

The crystal structure of AlAsO_4 at high pressure

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Abstract. Single-crystal structure determinations of the low-temperature quartz modification of AlAsO_4 were performed up to 4.87(7) GPa.

The refinements were carried out in space groups $P3_121$ and $P3_221$, respectively. At ambient conditions the lattice parameters are $a = 5.028(4)$ Å and $c = 11.228(3)$ Å. They decrease to $a = 4.800(3)$ Å and $c = 11.001(3)$ Å at 4.87(7) GPa.

The high pressure behaviour of AlAsO_4 is similar to that of the homeotypic compounds quartz and GeO_2 and to that of the isotypic compound AlPO_4 . With increasing pressure the c/a axial ratio increases, the AlO_4 and AsO_4 tetrahedra become more and more distorted. The decreasing (Al–O–As) angles indicate a cooperative tilting of the tetrahedra.

From the shortening of intertetrahedral O–O distances and the changes of the shape of the Dirichlet domains of the oxygen anions, it can be concluded that the oxygen packing changes with increasing pressure in the direction of an arrangement corresponding to a cubic body-centered lattice. As in the case of SiO_2 , GeO_2 and AlPO_4 it is mainly this effect which is responsible for the high-pressure behaviour of AlAsO_4 . The structural changes of AlAsO_4 at high temperature can be explained in an analogous way.

Introduction

The crystal structure of the low-temperature quartz modification of AlAsO_4 has been determined several times (Machatschki, 1936; Goiffon, Bayle, Astier, Jumas, Maurin and Philippot, 1983; Baumgartner, Behmer and

Preisinger, 1989). At ambient conditions AlAsO_4 crystallizes in the space group $P3_121$ or in the enantiomorphic space group $P3_221$. The crystal structure is analogous to that of quartz but the ordered distribution of the Al^{3+} and As^{5+} ions leads to a doubling of the lattice constant c .

The effect of temperature on the crystal structure of AlAsO_4 has been studied by Goiffon et al. (1983) at 173 K, by Goiffon, Jumas, Maurin and Phillippot (1986) at 373 K, and by Baumgartner et al. (1989) at 793 K and 1043 K. AlAsO_4 differs from AlPO_4 and quartz in that it shows no displacive $\alpha - \beta$ transformation¹. It decomposes at temperatures above 1400 K (Kosten and Arnold, 1980).

The effect of pressure on the crystal structure of quartz has been studied on single crystals by several groups (d'Amour, Denner and Schulz, 1979; Levien, Prewitt and Weidner, 1980; Glinnemann, 1987; Hazen, Finger, Hemley and Mao, 1989); the dependence of the structure on high temperature and high pressure has been determined by Ogata, Takéuchi and Kudoh (1987). Glinnemann, King, Schulz and Hahn (1990) investigated the structural changes of single crystals of trigonal GeO_2 , which is a high pressure model of quartz, and Jorgensen (1978) reported high-pressure crystal-structure refinements of SiO_2 and GeO_2 using neutron powder-diffraction data.

All compounds crystallizing with the α -quartz structure-type show high compressibilities which can be explained with the polyhedral approach of Hazen and Finger (1982) by a cooperative tilting of the tetrahedra. At the same time, however, the tetrahedra become more and more distorted when pressure is applied. These distortions cannot be explained by the polyhedral approach.

Another way to explain the high-pressure behaviour of quartz-type structures is to interpret the structural changes by changes of the oxygen packings. As shown by Sowa (1988), under high pressure in the low-temperature quartz structure-type the oxygen packing alters in the direction of an arrangement corresponding to a cubic body-centered lattice. These changes imply the tilting as well as the distortions of the tetrahedra.

There have been no single crystal investigations on AlAsO_4 at high pressure reported yet. But it is known that as in the case of SiO_2 where stishovite occurs as high-pressure phase a rutile-type high-pressure form of AlAsO_4 exists. Young, Sclar and Schwartz (1963) synthesized this modification at 9 GPa and 900°C. For GeO_2 the rutile structure-type is stable at ambient conditions.

