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High-pressure behavior and phase-stability of Al_5BO_9 , a mullite-type ceramic material

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Abstract

Phase stability, elastic behavior and pressure-induced structural evolution of synthetic boron-mullite Al_5BO_9 ($a=5.6780(7)$, $b=15.035(6)$ and $c=7.698(3)\text{\AA}$, space group $Cmc2_1$, $Z = 4$) were investigated up to 25.6(1) GPa by *in-situ* single-crystal synchrotron X-ray diffraction with a diamond anvil cell under hydrostatic conditions. No evidence of phase transition was observed up to 21.7(1) GPa. At 25.6(1) GPa, the refined unit-cell parameters deviated significantly from the compressional trend, and the diffraction peaks appeared broader than at lower pressure. At 26.7(1) GPa, the diffraction pattern was not indexable, suggesting amorphization of the material or a phase transition to an high-pressure polymorph. Fitting the P - V data up to 21.7(1) GPa with a second-order Birch-Murnaghan Equation-of-State, we obtained a bulk modulus $K_{T0}=164(1)$ GPa. The axial compressibilities, here described as linearized bulk moduli, are: $K_{T0(a)}=244(9)$, $K_{T0(b)}=120(4)$, and $K_{T0(c)}=166(11)$ GPa ($K_{T0(a)}: K_{T0(b)}: K_{T0(c)} = 2.03 : 1 : 1.38$). The structure refinements allowed a description of the main deformation mechanisms in response to the applied pressure. The stiffer crystallographic direction appears to be controlled by the infinite chains of edge-

sharing octahedra running along [100], making the structure less compressible along the *a*-axis than along the *b*- and *c*-axis.

Keywords: Al₅BO₉, mullite, Al₂O₃-B₂O₃-SiO₂, compressibility, elastic behavior, *P*-induced structure evolution.

Introduction

Ceramic materials with chemical composition belonging to the ternary system Al₂O₃-B₂O₃-SiO₂ have an increasing number of outstanding applications due to their high-temperature stability with low-thermal expansion, high-creep resistance, low-electric conductivity along with high chemical stability. Among the large number of applications, we recall: engineering ceramics, substrates for catalytic convertors, optically translucent ceramics for high-temperature furnace windows, fire-protecting lining in nuclear plants due to the low density and the capability of absorbing neutrons¹⁻⁸. Mullite (Al₂(Al_{2+2x}Si_{2-2x})O_{10-x} with $\sim 0.2 < x < \sim 0.9$ and B₂O₃ = 0)⁹⁻¹¹ is likely the most used ceramic compound of this class of materials.

A seminal review paper by Fischer and Schneider² on crystal-chemistry of boronaluminosilicates with mullite-type structures described the structural relationship in the Al₂O₃-B₂O₃-SiO₂ compounds. The authors showed that all boron-mullites can be derived from a hypothetical aristotype (with topological symmetry *P4/mbm*), in which the main building block is represented by chains of edge-sharing MO₆-octahedra running along [001]. A significant number of studies have been focused on the stability fields, solubility and crystal-chemistry of the compounds belonging to the ternary system Al₂O₃-B₂O₃-SiO₂^{1,2,12-35}.

Gatta *et al.*³⁶ investigated the elastic behavior and *P*-induced structural evolution of the boronaluminate Al_5BO_9 by means of *in-situ* single-crystal X-ray diffraction, with a diamond anvil cell, up to 7 GPa. The experiment was performed in order to elucidate the role of boron on the elastic features of mullite-type materials. A comparative elastic analysis was performed on the basis of the elastic parameters [*i.e.* stiffness coefficients, elastic compliances, Young's moduli, Poisson's ratios, bulk and shear moduli] of $2\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ and $2.5\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ mullite previously reported³⁷⁻⁴⁰. However, structure refinements of Al_5BO_9 at high pressure allowed only a preliminary description of the main deformation mechanisms. The stiffness of Al_5BO_9 (*i.e.* isothermal bulk modulus: 165(7) GPa³⁶) requires experiments at pressure higher than 7 GPa for a reliable description of the deformation mechanisms at the atomic scale. In this light, the aim of this study was the investigation of the elastic behavior and phase stability of Al_5BO_9 in response to pressure higher than 7 GPa, along with description of structure rearrangement at the atomic scale, by means of *in-situ* high-pressure single-crystal synchrotron diffraction experiments. We cannot exclude, for example, a change in the B-coordination in response to the applied pressure, with a potential variation of the elastic properties of this material.

The thermal behavior of Al_5BO_9 was recently reported by Fisch and Armbruster³⁴. The thermal expansion, along with the volume compression in response to the applied pressure, allows us to provide a *P-T-V* Equation-of-State of Al_5BO_9 .

Materials and methods

Sokolova *et al.*²⁰ described first the structure of $10\text{Al}_2\text{O}_3\cdot 2\text{B}_2\text{O}_3$ (Al_5BO_9 , $Z = 4$) in space group *Cmc*2₁ ($a = 5.6673(7)$, $b = 15.011(2)$, $c = 7.693(1)$ Å), consisting of

mullite-type octahedral chains (in this set running along [100]), linked by edge-sharing AlO_5 bipyramids alternating with AlO_4 tetrahedra and BO_3 triangular units (Fig. 1). In Al_5BO_9 , boron is only present on a three-fold coordinated site. A further boronaluminate $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$ ($\text{Al}_{4.91}\text{B}_{1.09}\text{O}_9$, $Z = 4$, commonly cited as $\text{Al}_{18}\text{B}_4\text{O}_{33}$) was also reported^{12,41,42}; in this case, 9% of aluminum tetrahedra are substituted by four-fold coordinated boron. Fischer and Schneider² assigned Al_5BO_9 to the "MUL-VIII.33, $Bb2_1m$: A_9B_2 " group, together with $\text{Al}_{18}\text{B}_4\text{O}_{33}$, $\text{Al}_9\text{BSi}_2\text{O}_{19}$ and $\text{Al}_{16.6}\text{Cr}_{1.4}\text{B}_4\text{O}_{33}$.

