mentioned thermal behavior of SiO₂ as described in Fig. 1. For some A³⁺B⁵⁺O₄ ternary oxides, very high temperatures for the α → β-quartz homeotype transformation were theoretically predicted [12] (AlAsO₄: 1140 °C, GaPO₄: 1656 °C, GaAsO₄: 1503 °C). For each case, a specific alternative process may occur during heating α-quartz homeotype, either transformation

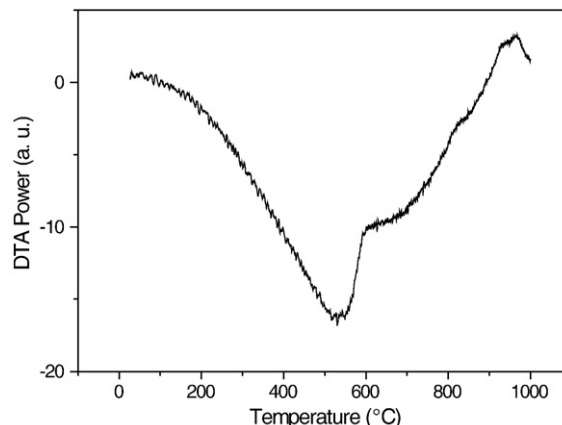


Fig. 3. DTA measurement upon the new GaAsO₄ polymorph.

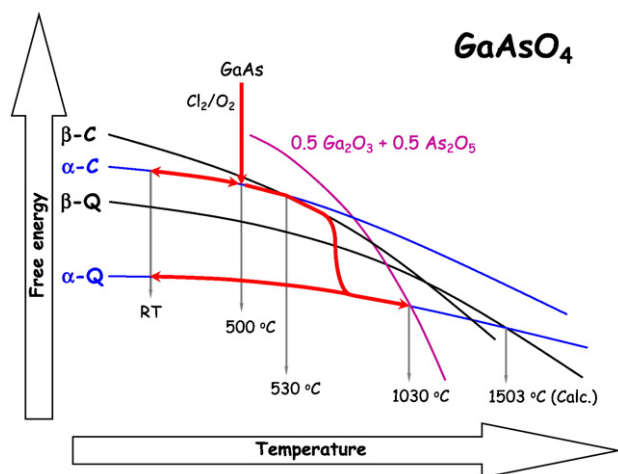


Fig. 4. Scheme of the hypothetical relative stability of the different GaAsO₄ polymorph as a function of temperature. The route of synthesis and thermal behavior of the new GaAsO₄ polymorph is presented. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

to the β -cristobalite homeotype (GaPO₄, 933 °C [12], 960 °C [13]) or chemical decomposition (AlAsO₄: 950 °C [12], GaAsO₄: 1030 °C [2]). Then, for the case of the GaAsO₄ system at atmospheric pressure, berlinite-GaAsO₄ type is reported as the thermodynamically stable phase up to its decomposition temperature.

Fig. 3 shows the result of the DTA measurement upon mixture containing the new GaAsO₄ polymorph. It is the main phase according to Table 1. At least one endothermic event is observed at about 530 °C. The XRD pattern (not shown) of the sample subsequently cooled at room temperature exhibited the absence of the new polymorph and the almost full presence of berlinite-GaAsO₄. This thermal behavior is compatible with that of GaPO₄ for which the α -cristobalite homeotype inverts during heating to the β -cristobalite homeotype (605 °C) and further, above 700 °C, relaxes to the α -quartz homeotype [13].

4. Conclusions

For GaAsO₄, as a member of A³⁺B⁵⁺O₄ ternary oxides potentially exhibiting silica polymorphism, the temperatures of all reconstructive transitions as indicated in Fig. 1 should be greater than the decomposition temperature. Therefore, a traditional thermal route to obtain the α -cristobalite homeotype is not feasible. On the contrary, it can be concluded that the gaseous phase synthesis [3] is a route which allowed obtaining the α -cristobalite homeotype of GaAsO₄ directly as a metastable phase at 500 °C, and also retained at room temperature. Thermal features shown in Fig. 3 could indicate at 530 °C the $\alpha \rightarrow \beta$ -cristobalite homeotype inversion. The further transformation

to stable berlinite-GaAsO₄ is observed after DTA measurement up to 1000 °C. It must be due to a thermal relaxation during heating above 530 °C.

This hypothetical behavior is schematized in Fig. 4. In this figure, the free energy of the different phases considered is qualitatively represented as a function of temperature. As observed, the relative stability decreases as y-axis increases in agreement with the features of Fig. 1. The α -cristobalite homeotype (new GaAsO₄ polymorph) could be metastable from RT up to temperatures between 530 and 1030 °C [2]. In this temperature range, the relaxation to the α -quartz homeotype (berlinite-GaAsO₄) occurs as indicated with the thick line (red in color version) that joins the curves of relative stability of new GaAsO₄ polymorph and berlinite-GaAsO₄. Finally, the figure presents the no viability of the formation of the β -quartz homeotype as a precursor of the new GaAsO₄ polymorph due to the decomposition of berlinite-GaAsO₄ into the individual Ga₂O₃-As₂O₅ oxides.

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