

Atomic-scale deformation mechanisms at high-pressure in inderborite, $\text{CaMg}[\text{B}_3\text{O}_3(\text{OH})_5]_2(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$

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Abstract

The high-pressure behavior of inderborite [ideally $\text{CaMg}[\text{B}_3\text{O}_3(\text{OH})_5]_2(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$, Sp. gr. $C2/c$ with $a \sim 12.14$, $b \sim 7.43$, $c \sim 19.23$ Å, $\beta \sim 90.3^\circ$ at room conditions] has been studied by two *in-situ* single-crystal synchrotron X-ray diffraction experiments up to about 10 GPa, using He as pressure-transmitting fluid. Between 8.11 (5) and 8.80(5) GPa, inderborite undergoes a first-order phase transition to its high-pressure polymorph, inderborite-II (with $a \sim 11.37$, $b \sim 6.96$, $c \sim 17.67$, $\beta \sim 96.8^\circ$



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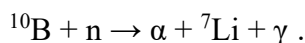
$\Delta V \sim 7.0\%$, space group unknown). The isothermal bulk modulus ($K_{V0} = \beta^{-1}_{P0,T0}$, where $\beta_{P0,T0}$ is the volume compressibility coefficient) of inderborite was found to be $K_{V0} = 41(1)$ GPa. The destructive nature of the phase transition prevented any structure resolution of inderborite-II or even the continuation of the experiments at pressures higher than 10.10(5) GPa. In the pressure range 0–8.11(5) GPa, the compressional anisotropy of inderborite, indicated by the ratio between the principal components of the Eulerian finite unit-strain ellipsoid, is $\epsilon_1:\epsilon_2:\epsilon_3 = 1.4:1.05:1$. The deformation mechanisms at the atomic scale in inderborite are here described. Our findings support the hypothesis of a quasi-linear correlation between the total H₂O content and *P*-stability range in hydrated borates, as the pressure at which inderborite undergoes the phase transition falls in line with most of the hydrate borates studied at high-pressure so far.

Keywords: inderborite, high-pressure, single crystal X-ray diffraction, elastic compressibility, phase transition.

1. Introduction

Boron is a strategic element used in a variety of products, including ant poisons, detergents (for bleaching), borosilicate glasses (such as Pyrex®), and ceramics, (ABE, 1952; Woods, 1994; Klotz and Moss, 1996; Yu *et al.*, 2018; Chen *et al.*, 2020; U.S.G.S, 2022). The strategic importance of boron, and the moderate supply risk due to its uneven distribution, has been recognized by the European Union, which has classified borates as critical raw material since 2014 (European Commission, 2014). Economically viable boron mineral deposits are irregularly distributed worldwide and are mostly represented by five main hydrated borates: ulexite, colemanite, borax, tinalconite, and kernite (Kistler and Helvacı, 1994; Helvacı and Alonso, 2000; Zheng *et al.*, 2005; García-Veigas and Helvacı, 2013). Other borate minerals, such as inderborite, meyerhofferite,

inoite, and tertschite, are often found in smaller weight fractions alongside these main minerals. Due to their low production cost, hydrated borates are believed to be good candidates as aggregates in neutron shielding concretes (Okuno, 2005; Okuno *et al.*, 2009; Glinicki *et al.*, 2018), because of the ^{10}B isotope (which accounts for about 20 % of natural boron) high cross-section for thermal neutrons (~ 3840 barns) (Carter *et al.*, 1953; Palmer and Swihart, 1996), leading to the reaction:



Inderborite, ideally $\text{CaMg}[\text{B}_3\text{O}_3(\text{OH})_5]_2(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$, Sp. gr. $C2/c$ with $a \sim 12.14$, $b \sim 7.43$, $c \sim 19.23$ Å, $\beta \sim 90.3^\circ$, was originally discovered at the Inder Lake borate deposit, western Kazakhstan, and later also at the Eskişehir district, Turkey (Kurkutova *et al.*, 1965; Palmer and Helvacı, 1997). The lower occurrence of inderborite, with respect to other most common borates, is attributed to its extremely narrow stability field in the $\text{CaO-MgO-B}_2\text{O}_3\text{-H}_2\text{O}$ system, as demonstrated by Birsoy and Özbaş (Birsoy and Özbaş, 2012). However, minor fractions of inderborite are commonly found associated to colemanite and ulexite in valuable ore deposits of hydrate borates (*e.g.*, Kirka and Sarıkaya deposits) (Palmer and Helvacı, 1997; Helvacı and Palmer, 2017). For example, inderborite was found in the ore debris nearby the Kuşkaya gallery of the Turkish Borax Mining Company, in the Sarıkaya borate deposits, alongside others borate minerals such as colemanite, borax, ulexite, kurnakovite and inderite (Baysal, 1973).

Kurkutova *et al.* (1966) were the first to determine the crystal structure of inderborite (Figure 1), although the complex hydrogen bond network was only later described by Burns and Hawthorne (Kurkutova *et al.*, 1965; Burns and Hawthorne, 1994). In a recent paper, based on a multi-methodological approach, the crystal chemistry (with a focus on the B isotopic composition) and structure of inderborite (based on a single-crystal neutron diffraction experiment) were re-investigated by Gatta *et al.* (2023). They confirmed that the chemical composition of the

inderborite from Inder (Kazakhstan) is virtually identical to the ideal one. The fundamental building block (FBB) of inderborite is a $[B_3O_3(OH)_5]^{2-}$ ring, consisting of 2 $B\phi_4$ tetrahedrons and one planar trigonal $B\phi_3$ unit (ϕ represents an O^{2-} anion, an OH^- hydroxyl group or a H_2O molecule). The same $\langle \Delta 2\phi \rangle$ unit (Δ stands for a $B\phi_3$ unit, whereas ϕ for a $B\phi_4$ tetrahedron), in which all oxygen atoms that are not shared between two boron atoms are protonated (Burns and Hawthorne, 1994), occurs also in kurnakovite, meyerhofferite, inyoite, inderite and solongoite, whereas in hydroboracite and colemanite is polymerized into chains (Hawthorne, 2012). In the crystal structure of inderborite, the $[B_3O_3(OH)_5]^{2-}$ rings are interconnected with the Ca-polyhedra and Mg-octahedra through the O1, O2, O3, O6, and O8 oxygen hinges. This results in the formation of continuous hetero-polyhedral sheets parallel to (100) (Fig. 1), connected through a complex hydrogen bonding network involving O7 and O4 as *acceptors*, respectively from the O3 and O6 hydroxyl groups and from the O10 H_2O molecule. A crucial role in providing stability to the crystal structure is attributed to the interstitial ("zeolitic") H_2O molecule O11, which occupies a key position between the sheets (Figure 1). O11 is connected, via hydrogen bonding, to O8 and O9: the former is an oxygen hinge that connects the Mg-octahedron with the B2-tetrahedron, whereas the latter is a H_2O molecule belonging only to the Mg-octahedron. This further connects the crystal structure along the [010] crystallographic direction. O9 is also a *donor* to O10, the only H_2O molecule of the complex Ca polyhedrons, providing the only weak connection between Ca- and Mg-polyhedrons.

Nowadays, inderborite remains an extremely poorly studied mineral. The only available Raman spectrum to date can be found on the <https://rruff.info/> website, and some important thermodynamic parameters (such as the thermal expansion coefficient and elastic compressibility) are still missing. As pointed out by Gatta et al. (2023), given the importance of the hydrogen

bonding network in inderborite, a compressional, thermal, or chemical perturbation of the H-bonding scheme could easily lead to a phase transition. On this basis, in this study we aim to: *i*) assess the stability range of inderborite with respect to pressure even for potential industrial utilization of this borates, *ii*) describe the structural evolution of inderborite, at the atomic scale, with increasing pressure. While inderborite will likely not be used as primary component in radiation shielding concretes, its association with major hydrated borates (*e.g.*, colemanite and borax) makes it imperative to investigate its stability under non-ambient conditions. Furthermore, its stability at high-pressure will allow to *iii*) draw comparisons with other hydrated borate structures studied so far, to strengthen the hypothesis of a correlation between the total H₂O content and the stability range of hydrated borates under pressure.