The Al_5BO_9 crystals used in this study and in those of Gatta *et al.*³⁶, Fisch *et al.*³² and Fisch and Armbruster³⁴ were synthesized by slow cooling of a starting mixture in a flux consisting of 0.50 g K_2CO_3 and 1.56 g MoO_3 corresponding to $1\text{K}_2\text{CO}_3 + 3\text{MoO}_3 \rightarrow \text{K}_2\text{Mo}_3\text{O}_{10} + \text{CO}_2\uparrow$.³³ The starting mixture was composed of Al_2O_3 and B_2O_3 mixed in a molar ratio of 9:2 (*i.e.* 0.03 g B_2O_3 and 0.19 g Al_2O_3). All oxides were ground for 10 min (using an agate mortar) and placed in a lid-covered platinum crucible. The mixture was then heated to 800°C (at a gradient of 100°C/h), and further heated to 1100°C (at a rate of 50°C/h). After 2h at 1100°C, the melt was slowly cooled down to 600°C (at 10°C/h). Yield was about 0.1 g of radially grown aggregates of needle-like whitish crystals, with a maximum size of about 0.2 x 0.2 x 0.8 mm³. Chemical and structure characterization of the crystals was performed on the basis of ¹¹B and ²⁷Al solid-state MAS-NMR, Raman and FTIR spectroscopy, Laser-ablation ICP-MS, single-crystal and powder X-ray diffraction at ambient^{32,33} and non-ambient conditions^{34,36}.

HP-synchrotron X-ray single-crystal diffraction experiments were performed at the Extreme Conditions Beamline P02.2 at PETRA III/DESY, using an incident beam with an energy of 42.7 keV (0.29036 Å in wavelength) and a focusing spot of ~ 8.5

(H) $\times 1.8$ (V) μm^2 , originating from a Compound Refractive Lenses (CRL) system consisting of 121 Be lenses with a radius of 50 μm (400 μm beam acceptance) and a focal length of 1221 mm. A platy single crystal of Al_5BO_9 ($\sim 60 \times 40 \times 5 \mu\text{m}^3$) was loaded in a symmetric diamond anvil cell (DAC), equipped with Boehler Almax design diamonds/seats with a 70° opening and 300 μm culets size. A 250 μm thick foil of rhenium was used as gasket, which was pre-indented to 60 μm and then drilled with a hole of 200 μm in diameter. The hole was the pressure chamber in which the crystal of Al_5BO_9 , along with some ruby spheres for pressure determination⁴³, was located. Neon was used as hydrostatic pressure transmitting medium⁴⁴. Pressure was increased with an automated pressure-driven system from Sanchez Technology and measured with the online ruby/alignment system powdered by a 100 mW 458 nm laser. Diffraction images were acquired on a PerkinElmer XRD 1621 flat panel detector, using an in-house script for collecting step-scan diffraction images. The sample to detector distance (402.34 mm) was calibrated using a CeO_2 standard (NIST 674a). The images were then converted with an in-house software script (Rothkirch *et al.*, *in preparation*) to conform with to the “Esperanto” format of the program CrysAlis⁴⁵. The diffraction data were first collected with the crystal in the DAC and without any P -medium (*i.e.* ambient pressure). A pure ω -scan ($-28 \leq \omega \leq +28^\circ$), with a step size of 1° and an exposure time of 1 s/frame was used for the data collected up to 8.3 GPa (*i.e.* P_3 , Table 1); the exposure was increased to 2 s/frame for the data collected at $P > 8.3$ GPa, in order to improve the quality of the data (diffraction data at P_3 are then not used for the description of the structure evolution). Bragg peaks were then indexed and their intensities were integrated and corrected for Lorentz-polarization effects, using the CrysAlis package⁴⁵. At any pressure, reflection conditions were consistent with those of the space group $Cmc2_1$. No evidence of

phase transition or anomalous elastic behavior was observed up to 21.7(1) GPa. At 25.6(1) GPa, the refined unit-cell parameters deviated significantly from the compressional trend (Fig. 2), and the diffraction peaks appeared broader than at lower pressure. At 26.7(1) GPa, the diffraction pattern was no longer indexable, suggesting amorphization of the material or a phase transition to a high-pressure polymorph with an irreversible corruption of the crystal, as shown by the diffraction patterns collected in decompression.

Integrated intensity data up to 25.6(1) GPa were used for isotropic structure refinements (against F) using the Jana2006 software⁴⁶, starting from the atomic coordinates of *Gatta et al.*³⁶. Neutral atomic scattering factors of B, Al and O from the *International Tables for Crystallography*⁴⁷ were used. In order to reduce the number of refined variables, isotropic displacement parameters were refined by grouping all of the Al-sites and all of the O-sites, adopting the same strategy of *Gatta et al.*³⁶.

Convergence was achieved in all the HP-refinements, with insignificant residues in the final difference-Fourier synthesis of the electron density, coupled with no significant correlations in the variance-covariance matrix of the refined parameters. Further details pertaining to the structural refinements are reported in Table 1. Refined atomic positions and displacement parameters are reported in Table 2. Bond distances are listed in Table 3.

