Crystal structure of moganite-type phosphorus oxynitride: relationship to other twinned-quartz-based structures

J. HAINES,[a]* C. CHATEAU,[a] J. M. LÉGER,[a] A. LE SAUZE,[b] N. DIOT,[b] R. MARCHAND[b] AND S. HULL[c]

[a]*Laboratoire de Physicochimie des Matériaux, CNRS, 1 Place Aristide Briand, 92195 Meudon CEDEX, France,* [b]*Laboratoire Verres et Céramiques, UMR CNRS 6512, Université de Rennes-1, Campus de Beaulieu, 35042 Rennes CEDEX, France, and* [c]*ISIS Science Division, Rutherford Appleton Laboratory, Didcot, Oxfordshire OX11 0QX, England. E-mail: haines@cnrs-bellevue.fr*

Abstract

The structure of moganite-type phosphorus oxynitride quenched from high-pressure high-temperature conditions has been refined using neutron powder diffraction data. This moganite-type structure, space group $I2/a$, $Z = 12$, is slightly less distorted with respect to the *Imab* aristotype than is moganite (a monoclinic form of silica). A close topological relationship has been identified between the moganite-type and orthorhombic BeH_2 structures indicating that SiO_2, PON and BeH_2 all adopt structures belonging to the twinned-quartz-based group. This group represents another possible structure type for systems composed of corner-sharing AX_4 tetrahedra. Structures of this group are obvious candidates for intermediate phases between the cristobalite and quartz types.

1. Introduction

A large number of important structures are built up from corner-sharing AX_4 tetrahedra. The structures adopted by silica provide several examples. These include the stable phases at ambient pressure with increasing temperature: α-quartz, β-quartz, HP-tridymite and β-cristobalite; the high-pressure phase coesite; and metastable phases such as α-cristobalite (Heaney, 1994). This rich variety of observed structures is owing to the many different ways tetrahedra can be linked to form extended corner-sharing arrays. It can be noted that a large number of compounds adopt these structure types or their distorted variants. In addition to the above silica structures, some lesser-known silica polymorphs have also been encountered, such as keatite and moganite. A significant quantity of moganite is in fact present in microcrystalline quartz varieties (Heaney & Post, 1992). Moganite has a monoclinic structure, space group $I2/a$, $Z = 12$ (Miehe & Graetsch, 1992), which can be considered to be built up from alternating layers of $(10\bar{1}1)$ slices of right- and left-handed quartz corresponding to a periodic Brazil-law twinning on the unit-cell scale. Until very recently moganite was considered to be the unique example of this structure type. A silica

analogue, phosphorus oxynitride (PON), which has a cristobalite-type structure (Boukbir *et al.*, 1989), was found to transform to a moganite-type phase at high temperature and high pressure (Chateau *et al.*, 1999). This moganite-type phase has a definite P–T range of stability, lying between those of the cristobalite-type and the higher-pressure quartz-type phases (Chateau *et al.*, 1999; Léger *et al.*, 1999).

Unlike silica, for which only rather poorly crystallized natural samples of moganite are available, moganite-type PON synthesized at high pressures and temperatures can be obtained as a well crystallized powder. It can be noted that for the structure refinements using X-ray data from natural samples of moganite the coordinates of one O atom had to be fixed based on distance-least-squares calculations, as unconstrained refinements led to unreasonable Si—O bond lengths. Until now the structure of moganite-type PON has only been refined from X-ray diffraction from a powder. Owing to the number of crystallographically independent atoms, particularly the relatively low scattering O and N atoms, it was not possible to refine the individual atomic displacement parameters. In the present work, we have thus refined the structure of moganite-type PON using neutron diffraction data, which improves our understanding of what was up to now a relatively lesser known structure type. A search of the literature has also permitted the identification of a very close topological relative of moganite. The structure of an orthorhombic modification of beryllium hydride has been reported and also appeared to be a unique example of a structure type (Smith *et al.*, 1988). In this paper, we show that this BeH_2 structure along with moganite and moganite-type PON belong to the same group of twinned-quartz-based structures.