The structure of AlPO_4 which shows close relationship to the α -quartz structure has already been investigated at high pressure (Sowa, Macavei and Schulz, 1990). The purpose of the present study was to determine the structure of AlAsO_4 , whose averaged cation size lies between that of SiO_2

¹ α -quartz = low-temperature quartz; β -quartz = high temperature quartz.

and GeO_2 at high pressure, and to ascertain the corresponding changes of the oxygen packing.

Experimental

Specimen

Synthetic Fe^{3+} doped AlAsO_4 crystals were kindly supplied by Prof. Lehmann (Münster). The crystals have been synthesized as described by Krauß and Lehmann (1975). The doping levels of Fe^{3+} was below 1% and should not have any influence on the crystal structure. The starting dimensions of the crystal used were approximately $1.5 \times 1.5 \times 3 \text{ mm}^3$. A thin cut parallel to $(\bar{1}20)$ was prepared with a thickness of $40 \mu\text{m}$. The crystal fragments used for the structure determinations had sizes of approximately $80 \times 100 \times 40 \mu\text{m}^3$.

Data collections

All measurements were carried out on an automated ENRAF-NONIUS CAD4 four-circle diffractometer using monochromatized MoK_α radiation.

At ambient conditions diffraction data of an AlAsO_4 crystal were first collected outside the diamond cell by the ω -scan technique. The fixed- ϕ mode (Finger and King, 1978) was used, and only those reflections that would be measured within the pressure cell were collected. This allows a comparison of this measurement and those performed at high pressure.

To find out systematic errors caused by the pressure cell, room-pressure data were also collected within the diamond-anvil cell. Because the crystal used in the first measurement was lost, another crystal of nearly the same dimensions was used.

The high-pressure investigations were carried out in a Merrill-Bassett type high-pressure cell (Merrill and Bassett, 1974). The crystal was fixed with silicone grease onto one of the diamond anvils. An Inconel 718 type gasket was employed which was preindented to $120 \mu\text{m}$. The $300 \mu\text{m}$ hole was obtained by spark erosion (Ahsbahs, 1984). A 4:1 mixture of methanol:ethanol was used as the pressure transmitting liquid (Piermarini, Block and Barnett, 1973) and a ruby splinter was inserted for the pressure calibration (Barnett, Block and Piermarini, 1973; Piermarini, Block, Barnett and Forman, 1975). The estimated error in pressure was $\pm 0.07 \text{ GPa}$. Following the data collection at 1.81 GPa the crystal moved slightly when a pressure of 3 GPa was applied. While reloading the pressure cell, the crystal was lost and another one of nearly the same size was used for the measurements at higher pressures. For centering of the crystal the method of Hamilton (1974) modified by King and Finger (1979) was applied.

Table 1. Details of data collections.

P/GPa	$\theta_{\max}/^\circ$	Number of intensity data				R_{int}	R_w	R
		meas.	used	independent				
				all	$F > 3\sigma(F)$			
0.0001	30	943	943	429	426	2.81	2.73	2.61
0.0001 MB-cell	30	894	835	337	312	3.07	3.58	4.34
1.81	30.5	938	859	388	358	3.65	4.92	5.45
2.99	31	916	856	386	351	3.61	4.05	5.26
4.87	31.5	924	857	422	373	3.63	4.24	6.20

$$R_{\text{int}} = \left(\frac{\sum_1^N \left\{ M \sum_1^N [w(\bar{F}_N - F_M)^2] \right\}}{\sum_1^N \left[(M-1) \sum_1^N w F_M^2 \right]} \right)^{1/2}$$

N = number of independent reflections

M = number of symmetrically equivalent reflections

$$R = \frac{\sum |F_v| - |F_c|}{\sum F_v}$$

$$R_w = \left(\frac{\sum_w (|F_v| - |F_c|)^2}{\sum_w F_v^2} \right)^{1/2}$$

Intensity data were collected by the ω -scan technique with the fixed- ϕ mode at four pressures, including ambient pressure, up to a maximum of 4.87 GPa. At room pressure, intensities of all accessible reflections up to $\theta = 30^\circ$ were collected. In order to always get the same number of reflections the θ range was stepwise extended to 31.5° at 4.87 GPa. The counting times were up to 5 min for the main reflections (hkl with $l = 2n$) and up to 8 min for the superstructure reflections (hkl with $l = 2n + 1$).