Elastic behavior

The evolution of the unit-cell parameters of Al_5BO_9 with pressure is shown in Fig. 2. The compressional behavior up to 21.7(1) GPa appears to be monotonic, without any evidence of phase transition or change in the compressional mechanisms. At $P > 22$ GPa, the deviation from the compressional trend suggests an impending phase

transition or the P -induced amorphization of Al_5BO_9 . The elastic behavior of Al_5BO_9 up to 21.7(1) GPa is here described with a Birch-Murnaghan Equation-of-State (BM-EoS)⁴⁸. This EoS is based upon the assumption that the high-pressure strain energy in a solid can be expressed as a Taylor series in the Eulerian finite strain, defined as:

$$f_E = [(V_0/V)^{2/3} - 1] / 2$$

where V_0 and V represent the unit-cell volume at ambient and HP conditions, respectively. Expansion in the Eulerian strain polynomial has the following form:

$$P(f_E) = 3K_{T0}f_E (1 + 2f_E)^{5/2} \{ 1 + 3/2(K' - 4)f_E + 3/2[K_{T0}K'' + (K' - 4)(K' - 3) + 35/9]f_E^2 + \dots \},$$

where K_0 represents the bulk modulus ($K_{T0} = -V_0(\partial P/\partial V)_{P=0} = 1/\beta_{V0}$, where β_{V0} is the volume compressibility coefficient at ambient conditions), K' and K'' represent its pressure derivatives (*i.e.* $K' = \partial K_{T0}/\partial P$; $K'' = \partial^2 K_0/\partial P^2$). Fitting the P - V data with a truncated second- and third-order (in energy) BM-EoS with the EOS-FIT5.2 program⁴⁹, using the data weighted by the uncertainties in P and V , we obtain: $V_0 = 657.3(2) \text{ \AA}^3$ and $K_{T0} = 164(1) \text{ GPa}$ ($\beta_{V0} = 0.0061(4) \text{ GPa}^{-1}$, $K' = \partial K_{T0}/\partial P = 4$ (fixed)) for a second-order fit; $V_0 = 657.3(3) \text{ \AA}^3$, $K_{T0} = 165(4) \text{ GPa}$ and $K' = 3.9(5)$ for a third-order fit.

The evolution of Eulerian finite strain vs. normalized stress ($F_E = P/[3f_E(1+2f_E)^{5/2}]$)⁴⁹ is shown in Fig. 2. The weighted linear regression through the data points leads to: $F_E(0) = 165(5) \text{ GPa}$. The value of the normalized stress extrapolated at ambient conditions ($F_E(0)$) and the bulk modulus (K_{T0}) refined on the basis of the second-order BM-EoS are in good agreement. The almost horizontal regression function suggests that the use of a truncated second-order BM-EoS is appropriate to describe the elastic behavior of Al_5BO_9 ⁴⁹.

The elastic anisotropy of Al_5BO_9 is here described on the basis of the “axial bulk moduli”, derived using a “linearized” BM-EoS.⁴⁹ In this case, a “virtual” volume in the EoS is used, calculated as: a^3 , b^3 or c^3 . The refined elastic parameters, accounting for uncertainties in P and length, are: $a_0 = 5.6783(7)$ Å, $K_{\text{T0}(a)} = 244(9)$ GPa ($\beta_{(a)} = 1/3K_{\text{T0}(a)} = 0.0014(1)$ GPa⁻¹) and $K'_{(a)} = 4.6(9)$ for the a -axis; $b_0 = 15.035(5)$ Å, $K_{\text{T0}(b)} = 120(4)$ GPa ($\beta_{(b)} = 1/3K_{\text{T0}(b)} = 0.0028(2)$ GPa⁻¹) and $K'_{(b)} = 2.5(4)$ for the b -axis; $c_0 = 7.700(4)$ Å, $K_{\text{T0}(c)} = 166(11)$ GPa ($\beta_{(c)} = 1/3K_{\text{T0}(c)} = 0.0020(2)$ GPa⁻¹) with $K'_{(c)} = 6.9(9)$ for the c -axis, with an anisotropic scheme: $K_{\text{T0}(a)} : K_{\text{T0}(b)} : K_{\text{T0}(c)} = 2.03 : 1 : 1.38$; $\beta_{(a)} : \beta_{(b)} : \beta_{(c)} = 1 : 2.0 : 1.4$.

Structural evolution with pressure

The structural refinement at room conditions confirms the structure model of Al_5BO_9 previously reported by Sokolova *et al.*²⁰ and Gatta *et al.*³⁶, which consists of edge-sharing octahedral chains (running along [100]) linked by edge-sharing AlO_5 bipyramids alternating with AlO_4 tetrahedra. Chains of edge-sharing MO_6 -octahedra represent the typical building blocks in all the mullite-type materials. Boron lies in small cavities and it is coordinated by three framework oxygen atoms, giving BO_3 triangular units (Fig. 1). At room- P , Al-octahedra and Al-tetrahedra are not so regular (octahedron: $\langle \text{Al1-O} \rangle_{\text{oct}} = 1.895$ Å and $\Delta(\text{Al1-O})_{\text{max}} = 0.113$ Å, where Δ is the difference between the longest and the shortest bond distance; tetrahedron: $\langle \text{Al4-O} \rangle_{\text{tet}} = 1.748$ Å and $\Delta(\text{Al4-O})_{\text{max}} = 0.072$ Å, Table 3). The two bipyramidal units are significantly distorted (with $\Delta(\text{Al2-O})_{\text{max}} = 0.450$ Å and $\Delta(\text{Al3-O})_{\text{max}} = 0.523$ Å, Table 3). The BO_3 triangular unit is almost regular, with $\text{B-O}_{\text{max}} = 1.39(1)$ Å and $\text{B-O}_{\text{min}} = 1.38(1)$ Å.

The structure refinements at non-ambient conditions show that the Al-polyhedra are compressed in response to the applied pressure. The evolution of the $\langle \text{Al}_i\text{-O} \rangle$ distances of the Al1-, Al3- and Al4-polyhedra follows almost monotonic trends of the compressional pattern (Fig. 3), even considering that the *e.s.d.* of the single Al_i-O distances is approximately $\pm 0.02 \text{ \AA}$ within the *P*-range investigated (Table 3). In contrast, the scattering of the data pertaining to the Al2-polyhedron does not allow a clear picture of its *P*-behavior (Fig. 3). The coordination shell of boron appears to be preserved within the *P*-range investigated, and the BO₃-unit appears to behave as a “rigid unit” (Table 3).