2. Experimental

Cristobalite-type phosphorus oxynitride was prepared as described previously (Boukbir *et al.*, 1989). In order to obtain moganite-type PON, 39 mg of the cristobalite-type phase were placed in a gold sample capsule and

treated at 2.5 GPa and between 1158–1173 K for 1 h in a belt-type apparatus (Chateau *et al.*, 1999). Temperature quenching was performed followed by slow decompression. The sample was analysed by X-ray diffraction, the results of which indicated the presence of traces of quartz-type PON and gold from the sample capsule in addition to the main moganite-type phase.

Time-of-flight (t.o.f.) neutron diffraction data were obtained on the Polaris medium-resolution diffractometer at the ISIS spallation source (Hull *et al.*, 1992). The PON powder was placed in a 2 mm diameter silica glass tube in the neutron beam. Data were collected over a time-of-flight range from 2002 to 19499 μs (d = 0.3237–3.1532 Å) at a diffraction angle $2\theta = 145°$ using a bank of ^{3}He ionization counters. The acquisition time was of the order of 24 h.

The background due to the silica tube was subtracted from the data, which were then converted from variable-step format to fixed-step format for use with the Rietveld refinement program *GSAS* (Larson & Von Dreele, 1994). A two-phase refinement was performed using the diffraction data (t.o.f. = 4074–19100 μs; d = 0.6570–3.0990 Å) in order to account for the presence of 1.6%(w/w) α-quartz-type PON, for which all structural parameters were fixed to the values given by Léger *et al.* (1999) and only the scale factor was varied. No diffraction lines from gold were detected by neutron diffraction. In the refinement, the cell constants, atomic positions, isotropic atomic displacement parameters, the scale factor and three line-shape parameters were varied for the moganite-type phase along with ten background parameters. It was assumed that, as had been found for the quartz-type phase (Léger *et al.*, 1999), N and O are completely disordered over the anion sites and thus the respective occupancies were fixed to 0.5. Attempts to

Table 1. *Experimental details for moganite-type PON*

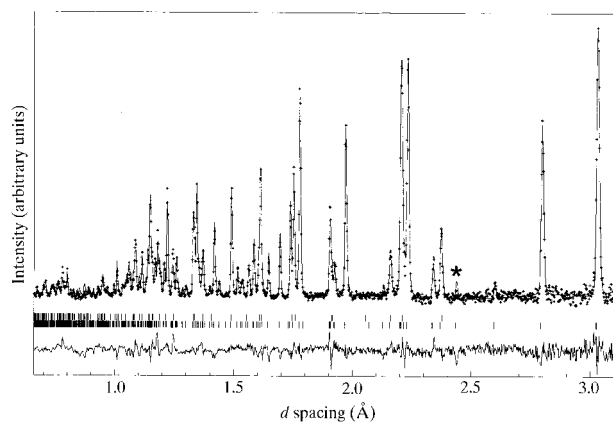| Crystal data	
Chemical formula	PON
Chemical formula weight	60.98
Cell setting	Monoclinic
Space group	$I2/a$
a (Å)	8.5194 (2)
b (Å)	4.7448 (1)
c (Å)	10.3970 (3)
β (°)	90.013 (6)
V (Å^3)	420.27 (1)
Z	12
Radiation type	Neutron
Specimen shape	Cylinder
Specimen preparation	Belt-type apparatus
Specimen preparation pressure (kPa)	2 500 000
Specimen preparation temperature (K)	1158–1173
Colour	Grey
Data collection	
Diffractometer	Polaris medium-resolution
Data collection method	Time-of-flight scans
Instrument location	Rutherford Appleton Laboratory, Chilton, Didcot, UK
Specimen mounting	Silica tube
Specimen mounted	Transmission mode
Temperature (K)	298
Absorption correction	None
Refinement	
R_p	0.110
R_{wp}	0.100
χ^2	3.3
Profile function	Type 3 time-of-flight profile function [pseudo-Voigt convoluted with back-to-back exponentials (Larson & Von Dreele, 1994)]
No. of parameters used	37
$(\Delta/\sigma)_{max}$	0.13
Structure refinement and source of atomic scattering factors	*GSAS* (Larson & Von Dreele, 1994)