Details of the data collections are summarized in Table 1.

Data reduction

All reflections which were shadowed by parts of the steel gasket as well as those overlapping with reflections of the diamonds or the ruby crystal were omitted. Also, reflections coinciding with beryllium or steel powder rings were removed.

The intensities of the reflections measured in the pressure cell were corrected by the method of Hazen (1976), and Finger and King (1978) with

respect to the absorption of the incident and diffracted X-ray beams in the diamond anvils and the beryllium parts of the cells.

Finally, corrections for the Lorentz- and polarization effects were applied.

Structure refinements

For the structure refinements the program SHELX76 (Sheldrick, 1976) was used. For reflections with $F > 3\sigma(F)$ measured outside the pressure cell, a weighting scheme of $1/\sigma(F)^2$ was used, for those measured inside the pressure cell it was $1/(\sigma^2(F) + 0.0002F^2)$. All other reflections were given small weights. Atomic form factors for neutral atoms were used (International Tables IV, 1974).

By taking into consideration anomalous scattering effects (International Tables IV, 1974) it could be seen that the structures of the crystals studied at room pressure and at 1.81 GPa correspond to a left hand quartz. They were refined in space group $P3_221$. The crystal used at 2.99 and 4.87 GPa showed the enantiomorphic structure which was refined in space group $P3_121$.

A refinement of the structure at ambient conditions with the program Prometheus (Zucker et al., 1983, modified by Belzner, 1987) showed that Dauphinée twinning can be neglected (twin fraction 99.8%). At higher pressures the twin fractions remained unchanged. The twin fractions of Brazil twins were about 10–20%. In the following only the atomic parameters in spacegroup $P3_121$ are given for comparison.

The oxygen atoms occupy two symmetrically different positions 6(c) x, y, z . The Al and P atoms lie on positions 3(a) $x, 0, 1/3$ and 3(b) $x, 0, 5/6$, respectively. At ambient conditions the positional parameters and anisotropic temperature factor coefficients refined from the data collected without a high pressure cell are in good agreement with the results of Goiffon et al. (1983) and Baumgartner et al. (1989)². However, the latter authors reported values of the tensor components U_{33} for all atoms which are up to twice the values yielded in this work. Due to the low precision of the anisotropic thermal parameters refined from the data collected at high pressure only the isotropic ones are reported here. The parameters refined from the data measured at ambient conditions in the high-pressure cell are in close agreement with those measured without a pressure cell.

The results of the refinements are summarized in Table 2.

² Anisotropic thermal parameters refined from data collected outside the pressure cell and $F_o - F_c$ lists can be ordered referring to the no. CSD 55012, name of the author and the citation of the paper at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

Table 2. Unit cell parameters and atomic parameters of AlAsO₄ at various pressures (GPa).

Pressure	0.0001	0.0001 MB-cell	1.81	2.99	4.87
$a/\text{\AA}$	5.028(4)	5.030(3)	4.945(4)	4.873(3)	4.799(3)
$c/\text{\AA}$	11.228(3)	11.234(3)	11.135(4)	11.071(4)	11.003(3)
c/a	2.2331	2.2334	2.2518	2.2719	2.2928
$V/\text{\AA}^3$	245.8(5)	246.2(4)	235.6(5)	227.7(4)	219.4(5)
Al x	0.4586(3)	0.4584(6)	0.4529(8)	0.4485(7)	0.4460(7)
$U/\text{\AA}^2$	0.0091(2)	0.0087(4)	0.0117(5)	0.0097(4)	0.0097(4)
As x	0.4574(1)	0.4576(2)	0.4517(3)	0.4453(2)	0.4404(2)
$U/\text{\AA}^2$	0.0078(2)	0.0075(2)	0.0082(3)	0.0080(2)	0.0080(2)
O1 x	0.4072(7)	0.406(1)	0.403(2)	0.401(1)	0.396(1)
y	0.2968(6)	0.296(1)	0.305(1)	0.312(1)	0.317(1)
z	0.3861(2)	0.3864(3)	0.3837(4)	0.3822(3)	0.3802(3)
$U/\text{\AA}^2$	0.0142(5)	0.0152(9)	0.013(1)	0.0118(9)	0.012(1)
O2 x	0.4040(7)	0.401(1)	0.395(2)	0.393(1)	0.389(1)
y	0.2837(6)	0.284(1)	0.294(1)	0.299(1)	0.306(1)
z	0.8804(2)	0.8803(3)	0.8774(4)	0.8757(3)	0.8740(3)
$U/\text{\AA}^2$	0.0137(5)	0.0149(9)	0.014(1)	0.0109(9)	0.0101(9)

Parenthesized figures represent e.s.d.'s.