2. Experimental procedures

The sample of inderborite used in this study comes from the type locality (Inder Deposit, Kazakhstan), and was provided by the late Dr. Renato Pagano. Crystals from the same sample were recently used for the experiments reported by Gatta *et al.* (2023). Inderborite is a light (1.92 g/cm³) and soft (3.5 on the Mohs scale) mineral with a prismatic habitus. Two single crystals, each measuring approximately 20x15x10 μm³, were selected for high-pressure experiments at the ID15b beamline, ESRF, Grenoble (France). The diffraction experiment employed a convergent monochromatic beam ($E \sim 30$ keV, $\lambda \sim 0.41$ Å and ~ 200 mA). Helium was used as the pressure-transmitting fluid (Klotz *et al.*, 2009), and a two ruby micro-spheres were added as pressure calibrants (pressure uncertainty ± 0.05 GPa; Mao *et al.*, 1986). The crystals were loaded in two different membrane-driven DACs (diamond anvil cells), with 600 μm culet Boehler-Almax design anvils. For each DAC, a stainless-steel foil (with thickness ~ 250 μm) was pre-indented to about 80 μm and then drilled by spark-erosion, leading to a *P*-chamber of ~ 300 μm in diameter. The

diffraction patterns were collected by an Eiger2X 9M detector, positioned about 180 mm from the sample. The sample-to-detector distance was calibrated using a Si standard and a vanadinite ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$) single crystal. A pure ω -scan ($-32^\circ \leq \omega \leq +32^\circ$) was used to collect the diffraction patterns, with a 0.5° step width and a 0.5 s exposure time per step. Further details on the beamline setup can be found in (Hanfland, 2016; Poreba *et al.*, 2022).

3. Data analysis

The *CrysAlisPro* package (Rigaku Oxford Diffraction, 2019) was used to index the diffraction peaks and integrate their intensities; corrections for Lorentz-polarization effects were also applied. The semi-empirical *ABSPACK* routine, implemented in *CrysAlisPro*, was used to account for X-ray absorption effects caused by the DAC components. Table 1 lists the unit-cell parameters at high pressure, and their evolution with P is shown in Figure 2. Selected diffraction patterns are also presented in Figure 3. *JANA2006* package (Petříček *et al.*, 2014) was used for all structure refinements, with the initial fractional coordinates taken from Burns and Hawthorne (Burns and Hawthorne, 1994) and Gatta *et al.* (2023). CIFs (crystallographic information files) are deposited as Supplementary Materials.

High-pressure data were collected up to 9.84(5) GPa, as the number and intensity of the observed reflections (*i.e.*, with $F_o^2 > 3\sigma(F_o^2)$) significantly decreased after the phase transition at 8.80(5) GPa (as Figure 3 shows), effectively ending the experiment. In both the experiments, crystals did not recover after the phase transition. This was the most destructive phase transition observed in hydrated borates to date (*e.g.*, Comboni *et al.*, 2020b, 2022b), since the number of observed reflections was barely enough to properly index the diffraction pattern of the high-pressure polymorph, inderborite-II, which was found to be metrically monoclinic. The space group has not unambiguously determined.