Fig. 1. Experimental data (+) and the calculated (solid line) diffraction profile from the Rietveld refinement of moganite-type PON using neutron diffraction data. The intensity is in arbitrary units and the difference profile is on the same scale. Vertical bars indicate the positions of all calculated reflections for the α-quartz-type phase (above) and the moganite-type phase (below). The 310 reflection is indicated by an asterisk (*).

vary the occupancy to allow for a degree of O/N ordering led to no significant change in the agreement factors R_p and R_{wp}.

3. Results

The observed reflection conditions are in agreement with the moganite space group $I2/a$. The presence of the weak 310 reflection at 2.4367 Å is inconsistent with the orthorhombic aristotype *Imab*. It can be noted that in the X-ray diffraction data for moganite-type PON (Chateau *et al.*, 1999) this reflection (which is calculated to be the strongest of the family $hk0$: $h, k \neq 2n$ present for $I2/a$ and not for *Imab*, with a relative intensity of 0.3%) could not be distinguished from the background noise. Owing to the low intensity of this reflection in the neutron data, Fig. 1, refinements in the $I2/a$ space group

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($\mathring{A}^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x	y	z	U_{eq}
P1	1.0	1/4	−0.0096 (32)	0	0.0127 (15)
P2	1.0	0.0021 (9)	0.2406 (6)	0.1653 (4)	0.0031 (7)
O3	0.5	−0.0112 (5)	0.0597 (5)	0.2912 (2)	0.0126 (8)
N3	0.5	−0.0112 (5)	0.0597 (5)	0.2912 (2)	0.0126 (8)
O4	0.5	0.1572 (5)	0.1811 (8)	0.0963 (4)	0.0323 (13)
N4	0.5	0.1572 (5)	0.1811 (8)	0.0963 (4)	0.0323 (13)
O5	0.5	−0.1362 (5)	0.2106 (9)	0.0701 (4)	0.0335 (14)
N5	0.5	−0.1362 (5)	0.2106 (9)	0.0701 (4)	0.0335 (14)

were also performed using *Imab* in addition to those using moganite-type starting positions (Miehe & Graetsch, 1992; Chateau *et al.*, 1999). In both cases the refinement converged to give the same structural parameters (Tables 1 and 2). Selected interatomic distances are given in Table 3.† An attempt at refinement in the orthorhombic space group *Imab* increased χ^2 from 3.3 to 3.9 and the R factors by 2%, and resulted in serious misfits between calculated and observed intensities for several reflections.

4. Discussion

As described by Miehe & Graetsch (1992) the moganite structure can be considered to be constructed from alternating layers of $(10\bar{1}1)$ slices of right- and left-handed quartz as indicated in Fig. 2(*a*). This corresponds to periodic twinning according to the Brazil law on the scale of the unit cell. Moganite is characterized by four-, six- and eight-membered rings of corner-sharing SiO_4 tetrahedra. In moganite, there are two crystallographically independent SiO_4 tetrahedra with $Si-O$ distances ranging from 1.603 to 1.630 and 1.596 to 1.636 Å, respectively. As mentioned above, it was necessary to fix the positions of one set of O atoms based on distance-least-squares calculations owing to the quality of the diffraction data obtained from poorly crystallized natural samples. No such constraints were necessary in the refinement of moganite-type PON using neutron diffraction data from the well crystallized synthetic sample obtained in the present study. The corresponding ranges for the two independent $P(O,N)_4$ tetrahedra are 1.543–1.564 and 1.530–1.582 Å. It can be noted that, as in the case of the quartz-type phases of SiO_2 and PON (Hazen *et al.*, 1989; Léger *et al.*, 1999), the distances are shorter in PON. The bond angles in PON are similar to those in moganite and are in fact closer to those obtained from the unconstrained refinement detailed in Miehe & Graetsch (1992).