The polyhedral distortions (here described by the evolution of the $\Delta(\text{Al}_i\text{-O})_{\text{max}}$) do not show any significant trend in response to the applied pressure (Table 3). However, at 25.6(1) GPa the Al-polyhedra appear to be more distorted than at lower pressure, likely for the impending phase transition at $P \sim 26 \text{ GPa}$.

The main deformation mechanisms in response to the applied pressure act through inert-polyhedral tilting. Viewing the structure of Al₅BO₉ down [100], the deformation of the pentagonal voids, inscribed in 5-membered rings of Al-polyhedra (*i.e.* Al1-Al3-Al4-Al1-Al3, Fig. 4) provide the key to describe the main deformation mechanisms on (100), and so the resulting elastic anisotropy of Al₅BO₉. The shortening of the O7-O5 and O7-O2 distances (Figs 4 and 5) contributes mainly to the compression along the *b*-axis, whereas the shorting of O3-O3 distances controls compression along the *c*-axis. Furthermore, both the *b*- and *c*-axes are affected by the shortening along the O3-O2 “diameter”. Between 0.0001 and 21.7(1) GPa, we observe a relative decrease by -6.9% and -6.3% of O7-O5 and O7-O2, respectively, whereas -4.7% and -3.3% is the relative shortening of O3-O2 and O3-O3, respectively.

Discussion and conclusions

This study follows the first experiments of Gatta *et al.*³⁶ on the high-pressure behavior of Al₅BO₉, previously investigated up to about 7 GPa. This material preserves its crystallinity, in the crystal structure first described by Sokolova *et al.*²⁰, at least up to 25-26 GPa. An irreversible phase transition towards a high-pressure polymorph or towards an amorphous phase occurs at $P > 26$ GPa. A similar behavior was observed in a very recent study by Kalita *et al.*⁵⁰ on 2:1 and 3:2 Al_{4+2x}Si_{2-2x}O_{10-x} mullite: both the materials experience irreversible amorphization at $P > 20-22$ GPa.

Al₅BO₉ is a significantly stiff material. Its isothermal bulk modulus, obtained in this study by a second-order BM-EoS fit, is 164(1) GPa. This value is in good agreement with the experimental findings of Gatta *et al.*³⁶ (*i.e.* 165(7) GPa), based on data collected up to about 7 GPa. A similar compressional behavior is also observed for mullite [adiabatic bulk modulus of 2:1-mullite: $K_S = 169.1$ GPa⁴⁰; $K_S = 169.2$ GPa³⁸; 2.5:1-mullite: $K_S = 173.6$ GPa³⁹; $K_S = 171.6$ GPa³⁷; values recalculated by Schreuer *et al.*⁴⁰ as average of Voigt and Reuss model].

The elastic anisotropy of Al₅BO₉ observed in this study (*i.e.* $\beta_{(a)} : \beta_{(b)} : \beta_{(c)} = 1 : 2.0 : 1.4$) is in good agreement with the anisotropic scheme obtained by Gatta *et al.*³⁶ (*i.e.* $\beta_{(a)} : \beta_{(b)} : \beta_{(c)} = 1 : 2.4 : 1.2$).

The previous experiments showed that mullite-type materials are stiffer along the direction of the infinite chains of edge-sharing octahedra, making the structure more compressible on the plane perpendicular to the chains (see Gatta *et al.*³⁶ and references therein). The limited P -range investigated by Gatta *et al.*³⁶ did not allow a thorough description of the main P -induced mechanisms at the atomic scale, because up to 7 GPa all the building block units of the structure (*i.e.* Al-polyhedra, BO₃-unit) behave as rigid units. In this study, the higher P -range investigated allowed a

description of the compressional behavior of the chemical bonds, along with the slight intra-polyhedral deformation and noticeable inter-polyhedral tilting.

In Al_5BO_9 , the chains of edge-sharing octahedra run along $[100]$. The octahedral chains act as "pillars": the deformation along the chain direction is controlled by compression of the octahedral bonds (Figs 1 and 3, Table 3), as polyhedral tilting cannot occur along the chain direction in order to accommodate the deformation energy. In contrast, the presence of voids on the plane perpendicular to the octahedral chains (in this case: (100) , Fig. 4) allows to accommodate the strain energy by polyhedral tilting, making the structure more compressible on this plane. In other words, the structure is more compressible on (100) than along $[100]$ because on (100) there is the combined effect of P -induced bonds compression and polyhedral tilting, whereas along $[100]$ only bond compression occurs. Polyhedral tilting is energetically less costly than bond compression⁵¹, and is usually-predominant at low- P regime. The inter-polyhedral tilting on (100) , and in particular the non isotropic compression of the pentagonal voids, allows to explain the axial anisotropy with $\beta_{(b)} > \beta_{(c)}$: the pronounced shortening of the O7-O5 and O7-O2 distances (*i.e.* -6.9% and -6.3%, respectively, for a $\Delta P = 21.6$ GPa) contributes mainly to the compression along $[010]$, whereas the less pronounced shorting of the O3-O3 distance (*i.e.* -4.7%, for a $\Delta P = 21.6$ GPa) controls compression along $[001]$.

The *in-situ* high-temperature diffraction experiments performed by Fisch and Armbruster³⁴ on Al_5BO_9 up to 1273 K led to the following thermo-elastic anisotropy: $\alpha_{(a)} : \alpha_{(b)} : \alpha_{(c)} = 1 : 2.47 : 1.85$ [where $\alpha_{(i)}$ are the axial expansion coefficients, $\alpha_{(i)} = 1/l_i \cdot (\partial l_i / \partial T)$]. The most expandable direction corresponds to the most compressible one (*i.e.* $[010]$), whereas the less expandable direction corresponds to the stiffer one (*i.e.* $[100]$). If we combine the elastic parameters obtained in this study and the

thermal data of Fisch and Armbruster³⁴, a P - T - V EoS of Al_5BO_9 , valid at a first approximation, can be obtained:

$$V_{(P,T)} \sim V_{(P_0,T_0)}[1 - \beta\Delta P + \alpha\Delta T] = V_{(P_0,T_0)}[1 - 0.0061(4)\cdot\Delta P + 1.36(2)\cdot 10^{-5}\cdot\Delta T]$$

(with $\beta = 1/K_{T0}$ in GPa^{-1} and α in K^{-1}).