Results

The pressure dependence of the lattice constants can be expressed by

$$a = a_0 - d_1 P + d_2 P^2.$$

For AlAsO₄ it has been calculated:

$$a = 5.03(1) - 0.06(1) P + 0.002(3) P^2$$

$$c = 11.23(1) - 0.06(1) P + 0.003(2) P^2$$

with a and c in \AA and P in GPa.

As in the α -quartz modifications of SiO₂, GeO₂ and AlPO₄ the lattice constant a is more compressible than c . The cell edge compressibilities are not linear with pressure, whereas the increase in the c/a ratio is nearly linear. In Fig. 1 the dependence of c/a ratio on the pressure is represented. In all following figures only the data of SiO₂ and GeO₂ from Levien et al. (1980) and Glinnemann et al. (1990), respectively, are included. These data are more precise than the data from other measurements. In all these figures $c/2a$ is given for AlAsO₄ and AlPO₄.

The bulk modulus of AlAsO₄ in 36 GPa (Birch-Murnaghan equation of state with $k' = 4$). The compressibility is similar to those of quartz, GeO₂

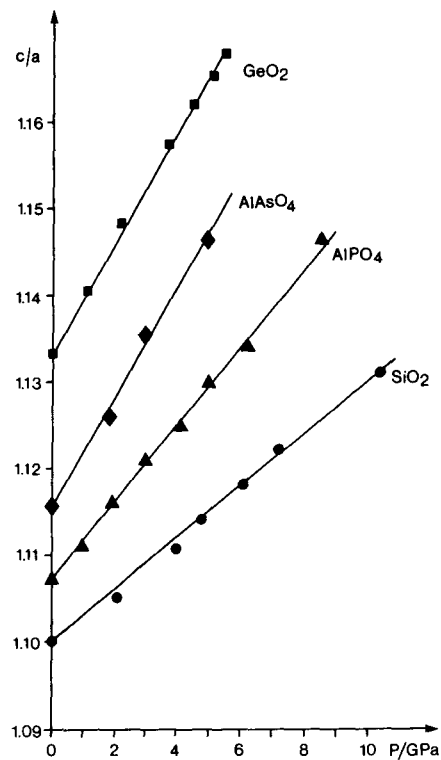


Fig. 1. c/a ratios of SiO₂, GeO₂, AlPO₄, and AlAsO₄ versus pressure. For AlPO₄ and AlAsO₄ $c/2a$ is given.

and AlPO₄, the bulk moduli of which are 42 GPa, 39 GPa and 36 GPa, respectively (calculated from the data of Glinnemann et al., 1990 and Sowa et al., 1990).

The shifts of the oxygen position parameters in AlAsO₄ with increasing pressure are analogous to the shifts of the corresponding coordinates in SiO₂ and GeO₂. Fig. 2 shows the oxygen positions in quartz-type structures of SiO₂, GeO₂ and AlAsO₄ versus c/a ratio. Due to the ordering of Al and As atoms in AlAsO₄ the oxygen atoms occupy two symmetrically different positions. The different sizes of the AlO₄ and AsO₄ tetrahedra give rise to the deviations of the oxygen positions from the coordinates of the oxygen atoms in SiO₂/GeO₂.

Bonding distances and angles are given in Table 3. The decrease of the Al–O–As angles under pressure is clearly visible, indicating that cooperative tilting of the tetrahedra takes place. The same effect has been found in SiO₂, GeO₂ and AlPO₄ at high pressures, where reductions of the Si–O–Si, Ge–O–Ge, and Al–O–P angles, respectively, occur.