The structure of moganite-type PON, Fig. 2(*b*), is less distorted from the orthorhombic *Imab* aristotype, Fig.

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† Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR0087). Services for accessing these data are described at the back of the journal.

Table 3. *Selected geometric parameters* ($\mathring{A}$, °)

P1—O4	1.564 (10)	P2—O3	1.569 (4)
P1—O4^i	1.564 (10)	P2—O3^{iv}	1.582 (3)
P1—O5^{ii}	1.543 (10)	P2—O4	1.530 (7)
P1—O5^{iii}	1.543 (10)	P2—O5	1.545 (6)
O5^{ii}—P1—O5^{iii}	103.6 (10)	O3—P2—O4	110.7 (4)
O5^{ii}—P1—O4	110.0 (2)	O3^{iv}—P2—O5	108.0 (3)
O5^{ii}—P1—O4^i	111.9 (2)	O3^{iv}—P2—O4	105.6 (4)
O5^{iii}—P1—O4	111.9 (2)	O5—P2—O4	110.0 (2)
O5^{iii}—P1—O4^i	110.0 (2)	P2—O3—P2^v	139.3 (2)
O4—P1—O4^i	109.3 (10)	P1^{ii}—O5—P2	147.0 (5)
O3—P2—O3^{iv}	106.7 (2)	P1—O4—P2	147.5 (5)
O3—P2—O5	115.4 (4)		

Symmetry codes: (i) $\frac{1}{2}-x, y, -z$; (ii) $-x, -y, -z$; (iii) $\frac{1}{2}+x, -y, z$; (iv) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

2(*c*), than that of silica. In particular, the tetrahedra in silica are tilted to a greater extent in the *ac* plane with respect to the orientations in the aristotype. This agrees well with the observed intensity of the *Imab* forbidden 310 reflection, which is visible in the X-ray data of Miehe & Graetsch (1992) with a relative intensity of 0.6%, but was not distinguished from the background in the case of X-ray data for PON (Chateau *et al.*, 1999). These two examples of the moganite structure type, however, bear a very strong resemblance to one another.