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Tables and Figure captions

Table 1. Details pertaining to the data collections and refinements of Al_5BO_9 at different pressures.

Table 2. Atomic coordinates and displacement parameters ($\text{\AA}^2$) of Al_5BO_9 at different pressures. P -values are given in Table 1.

Table 3. Intra-polyhedral bond distances ($\text{\AA}$) at different pressures. P -values are given in Table 1.

Figure 1. Two views of the crystal structure of Al_5BO_9 (in $Cmc2_1$). Al-polyhedra (*i.e.* octahedra, distorted bipyramids, and tetrahedra) in dark grey; triangular BO_3 -unit in white. The edge-sharing octahedral chains running along $[100]$ are well evident.

Figure 2. Evolution of the unit-cell parameters of Al_5BO_9 with pressure and third-order Birch-Murnaghan Equation-of-State fit (error bars are smaller than the symbols). Eulerian finite (f_E) strain vs Normalized Stress (F_E) plot, with the weighted linear regression through the data points.

Figure 3. Evolution of the average bond distances of Al1, Al2, Al3 and Al4 polyhedra (see Table 3 for details). We assumed error bars calculated as: $\Sigma\sigma(\text{Al}_i\text{-O}_j)/n_i$, where n is the coordination number of any given polyhedron (i). Data pertaining to P_3 are not plotted.

Figure 4. Configuration of the pentagonal voids (inscribed in 5-membered rings of polyhedra, *i.e.* Al1-Al3-Al4-Al1-Al3). The "diameters" of the voids (*i.e.* O7-O5, O7-O2, O3-O3, O3-O2 and O3-O5) are shown as dashed lines

Figure 5. Evolution of the O7-O5, O3-O2, O3-O3, O2-O7, and O3-O5 distances (*i.e.* "diameters" of the voids represented by the 5-membered ring of polyhedra). Data pertaining to P_3 are not plotted.

Table 1. Details pertaining to the data collections and refinements of Al_5BO_9 at different pressures.

P (GPa)	P_0 (0.0001)*	P_1 (1.6(1))	P_2 (5.3(1))	P_3 (8.3(1))	P_4 (10.3(1))	P_5 (12.0(1))	P_6 (15.0(1))	P_7 (17.2(1))	P_8 (19.4(1))	P_9 (21.7(1))	P_{10} (25.6(1))
Temperature (K)	298	298	298	298	298	298	298	298	298	298	298
X-ray wavelength (Å)	0.28988	0.28988	0.28988	0.28988	0.28988	0.28988	0.28988	0.28988	0.28988	0.28988	0.28988
Scan type	ω	ω	ω	ω	ω	ω	ω	ω	ω	ω	ω
Scan width ($^\circ$ /frame)	1	1	1	1	1	1	1	1	1	1	1
Exposure (s/frame)	1	1	1	1	2	2	2	2	2	2	2
Space Group	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$
Cell dim. (Å)	a	5.6780(7)	5.668(1)	5.640(1)	5.620(1)	5.604(1)	5.596(2)	5.579(2)	5.562(1)	5.549(1)	5.541(1)
	b	15.035(6)	14.970(7)	14.826(7)	14.724(7)	14.658(7)	14.590(7)	14.492(7)	14.429(6)	14.350(6)	14.308(7)
	c	7.698(3)	7.677(2)	7.626(2)	7.593(2)	7.568(2)	7.553(2)	7.519(2)	7.497(2)	7.481(2)	7.463(2)
Z	4	4	4	4	4	4	4	4	4	4	4
Maximum 2θ ($^\circ$)	26.0	26.6	26.6	26.2	26.1	26.1	25.0	24.4	24.4	26.2	26.4
Measured reflections	577	527	525	469	505	490	481	481	449	467	456
Unique reflections	391	383	397	347	381	361	356	360	341	339	330
Unique reflections with $I > 3\sigma(I)$	285	160	231	111	251	236	153	199	223	165	163
R_{int}	0.089	0.098	0.055	0.106	0.040	0.072	0.103	0.064	0.051	0.075	0.077
N. refined par.	30	30	30	30	30	30	30	30	30	30	30
$R_1, I > 3\sigma(I)$	0.069	0.096	0.086	0.115	0.076	0.085	0.074	0.069	0.058	0.080	0.098
wR_2 , all refl.	0.079	0.154	0.115	0.179	0.099	0.111	0.108	0.109	0.089	0.120	0.152
Goof	1.18	1.41	1.57	1.44	1.48	1.55	1.06	1.27	1.26	1.32	1.61
Residues ($e^-/\text{\AA}^3$)	-0.5/+0.5	-1.1/+1.5	-1.4/+1.4	-1.2/+1.4	-1.2/+1.3	-1.3/+1.3	-0.7/+1.0	-1.0/+1.0	-0.8/+0.8	-1.2/+1.1	-1.3/+1.3

*With the crystal in the DAC without P -medium.

Structure refinements against F . $R_{\text{int}} = \Sigma |F_{\text{obs}}^2 - F_{\text{calc}}^2(\text{mean})| / \Sigma (F_{\text{obs}}^2)$; $R_1 = \Sigma (|F_{\text{obs}}| - |F_{\text{calc}}|) / \Sigma |F_{\text{obs}}|$; $wR_2 = (\Sigma (w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2) / \Sigma (w(F_{\text{obs}}^2)^2))^{0.5}$, $w = 1/(\sigma^2(F_{\text{obs}}^2))$.

Table 2. Atomic coordinates and displacement parameters ($\text{\AA}^2$) of Al_5BO_9 at different pressures. P -values are given in Table 1.