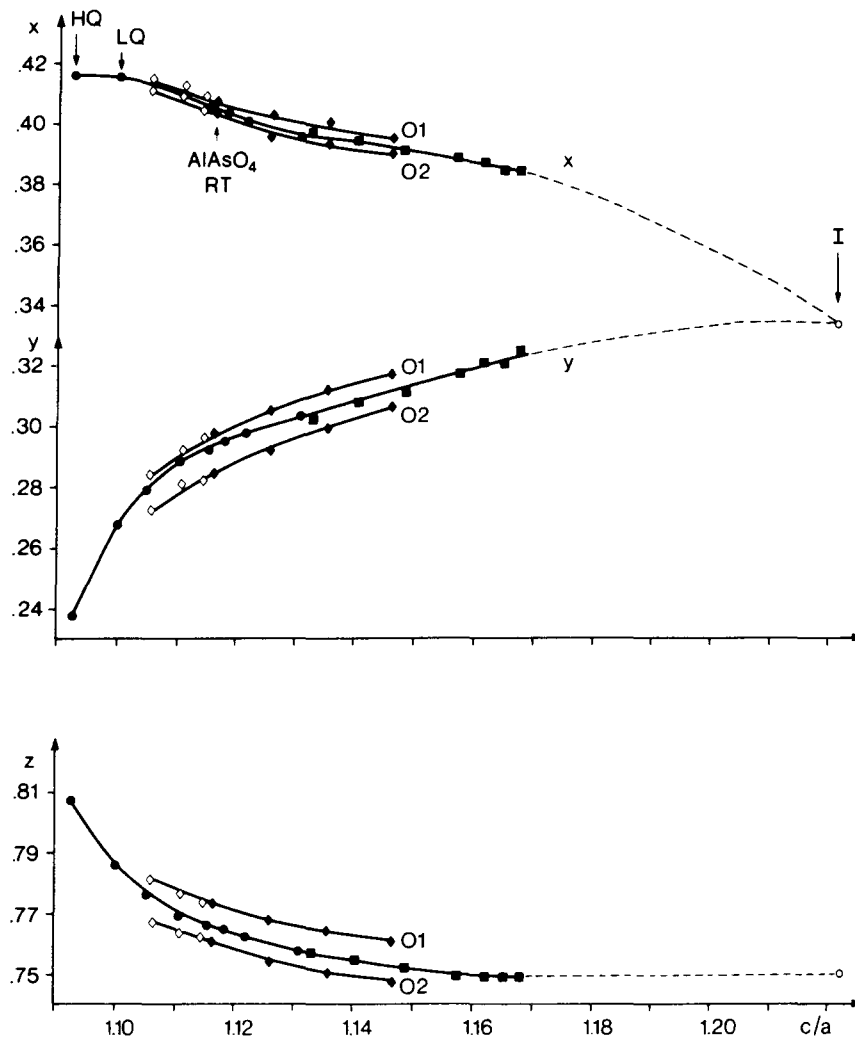


Fig. 2. Oxygen positions in quartz and quartz-type structures of GeO_2 and AlAsO_4 versus c/a ratio. HQ = high-temperature quartz (data from Wright and Lehmann, 1981), LQ = low-temperature quartz, $I = I$ lattice. $\bullet = \text{SiO}_2$, $\blacksquare = \text{GeO}_2$, $\blacklozenge = \text{AlAsO}_4$ (high pressure), $\diamond = \text{AlAsO}_4$ (high temperature, data from Goiffon et al., 1986, and Baumgartner et al., 1989), RT = room temperature. For AlAsO_4 $c/2a$ is given and the coordinate z is doubled.

From the altering of the tetrahedral O–O distances and the O–Al–O and O–As–O angles it can be seen that in AlAsO_4 the tetrahedra become more and more distorted when pressure is applied.

Table 3. Bond distances (Å) and angles (°) of AlAsO₄ at various pressures (GPa).