Relevant interatomic distances, average bond lengths, angles, polyhedral volumes, distortion index (defined as $D = \frac{1}{n} \sum_{i=1}^n \frac{|l_i - l_{av}|}{l_{av}}$, where l_i is the distance from the central atom to the i^{th} coordinating atom, and l_{av} is the average bond length; Baur, 1974), quadratic elongation (defined as $\langle \lambda \rangle = \frac{1}{n} \sum_{i=1}^n \left(\frac{l_i}{l_0}\right)^2$, where l_0 is the center-to-vertex distance of a regular polyhedron of the same volume and l_i is the actual center-to-vertex length; Robinson *et al.*, 1971)) and bond angle variance (defined as $\sigma^2 = \frac{1}{m-1} \sum_{i=1}^m (\phi_i - \phi_0)^2$ where m is the number of faces in the polyhedron $\times 3/2$, *i.e.*, number of bond angles, ϕ_i is the i^{th} bond angle, and ϕ_0 is the ideal bond angle for a regular polyhedron *e.g.*, 90° for an octahedron; Robinson *et al.*, 1971) have been calculated using the tools implemented in the *VESTA* software (Momma and Izumi, 2008), and listed in Table S1. Relevant interatomic angles and distances are reported in Table 2.

To describe the isothermal behaviour of inderborite, a second-order Birch-Murnaghan Equation of State (BM-EoS) was fitted to the P - V data (Birch, 1947). This EoS allows to refine the bulk modulus (K_{V0} or $K_{P0,T0}$, defined as $-V_0(\partial P/\partial V)_{T0} = \beta^{-1}_{P0,T0}$, where $\beta_{P0,T0}$ is the volume compressibility coefficient at room conditions) and its P -derivatives ($K' = \partial K_{P0,T0}/\partial P$ and $K'' = \partial^2 K_{P0,T0}/\partial P^2$). When truncated to the second order in energy, *i.e.* with $K' = \partial K_{P0,T0}/\partial P = 4$, the EoS transforms to:

$$P(fe) = 3K_{P0,T0} fe(1 + 2fe)^{5/2},$$

where fe (defined as $fe = \left[\left(\frac{V_0}{V}\right)^{2/3} - 1 \right] / 2$) is the Eulerian finite strain. The truncation to the second order in energy is reasonable when the experimental data plot following a horizontal trend in the diagram with Eulerian strain vs. “normalised pressure” (F , defined as $F = P/[3fe(1 + 2fe)^{5/2}]$). The BM-EoS parameters (listed in Table 3) were refined by minimizing the differences between

the EoS curves and the experimental data, which were weighted by their uncertainties in P and V . The fitting was carried out using the EOS-FIT7-GUI software (Angel *et al.*, 2014; Gonzalez-Platas *et al.*, 2016). An estimated uncertainty of ± 0.05 GPa was considered for pressure (Mao *et al.*, 1986) during the data fitting. The fe - F plot is shown in Figure S1.

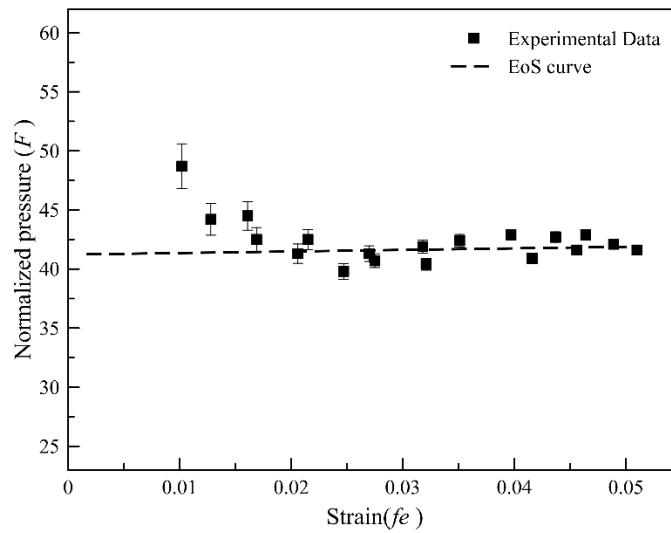


Figure S1: Normalized pressure $F = P/[3fe(1 + 2fe)^{5/2}]$ vs. Eulerian **finite** strain $fe = \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] / 2$ plot, based on the first data set collected at high pressure.