<i>Sites</i>	<i>P</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>Uiso</i>
Al1 8b	P_0^*	0.2517(5)	0.1163(3)	0.33383	0.0094(5)
	P_1	0.2510(9)	0.1180(7)	0.33664	0.0182(11)
	P_2	0.2518(8)	0.1181(6)	0.33664	0.0125(8)
	P_3	0.2520(14)	0.1225(10)	0.33664	0.0165(14)
	P_4	0.2511(7)	0.1179(5)	0.33664	0.0087(7)
	P_5	0.2512(8)	0.1172(6)	0.33664	0.0079(8)
	P_6	0.2513(8)	0.1178(5)	0.33664	0.0124(7)
	P_7	0.2508(8)	0.1181(5)	0.33664	0.0107(7)
	P_8	0.2510(6)	0.1172(4)	0.33664	0.0111(6)
	P_9	0.2501(9)	0.1172(6)	0.33664	0.0097(8)
	P_{10}	0.2495(11)	0.1158(7)	0.33664	0.0172(10)
Al2 4a	P_0^*	0	0.2554(4)	0.5231(9)	0.0094(5)
	P_1	0	0.2548(8)	0.5290(19)	0.0182(11)
	P_2	0	0.2549(6)	0.5233(15)	0.0125(8)
	P_3	0	0.2539(11)	0.533(3)	0.0165(14)
	P_4	0	0.2559(6)	0.5220(13)	0.0087(7)
	P_5	0	0.2557(7)	0.5238(14)	0.0079(8)
	P_6	0	0.2555(6)	0.5235(14)	0.0124(7)
	P_7	0	0.2563(6)	0.5217(14)	0.0107(7)
	P_8	0	0.2560(5)	0.5196(11)	0.0111(6)
	P_9	0	0.2573(7)	0.5206(16)	0.0097(8)
	P_{10}	0	0.2568(8)	0.5229(18)	0.0172(10)
Al3 4a	P_0^*	0	0.4449(4)	0.5184(10)	0.0094(5)
	P_1	0	0.4445(7)	0.524(2)	0.0182(11)
	P_2	0	0.4465(6)	0.5202(17)	0.0125(8)
	P_3	0	0.4443(12)	0.527(3)	0.0165(14)
	P_4	0	0.4450(6)	0.5209(15)	0.0087(7)
	P_5	0	0.4450(7)	0.5219(17)	0.0079(8)
	P_6	0	0.4452(6)	0.5269(17)	0.0124(7)
	P_7	0	0.4442(6)	0.5264(16)	0.0107(7)
	P_8	0	0.4454(5)	0.5296(13)	0.0111(6)
	P_9	0	0.4443(7)	0.5284(17)	0.0097(8)
	P_{10}	0	0.4450(8)	0.528(2)	0.0172(10)
Al4 4a	P_0^*	0	0.2981(4)	0.1688(10)	0.0094(5)
	P_1	0	0.2981(8)	0.170(2)	0.0182(11)
	P_2	0	0.2994(7)	0.1678(17)	0.0125(8)
	P_3	0	0.2977(12)	0.167(3)	0.0165(14)
	P_4	0	0.2994(6)	0.1660(15)	0.0087(7)
	P_5	0	0.3000(7)	0.1665(17)	0.0079(8)
	P_6	0	0.3021(7)	0.1684(16)	0.0124(7)
	P_7	0	0.3018(6)	0.1658(16)	0.0107(7)
	P_8	0	0.3018(6)	0.1671(12)	0.0111(6)
	P_9	0	0.3030(8)	0.1667(17)	0.0097(8)
	P_{10}	0	0.3034(9)	0.163(2)	0.0172(10)
B 4a	P_0^*	0	0.0177(13)	0.0534(19)	0.005(3)
	P_1	0	0.018(2)	0.054(4)	0.018(7)
	P_2	0	0.0219(19)	0.052(3)	0.011(6)
	P_3	0	0.026(3)	0.053(4)	0.002(8)
	P_4	0	0.0193(19)	0.053(3)	0.007(5)
	P_5	0	0.022(2)	0.049(3)	0.007(6)
	P_6	0	0.019(2)	0.057(3)	0.007(5)
	P_7	0	0.021(2)	0.056(3)	0.007(5)
	P_8	0	0.0167(19)	0.060(2)	0.012(5)
	P_9	0	0.018(2)	0.060(3)	0.004(6)
	P_{10}	0	0.015(3)	0.059(4)	0.018(9)
O1 4a	P_0^*	0	0.3285(10)	0.7104(18)	0.0123(9)
	P_1	0	0.327(2)	0.707(3)	0.0219(18)
	P_2	0	0.3281(17)	0.710(3)	0.0143(14)