A search of the literature concerning related compounds revealed another example of an AX_2 structure with a body-centred cell containing 12 formula units and with similar cell-constant ratios: that of orthorhombic BeH_2 (Smith *et al.*, 1988), which has the same space group as the moganite aristotype, *Imab*. Interestingly, the atomic positions in orthorhombic BeH_2 are very close to those in the moganite aristotype, except for the y values for two atoms $A2$ and $X1$, which are significantly different (Table 4). This is quite unusual as two-thirds of the A and one-third of the X atoms shift significantly along $\mathbf{b}$, whereas the remaining atoms are essentially unshifted. At first glance, interconversion between a BeH_2-type and a moganite aristotype structure could be considered as a reconstructive process in which the tetrahedra centred by $A2$ are rotated by 180° about a series of axes parallel to $\mathbf{c}$, or in which $A2$ and
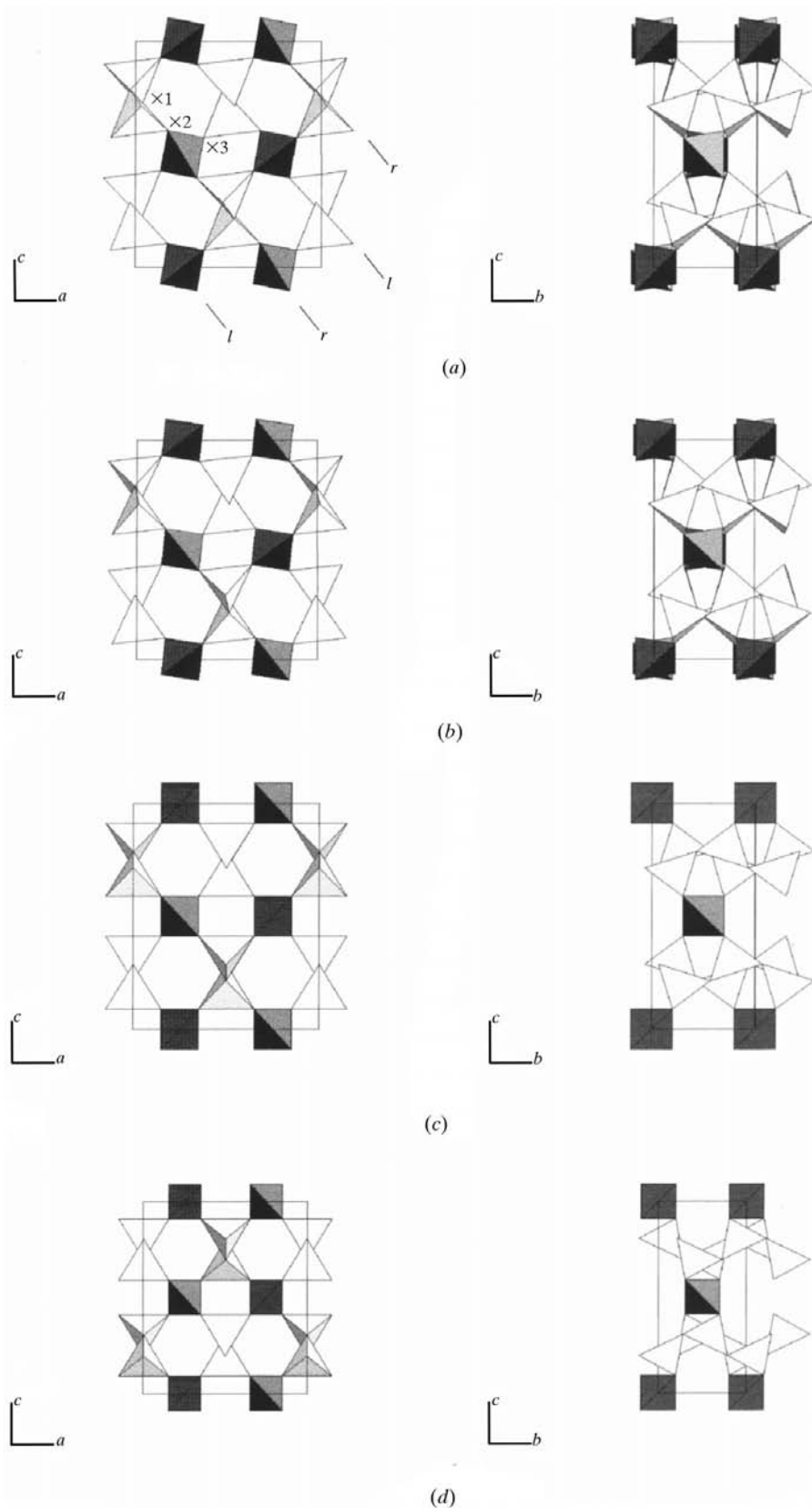
Fig. 2. Polyhedral representations of the crystal structures of (*a*) moganite (SiO$_2$), (*b*) moganite-type PON, (*c*) the *Imab* aristotype of moganite and (*d*) orthorhombic BeH$_2$. Dark and light polyhedra represent tetrahedra centred by *A*1 [*A*1(*X*2)$_2$(*X*3)$_2$] and those centred by *A*2 [*A*2(*X*1)$_2$*X*2*X*3] forming the (*A*$_2$*X*$_6$)$_n$ chains, respectively. The *X*1 atoms link the *A*2-centred tetrahedra to form the chains; *X*2 and *X*3 link the chains to the *A*1-centred tetrahedra. (Note: in *Imab* *X*2 = *X*3.) In (*a*) the diagonal alternating layers of (10$\bar{1}$1) slices of right- and left-handed quartz are indicated by r and l, respectively and the crystallographically distinct *X* atoms are also indicated.