Table 1 Evolution of the unit-cell parameters of inderborite with pressure obtained from the two independent experiments (*high-pressure polymorph).

	<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)
First dataset	0.0001	12.1300(5)	7.4253(2)	19.1940(4)	90.324(6)	1728.80(7)
	0.43(5)	12.0977(4)	7.4114(6)	19.1495(3)	90.332(3)	1716.9(2)
	0.61(5)	12.0820(4)	7.4028(6)	19.1256(3)	90.351(3)	1710.6(2)
	1.19(5)	12.0212(4)	7.3744(6)	19.0295(3)	90.382(3)	1686.9(4)
	1.80(5)	11.9696(5)	7.3425(7)	18.9417(4)	90.418(4)	1664.7(2)
	2.35(5)	11.9198(4)	7.3170(6)	18.8554(3)	90.444(3)	1644.5(4)
	2.82(5)	11.8804(4)	7.2925(6)	18.7842(3)	90.457(3)	1627.4(4)
	3.33(5)	11.8361(4)	7.2664(6)	18.6986(3)	90.483(3)	1608.1(4)
	3.84(5)	11.8093(4)	7.2487(6)	18.6366(4)	90.534(3)	1595.3(2)
	4.54(5)	11.7653(4)	7.2194(7)	18.5425(4)	90.566(3)	1574.9(2)
	6.23(5)	11.6781(5)	7.1664(7)	18.3259(4)	90.629(4)	1533.6(2)
	7.08(5)	11.6443(5)	7.1444(7)	18.2319(4)	90.638(3)	1516.7(2)
	7.80(5)	11.6192(5)	7.1256(8)	18.1556(4)	90.629(3)	1503.1(2)
	8.11(5)	11.5986(5)	7.1162(8)	18.1089(4)	90.623(3)	1494.6(2)
	8.80(5)*	11.37(1)	6.964(5)	17.672(12)	96.8(2)	1390(6)
10.10(5)*	11.49(1)	6.99(2)	17.33(4)	95.7(2)	1385(6)	
	<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)
Second dataset	0.0001	12.139(6)	7.4286(3)	19.1975(5)	90.352(6)	1731.2(8)
	0.35(5)	12.110(5)	7.4128(2)	19.1484(5)	90.371(6)	1718.9(8)
	0.86(5)	12.065(6)	7.3902(2)	19.0812(5)	90.402(6)	1701.3(8)
	1.56(5)	12.008(5)	7.3589(2)	18.9832(5)	90.402(7)	1677.4(8)
	2.32(5)	11.931(7)	7.3231(3)	18.8708(6)	90.425(8)	1648.7(10)
	3.05(5)	11.875(6)	7.2868(3)	18.7546(6)	90.515(7)	1622.8(8)
	3.81(5)	11.830(6)	7.2477(3)	18.6346(5)	90.516(7)	1597.7(8)
	4.67(5)	11.802(6)	7.2110(3)	18.5194(6)	90.592(7)	1575.9(8)
	5.30(5)	11.764(7)	7.1928(3)	18.4533(7)	90.636(9)	1561.4(9)
	6.20(5)	11.719(6)	7.1655(3)	18.3571(6)	90.555(8)	1541.4(8)
	6.90(5)	11.674(7)	7.1460(3)	18.2757(7)	90.603(9)	1524.5(10)
	7.45(5)	11.654(7)	7.1305(3)	18.2115(6)	90.638(9)	1513.3(9)
	8.96(5)*	11.435(2)	6.932(8)	17.453(12)	96.05(8)	1375(2)

Figure 1: Inderborite structure, based on the model proposed by Gatta *et al.* (2023), viewed perpendicular to the (100) plane. Ca-polyhedrons in *indigo*, Mg-polyhedrons in *orange*, boron polyhedrons in *green*, hydrogen in small *pale pink spheres*.