	P_3	0	0.0323(3)	0.701(5)	0.015(2)
	P_4	0	0.3271(15)	0.707(3)	0.0112(12)
	P_5	0	0.3269(18)	0.703(3)	0.0113(14)
	P_6	0	0.3249(17)	0.717(3)	0.0162(13)
	P_7	0	0.3263(16)	0.710(3)	0.0133(13)
	P_8	0	0.3241(14)	0.710(2)	0.0161(11)
	P_9	0	0.3245(19)	0.713(3)	0.0144(16)
	P_{10}	0	0.330(2)	0.703(4)	0.033(2)
O2	P_0^*	0.2562(11)	0.1897(7)	0.5379(14)	0.0123(9)
8b	P_1	0.257(2)	0.1914(13)	0.535(3)	0.0219(18)
	P_2	0.254(2)	0.1934(11)	0.539(2)	0.0143(14)
	P_3	0.257(4)	0.192(2)	0.560(4)	0.015(2)
	P_4	0.2536(18)	0.1901(11)	0.540(2)	0.0112(12)
	P_5	0.255(2)	0.1882(12)	0.543(2)	0.0113(14)
	P_6	0.254(2)	0.1878(11)	0.542(2)	0.0162(13)
	P_7	0.255(2)	0.1892(10)	0.541(2)	0.0133(13)
	P_8	0.2528(15)	0.1877(9)	0.5402(17)	0.0161(11)
	P_9	0.252(2)	0.1865(12)	0.544(2)	0.0144(16)
	P_{10}	0.253(3)	0.1884(18)	0.544(3)	0.033(2)
O3	P_0^*	0	0.4525(10)	0.9063(19)	0.0123(9)
4a	P_1	0	0.4566(18)	0.902(4)	0.0219(18)
	P_2	0	0.4549(14)	0.907(3)	0.0143(14)
	P_3	0	0.454(3)	0.899(5)	0.015(2)
	P_4	0	0.4549(13)	0.904(3)	0.0112(12)
	P_5	0	0.4548(15)	0.904(3)	0.0113(14)
	P_6	0	0.4532(15)	0.913(3)	0.0162(13)
	P_7	0	0.4544(14)	0.903(3)	0.0133(13)
	P_8	0	0.4528(12)	0.909(2)	0.0161(11)
	P_9	0	0.4526(16)	0.911(3)	0.0144(16)
	P_{10}	0	0.450(2)	0.891(4)	0.033(2)
O4	P_0^*	0	0.0443(9)	0.4206(19)	0.0123(9)
4a	P_1	0	0.0408(16)	0.418(4)	0.0219(18)
	P_2	0	0.0447(12)	0.425(3)	0.0143(14)
	P_3	0	0.040(2)	0.424(5)	0.015(2)
	P_4	0	0.0445(12)	0.419(3)	0.0112(12)
	P_5	0	0.0448(14)	0.418(3)	0.0113(14)
	P_6	0	0.0438(14)	0.418(3)	0.0162(13)
	P_7	0	0.0440(13)	0.420(3)	0.0133(13)
	P_8	0	0.0424(12)	0.417(2)	0.0161(11)
	P_9	0	0.0401(16)	0.411(3)	0.0144(16)
	P_{10}	0	0.040(2)	0.405(4)	0.033(2)
O5	P_0^*	0	0.3514(11)	0.3711(16)	0.0123(9)
4a	P_1	0	0.353(2)	0.363(3)	0.0219(18)
	P_2	0	0.3521(16)	0.379(3)	0.0143(14)
	P_3	0	0.353(3)	0.359(4)	0.015(2)
	P_4	0	0.3548(16)	0.370(2)	0.0112(12)
	P_5	0	0.3559(18)	0.371(3)	0.0113(14)
	P_6	0	0.3520(18)	0.373(3)	0.0162(13)
	P_7	0	0.3551(17)	0.368(2)	0.0133(13)
	P_8	0	0.3544(15)	0.369(2)	0.0161(11)
	P_9	0	0.355(2)	0.368(3)	0.0144(16)
	P_{10}	0	0.362(3)	0.364(4)	0.033(2)
O6	P_0^*	0	0.1897(11)	0.2660(18)	0.0123(9)
4a	P_1	0	0.187(2)	0.254(3)	0.0219(18)
	P_2	0	0.1915(16)	0.262(3)	0.0143(14)
	P_3	0	0.182(3)	0.234(4)	0.015(2)
	P_4	0	0.1891(15)	0.258(3)	0.0112(12)
	P_5	0	0.1893(18)	0.256(3)	0.0113(14)
	P_6	0	0.1924(18)	0.263(3)	0.0162(13)
	P_7	0	0.1899(16)	0.258(3)	0.0133(13)
	P_8	0	0.1925(15)	0.262(2)	0.0161(11)
	P_9	0	0.191(2)	0.259(3)	0.0144(16)
	P_{10}	0	0.189(2)	0.246(4)	0.033(2)
O7	P_0^*	0.2112(10)	0.0482(7)	0.1243(14)	0.0123(9)
8b	P_1	0.214(2)	0.0444(14)	0.123(3)	0.0219(18)
	P_2	0.2147(15)	0.0467(11)	0.126(2)	0.0143(14)
	P_3	0.213(2)	0.0457(19)	0.137(3)	0.015(2)

P_4	0.2151(16)	0.0484(10)	0.127(2)	0.0112(12)
P_5	0.2139(18)	0.0483(12)	0.131(2)	0.0113(14)
P_6	0.2163(17)	0.0471(11)	0.131(2)	0.0162(13)
P_7	0.2149(16)	0.0482(11)	0.131(2)	0.0133(13)
P_8	0.2141(14)	0.0472(9)	0.1317(18)	0.0161(11)
P_9	0.216(2)	0.0472(12)	0.135(2)	0.0144(16)
P_{10}	0.215(2)	0.0448(16)	0.136(3)	0.033(2)

* With the crystal in the DAC without P -medium.

Note: Isotropic displacement parameters were refined by grouping all of the Al-sites and all of the O-sites.

Table 3. Intra-polyhedral bond distances (Å) at different pressures. P -values are given in Table 1.