Table 4. *Data for twinned-quartz-based AX$_2$ structures*

	SiO$_2$ (moganite) A = Si, X = O	PON (moganite type) A = P, X = O, N	PON (*Imab* structural model) A = P, X = O, N	SiO$_2$ (moganite aristotype) A = Si, X = O	BeH$_2$ A = Be, X = H
Reference	Miehe & Graetsch (1992)	This work	This work	After Miehe & Graetsch (1992)	Smith *et al.* (1988)
Space group	*I2/a, Z* = 12	*I2/a, Z* = 12	*Imab, Z* = 12	*Imab, Z* = 12	*Imab, Z* = 12
Cell constants					
a (Å)	8.758 (2)	8.5194 (2)	8.5190 (2)	8.758	7.707 (3)
b (Å)	4.876 (1)	4.7448 (1)	4.7446 (1)	4.876	4.160 (2)
c (Å)	10.715 (2)	10.3970 (3)	10.3976 (3)	10.715	9.082 (4)
β (°)	90.08 (3)	90.013 (6)	90	90	90
$A1$					
Site	4(*e*)	4(*e*)	4(*a*)	4(*a*)	4(*a*)
x	1/4	1/4	1/4	1/4	1/4
y	−0.0092 (17)	−0.0096 (32)	0	0	0
z	0	0	0	0	0
$A2$					
Site	8(*f*)	8(*f*)	8(*j*)	8(*j*)	8(*j*)
x	0.0115 (4)	0.0021 (9)	0	0	0
y	0.2533 (6)	0.2406 (6)	0.2403 (7)	0.25	0.1253 (11)
z	0.1678 (2)	0.1653 (4)	0.1652 (4)	0.17	0.1699 (6)
$X1$					
Site	8(*f*)	8(*f*)	8(*j*)	8(*j*)	8(*j*)
x	−0.0314 (12)	−0.0112 (5)	0	0†	0
y	0.0680 (13)	0.0597 (5)	0.0619 (5)	0.07†	0.2823 (32)
z	0.2860 (5)	0.2912 (2)	0.2928 (3)	0.29†	0.3055 (21)
$X2$					
Site	8(*f*)	8(*f*)	16(*k*)	16(*k*)	16(*k*)
x	0.1711‡	0.1572 (5)	0.1470 (3)	0.15	0.1515 (9)
y	0.1770‡	0.1811 (8)	0.1944 (4)	0.20	0.1949 (14)
z	0.1050‡	0.0963 (4)	0.0838 (2)	0.09	0.0895 (15)
$X3$					
Site	8(*f*)	8(*f*)	—	—	—
x	−0.1343 (5)	−0.1362 (5)	—	—	—
y	0.2148 (12)	0.2106 (9)	—	—	—
z	0.0739 (8)	0.0701 (4)	—	—	—

† For chain inversion, the $X1$ atom corresponding to $X1$ in BeH$_2$ is at the equivalent position (0, 0.57, 0.21).   ‡ Coordinates fixed using distance-least-squares.

$X1$ are shifted along **b**, also implying the breaking of bonds. If this were true, orthorhombic BeH$_2$ would represent a topologically distinct structure type for AX_2 compounds with a different arrangement of corner-sharing tetrahedra.

Miehe & Graetsch (1992) described the α-quartz (*q*) and moganite (*m*) structures as chain silicates, in which interstitial vacant sites □ with pseudotetragonal disphenoid configuration are included in the formula. The formula for quartz is thus Si^q□^{q}Si[Si$_2$O$_6$]$_2$ and that of moganite □^{m}Si^{m}Si[Si$_2$O$_6$]$_2$ with the Si$_2$O$_6$ chains running along **b** (moganite), Fig. 2. In order to transform quartz to moganite one must replace □^{q} by Si^m and Si^q by □^{m} (this corresponds to the displacement of one-quarter of the Si atoms by ∼**b**/2) and at the same time invert the Si—O—Si angles in one half of the Si$_2$O$_6$ chains. Such a transformation is evidently reconstruc-