Pressure	0.0001	0.0001 MB-cell	1.81	2.99	4.87
Al—O1	1.741(3)	1.743(6)	1.742(7)	1.734(5)	1.735(5)
Al—O2	1.751(3)	1.752(4)	1.748(5)	1.746(5)	1.738(5)
O2—O1	2.803(4)	2.800(7)	2.776(8)	2.756(6)	2.738(7)
O2—O1	2.886(4)	2.900(7)	2.916(8)	2.914(6)	2.922(6)
O2—O2	2.883(5)	2.876(8)	2.863(9)	2.861(7)	2.858(7)
O1—O1	2.843(5)	2.843(9)	2.846(11)	2.843(9)	2.830(10)
O1—Al—O1	109.5(2)	109.3(4)	109.6(5)	110.1(4)	109.3(4)
O2—Al—O2	110.9(2)	110.3(6)	109.9(4)	110.0(3)	110.6(3)
O1—Al—O2	111.5(1)	112.1(2)	113.3(3)	113.7(2)	114.6(2)
O1—Al—O2	106.8(1)	106.5(2)	105.4(2)	104.7(2)	104.1(2)
As—O1	1.669(2)	1.668(4)	1.666(5)	1.665(4)	1.672(4)
As—O2	1.664(3)	1.676(5)	1.685(6)	1.667(5)	1.668(5)
O2—O1	2.697(4)	2.712(7)	2.706(8)	2.678(6)	2.673(7)
O2—O1	2.757(4)	2.770(7)	2.789(8)	2.780(8)	2.800(8)
O2—O2	2.687(5)	2.691(9)	2.700(11)	2.690(9)	2.699(9)
O1—O1	2.733(5)	2.726(8)	2.721(9)	2.712(7)	2.715(7)
O1—As—O1	109.9(2)	109.6(3)	109.5(4)	109.1(3)	108.6(3)
O2—As—O2	107.7(2)	106.8(4)	106.5(4)	107.6(3)	108.0(3)
O1—As—O2	111.6(1)	111.9(3)	112.7(3)	113.2(2)	113.9(2)
O1—As—O2	108.0(1)	108.4(2)	107.8(2)	107.0(2)	106.3(2)
Al—O1—As	135.6(2)	135.6(3)	132.7(4)	130.9(3)	128.4(3)
Al—O2—As	134.8(2)	134.0(3)	130.3(4)	129.0(3)	126.9(3)

Parenthesized figures represent e.s.d.'s.

Comparing room-temperature and low-temperature data of several compounds with quartz and isotypic or homeotypic structures Goiffon et al. (1983) found that the higher the c/a ratio the more distorted are the tetrahedra. The authors suppose that the c/a ratio is a measure for the distortion of the quartz structure. This assumption is confirmed in high-pressure structural investigations on SiO₂, GeO₂, AlPO₄, and AlAsO₄ which show increasing distortions of the tetrahedra with increasing c/a ratios.

Discussion

As has been shown for the quartz-type structures of SiO₂, GeO₂ and AlPO₄ (Sowa, 1988, Sowa et al., 1990) the high-pressure behaviour of AlAsO₄ is also characterized by changes of the oxygen packing. Such changes do not only occur at high pressure. Also increasing temperatures cause analogous structural variations which take an opposite direction as under high pressure. It can be seen in Fig. 2 that the oxygen positional parameters at 373 K

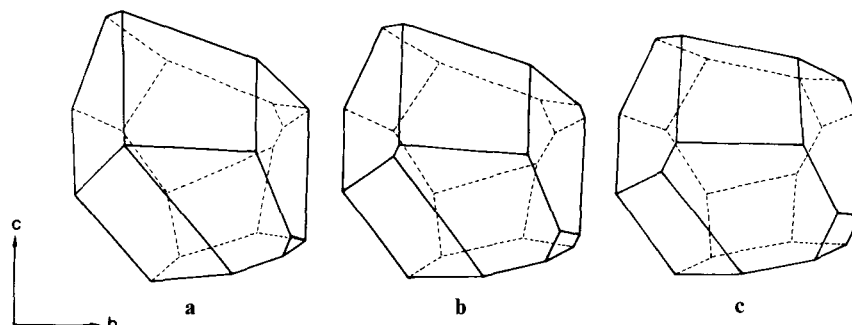


Fig. 3. Dirichlet domains of the oxygen anions O1 in AlAsO_4 (a) at 1023 K (Baumgartner et al., 1989), (b) at ambient conditions, (c) at 4.87 GPa.

(Goiffon et al., 1986), 773 K, and 1023 K (Baumgartner et al., 1989) lie on the same curves as the parameters at high pressures do.