	P_0	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}
Al1—O3	1.829(10)	1.868(19)	1.850(15)	1.85(3)	1.829(14)	1.816(15)	1.821(15)	1.806(14)	1.792(12)	1.795(16)	1.72(2)
Al1—O6	1.886(11)	1.87(2)	1.877(17)	1.84(3)	1.850(15)	1.859(17)	1.854(17)	1.834(16)	1.848(14)	1.839(19)	1.85(2)
Al1—O2	1.902(11)	1.88(2)	1.902(18)	1.98(3)	1.866(16)	1.870(18)	1.850(17)	1.841(16)	1.828(14)	1.839(18)	1.84(2)
Al1—O1	1.903(10)	1.91(2)	1.880(16)	1.91(3)	1.885(15)	1.902(17)	1.849(16)	1.860(15)	1.874(13)	1.862(17)	1.86(2)
Al1—O4	1.905(10)	1.937(18)	1.912(14)	1.98(2)	1.877(13)	1.863(15)	1.869(15)	1.866(14)	1.858(12)	1.857(16)	1.82(2)
Al1—O7	1.942(11)	1.99(2)	1.938(17)	1.90(3)	1.893(16)	1.863(18)	1.864(17)	1.855(16)	1.844(14)	1.820(19)	1.80(2)
<Al1-O>	1.895	1.909	1.893	1.91	1.867	1.862	1.851	1.844	1.841	1.835	1.82
$\Delta(\text{Al1-O})_{\text{max}}$	0.11(2)	0.12(4)	0.09(4)	0.13(6)	0.06(3)	0.09(3)	0.05(3)	0.06(3)	0.08(3)	0.07(4)	0.14(4)
Al2—O2 x 2	1.762(9)	1.739(17)	1.703(14)	1.72(2)	1.723(13)	1.740(15)	1.731(14)	1.723(13)	1.718(11)	1.733(16)	1.71(2)
Al2—O1	1.813(16)	1.74(3)	1.79(2)	1.63(4)	1.75(2)	1.71(3)	1.77(2)	1.74(2)	1.73(2)	1.73(3)	1.69(3)
Al2—O5	1.858(16)	1.95(3)	1.81(2)	1.97(4)	1.85(2)	1.86(3)	1.80(3)	1.83(2)	1.81(2)	1.80(3)	1.90(4)
Al2—O6	2.212(16)	2.34(3)	2.20(3)	2.50(4)	2.22(2)	2.24(3)	2.16(3)	2.20(3)	2.13(2)	2.17(3)	2.25(3)
<Al2-O>	1.881	1.90	1.84	1.91	1.85	1.86	1.84	1.84	1.82	1.83	1.85
$\Delta(\text{Al2-O})_{\text{max}}$	0.45(2)	0.60(5)	0.50(4)	0.87(6)	0.50(3)	0.53(4)	0.43(4)	0.48(4)	0.41(3)	0.44(4)	0.56(5)
Al3—O3	1.768(16)	1.75(3)	1.70(2)	1.79(4)	1.71(2)	1.71(2)	1.70(2)	1.73(2)	1.72(2)	1.71(3)	1.79(3)
Al3—O5	1.806(17)	1.84(3)	1.77(2)	1.85(4)	1.75(2)	1.73(3)	1.78(3)	1.75(2)	1.77(2)	1.76(3)	1.69(4)
Al3—O7 x 2	1.834(8)	1.797(15)	1.802(12)	1.82(2)	1.792(12)	1.802(13)	1.770(13)	1.771(12)	1.764(10)	1.765(14)	1.766(18)
Al3—O1	2.291(16)	2.25(3)	2.27(3)	2.22(5)	2.23(2)	2.20(3)	2.25(3)	2.19(3)	2.20(2)	2.20(3)	2.08(3)
<Al3-O>	1.906	1.89	1.87	1.90	1.85	1.85	1.85	1.84	1.84	1.84	1.82
$\Delta(\text{Al3-O})_{\text{max}}$	0.52(3)	0.50(6)	0.57(5)	0.43(9)	0.52(4)	0.49(5)	0.55(5)	0.46(5)	0.48(4)	0.49(6)	0.39(6)
Al4—O2 x 2	1.722(9)	1.73(2)	1.704(16)	1.60(3)	1.686(14)	1.668(15)	1.673(15)	1.660(15)	1.675(11)	1.658(16)	1.63(2)
Al4—O6	1.794(17)	1.78(3)	1.75(3)	1.77(4)	1.76(2)	1.75(3)	1.74(3)	1.76(2)	1.72(2)	1.74(3)	1.74(4)
Al4—O5	1.752(15)	1.70(3)	1.79(2)	1.67(4)	1.75(2)	1.75(2)	1.70(2)	1.70(2)	1.689(19)	1.67(3)	1.70(3)
<Al4-O>	1.748	1.74	1.74	1.66	1.72	1.71	1.70	1.69	1.69	1.68	1.67
$\Delta(\text{Al4-O})_{\text{max}}$	0.07(2)	0.08(5)	0.09(4)	0.17(7)	0.07(3)	0.08(3)	0.07(3)	0.10(3)	0.05(3)	0.08(5)	0.11(5)
B1—O4	1.38(2)	1.37(4)	1.38(3)	1.39(5)	1.38(3)	1.39(3)	1.38(3)	1.38(3)	1.36(3)	1.38(4)	1.38(5)
B1—O7 x 2	1.395(11)	1.38(2)	1.385(16)	1.39(2)	1.396(16)	1.401(18)	1.392(17)	1.379(16)	1.376(15)	1.386(19)	1.38(3)

Figure 1. Two views of the crystal structure of Al_5BO_9 (in $Cmc2_1$). Al-polyhedra (*i.e.* octahedra, distorted bipyramids, and tetrahedra) in dark grey; triangular BO_3 -unit in white. The edge-sharing octahedral chains running along $[100]$ are well evident.

Figure 2. Evolution of the unit-cell parameters of Al_5BO_9 with pressure. For the unit-cell parameters, the third-order Birch-Murnaghan Equation-of-State fit is shown.

Eulerian finite (f_E) strain vs Normalized Stress (F_E) plot. The weighted linear regression through the data points is shown. Error bars are smaller than the symbols.

Figure 3. Evolution of the average bond distances of Al1, Al2, Al3 and Al4 polyhedra (see Table 3 for details). We assumed error bars calculated as: $\Sigma\sigma(\text{Al}_i\text{-O}_j)/n_i$, where n is the coordination number of any given polyhedron (i). Data pertaining to P_3 are not plotted.

Figure 4. Configuration of the pentagonal voids (inscribed in 5-membered rings of polyhedra, *i.e.* Al1-Al3-Al4-Al1-Al3). The "diameters" of the voids (*i.e.* O7-O5, O7-O2, O3-O3, O3-O2 and O3-O5) are shown as dashed lines.

Figure 5. Evolution of the O7-O5, O3-O2, O3-O3, O2-O7, and O3-O5 distances (*i.e.* "diameters" of the voids represented by the 5-membered ring of polyhedra). Data pertaining to P_3 are not plotted.