tive. The corresponding formula for BeH$_2$ is the same as that of moganite (Be replaces Si, H replaces O); however, in BeH$_2$ all the A_2X_6 chains are inverted with respect to moganite. Upon inspection of the SiO$_2$ aristotype and BeH$_2$-type structures, one can see that inversion of the chains can occur *via* a tilt of the $A2$-centred tetrahedra about axes parallel to **a** passing through $X2$. This tilt only involves $A2$ and $X1$ such that $X1$ originally at (0, 0.57, 0.21) in the SiO$_2$ aristotype would shift to (0, 0.28, 0.31) in a hypothetical BeH$_2$-type silica. The structural topology is thus retained as only a tilt of certain tetrahedra occurs and no bonds are broken, as in the case of interconversion between Dauphiné twins. An intermediate state, also *Imab*, between the BeH$_2$-type and the moganite aristotype structures can be imagined, in which the chains resemble those in β-quartz, but with, in addition, a mirror plane

along the chain axis (*i.e.* straight chains aligned parallel to **b**).

The close topological relationship between the moganite and BeH_2 types indicates that it would not be impossible for both to occur for the same compound, particularly at different pressures and temperatures. A hypothetical BeH_2-type silica with the same unit-cell volume as moganite would exhibit similar bond distances. A notable difference between the two structure types is that the $A-X-A$ angles are about 10–20° smaller in the BeH_2 structure type yielding $X1-X1-X2$ angles close to 180°, Fig. 2. These $A-X-A$ angles close to 130° are similar to the $Ge-O-Ge$ angles in α-quartz-type GeO_2 (Smith & Isaacs, 1964) and the $Si-O-Si$ angles in quartz at high pressure (Hazen *et al.*, 1989; Glinnemann *et al.*, 1992). The moganite and BeH_2 structure types could be easily identified as they would have very different diffracted line intensities for a given compound.

Symmetrized and distorted variants of the moganite and BeH_2 structure types are also possible. The higher-symmetry orthorhombic moganite aristotype and the intermediate *Imab* structure are obvious candidates for high-temperature phases. A hypothetical intermediate state in silica would exhibit distances similar to those in high-temperature β-quartz. A slightly distorted variant of BeH_2 with monoclinic symmetry, bearing the same relationship to BeH_2 as moganite does to the *Imab* aristotype, might also exist at low temperature, for example. It can be noted that the X-ray powder diffraction pattern of such a monoclinic phase would be virtually indistinguishable from orthorhombic BeH_2 with the strongest *Imab* forbidden reflection having a relative intensity of 0.16% and such a structure cannot be ruled out as a candidate for BeH_2 at ambient temperature, which up to the present date has only been refined using X-ray diffraction data from a powder (Smith *et al.*, 1988).

In PON, the recovery of the moganite-type phase from high pressures and high temperatures inferred a P–T field of stability between those of the cristobalite- and quartz-type phases (Chateau *et al.*, 1999). Owing to their intermediate densities, structures of this twinned-quartz-based group are obvious candidates for phases lying between the cristobalite type and the quartz type in phase diagrams of AX_2 compounds. Similarly, many ABX_4 and ABX_2 compounds which adopt cristobalite- or quartz-related structures (O'Keeffe & Hyde, 1976; Philippot *et al.*, 1996) may also exhibit structures belonging to this group.

5. Conclusions

The structure of moganite-type phosphorus oxynitride prepared at high pressure has been refined using neutron powder diffraction data. Moganite-type PON is slightly less distorted with respect to the *Imab* aristotype than is moganite. These moganite-type structures and orthorhombic BeH_2 are shown to belong to the same group of twinned-quartz-based derivatives. This group provides another example of a possible structure type for systems composed of corner-sharing AX_4 tetrahedra.

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