Fig. 3 shows the resultant Dirichlet domains (calculated only with oxygen neighbours) of the oxygen atoms O1 at 1023 K, ambient conditions and 4.87 GPa, respectively. At high pressure these Dirichlet domains are similar to the polyhedra in GeO_2 , whereas at high temperatures a resemblance with the corresponding polyhedra in SiO_2 at low pressure can be noted (see Sowa, 1988). The polyhedra around O2 show nearly identical shapes as those around O1.

Changes of the oxygen packing can be recognized by looking at the O–O distances in quartz-type structures. Due to the different cation sizes the O–O distances in SiO_2 , GeO_2 and AlAsO_4 are not directly comparable. It is therefore necessary to standardize these structures. That can be done by calculating the distances in unit cells with $a = 1$ and c equal to the axial ratio. Figs. 4 and 5 show these normalized O–O distances in AlAsO_4 and $\text{SiO}_2/\text{GeO}_2$, respectively, versus the c/a ratio which is a measure for pressure. At low pressure, each oxygen atom in SiO_2 is surrounded by six others with nearly equal distances, whereas in AlAsO_4 each oxygen atom has six nearest oxygen neighbours with different distances. With increasing c/a ratio the number of neighbours increases, but the O–O distances are not of the same length. In Fig. 5 the connecting lines between the measuring points are extended to the corresponding distances in a cubic I lattice at $c/a = \sqrt{3}/\sqrt{2}$. In this case each oxygen atom would be surrounded by eight neighbours. As in GeO_2 and AlPO_4 at high pressures, intertetrahedral O–O distances in AlAsO_4 occur which are shorter than intratetrahedral distances. These displacements of the oxygen atoms imply tetrahedral distortions, because a cubic I lattice contains only flattened tetrahedra. Further increase in pressure should result in increasing distortions of the tetrahedra. High-pressure investigations on quartz-powder samples confirm the presumption that the cations would not tolerate such strongly distorted coordination polyhedra. Hemley, Jephcoat, Mao, Ming and Manghnani (1988)

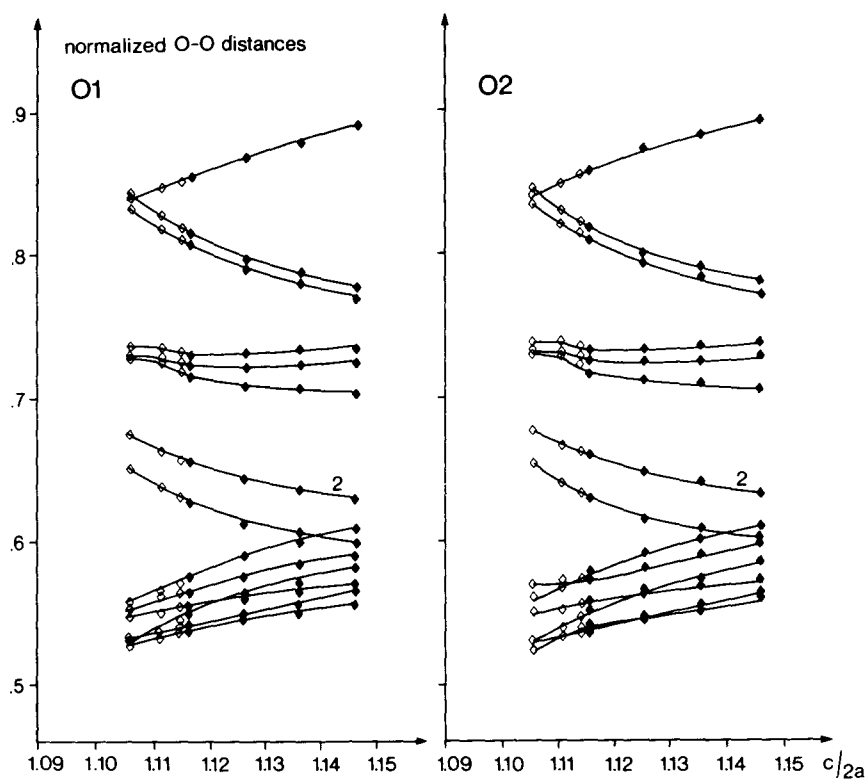


Fig. 4. Normalized O–O distances in AlAsO_4 versus $c/2a$ ratio. With one exception, the distances appear only once. \blacklozenge = high-pressure data, \diamond = high-temperature data (Goiffon et al., 1986, and Baumgartner et al., 1989).

reported energy dispersive X-ray scattering studies with synchrotron radiation showing that the quartz sample became amorphous at pressures of 25–35 GPa. In AlAsO_4 an amorphization probably also takes place at higher pressure.

From Fig. 2 and Fig. 4 the analogous behaviour of the AlAsO_4 structure at high temperatures becomes obvious, indicating that AlAsO_4 displays the “inverse relationship” of temperature and pressure. Such behaviour has already been supposed for the α -quartz structure of SiO_2 by Hazen and Finger (1982). It can also be understood that AlAsO_4 shows no displacive α – β transformation. At 1023 K it does not even attain a crystal structure corresponding to the low-temperature quartz structure of SiO_2 at ambient conditions. From Fig. 2 and 4 it can be concluded that a phase transition to the high-temperature quartz modification is expected to occur at higher temperatures. But the compound decomposes before the transition temperature is reached (Kosten and Arnold, 1980).

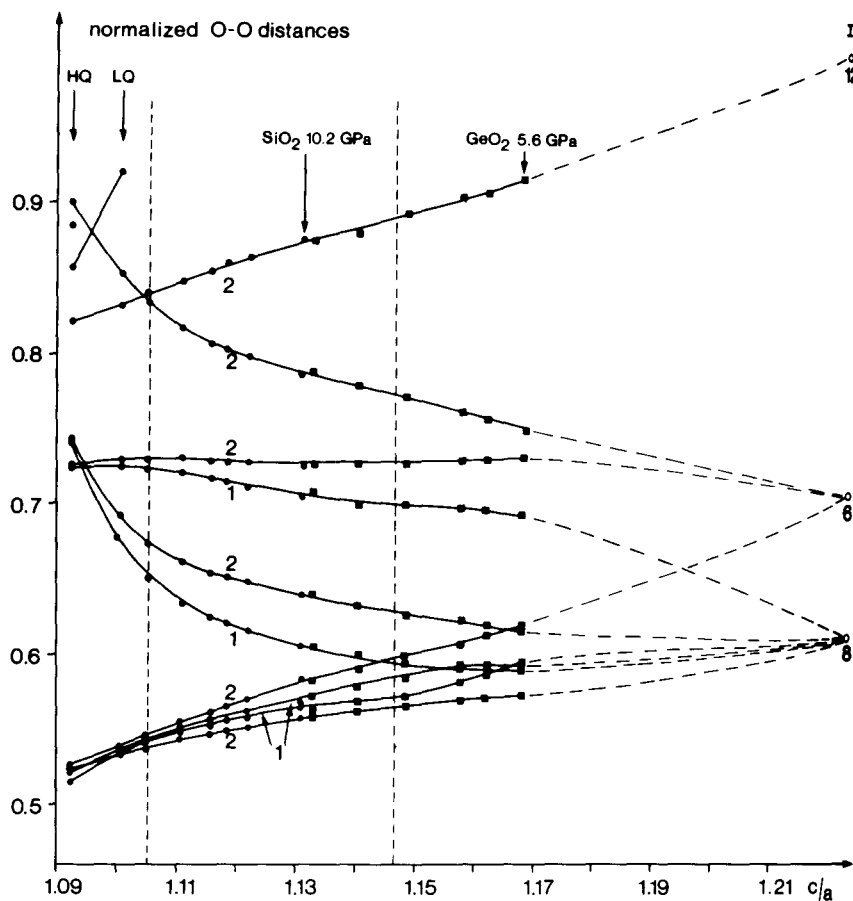


Fig. 5. Normalized O—O distances in SiO_2 and GeO_2 versus c/a ratio. The number of distances is also given. HQ = high-temperature quartz (data from Wright and Lehmann, 1981). LQ = low-temperature quartz, $I = I$ lattice. ● = SiO_2 , ■ = GeO_2 . The examined $c/2a$ range for AlAsO_4 is marked by broken lines.

For the calculations of the Dirichlet domains and O—O distances the program DIDO (Fischer and Koch, 1984) was used.

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