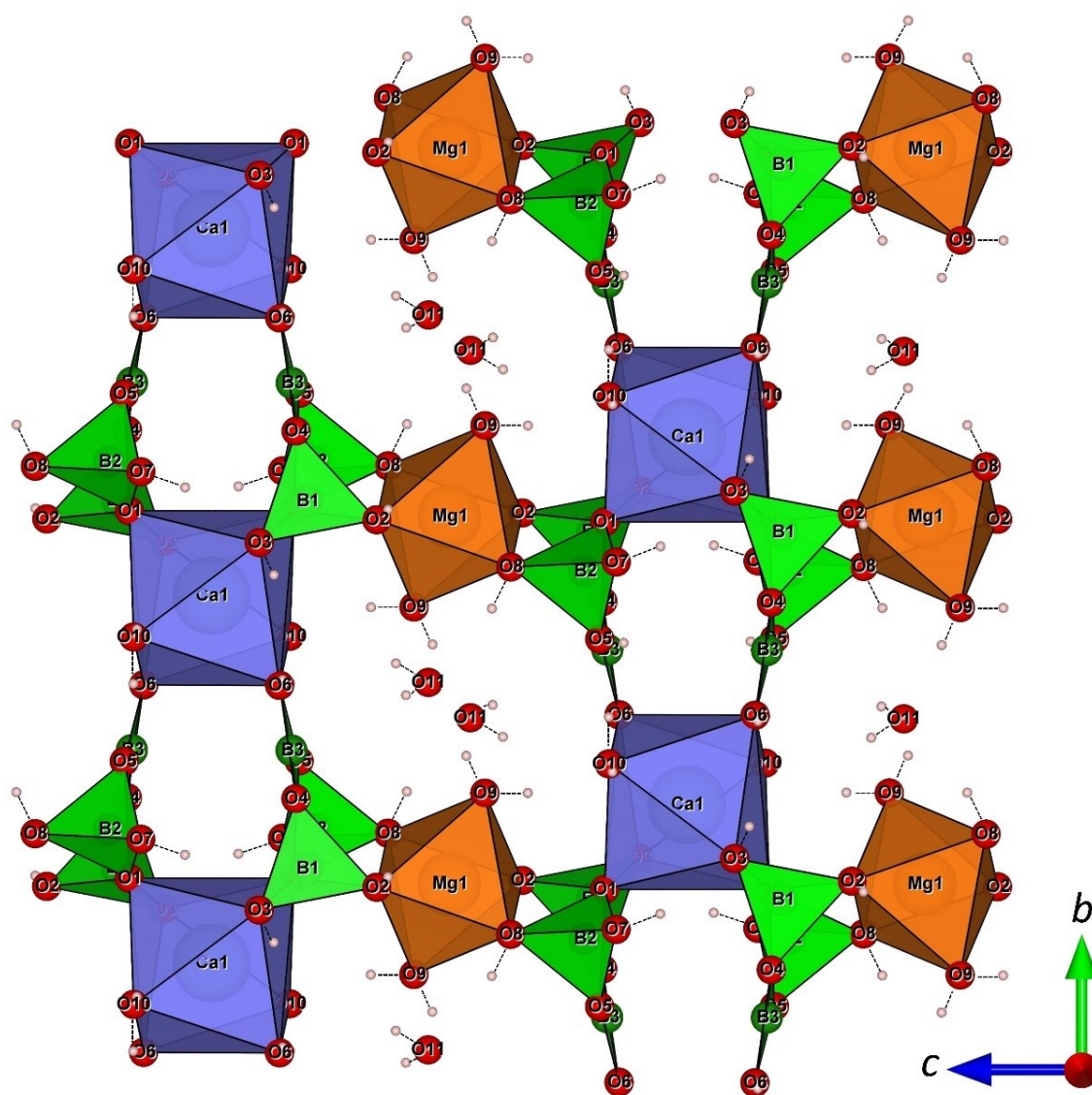


Figure 2: Evolution with pressure of the unit-cell parameters of inderborite: first dataset in black squares, second dataset in red diamonds, inderborite-II in green circles. E.s.ds are smaller than symbols.

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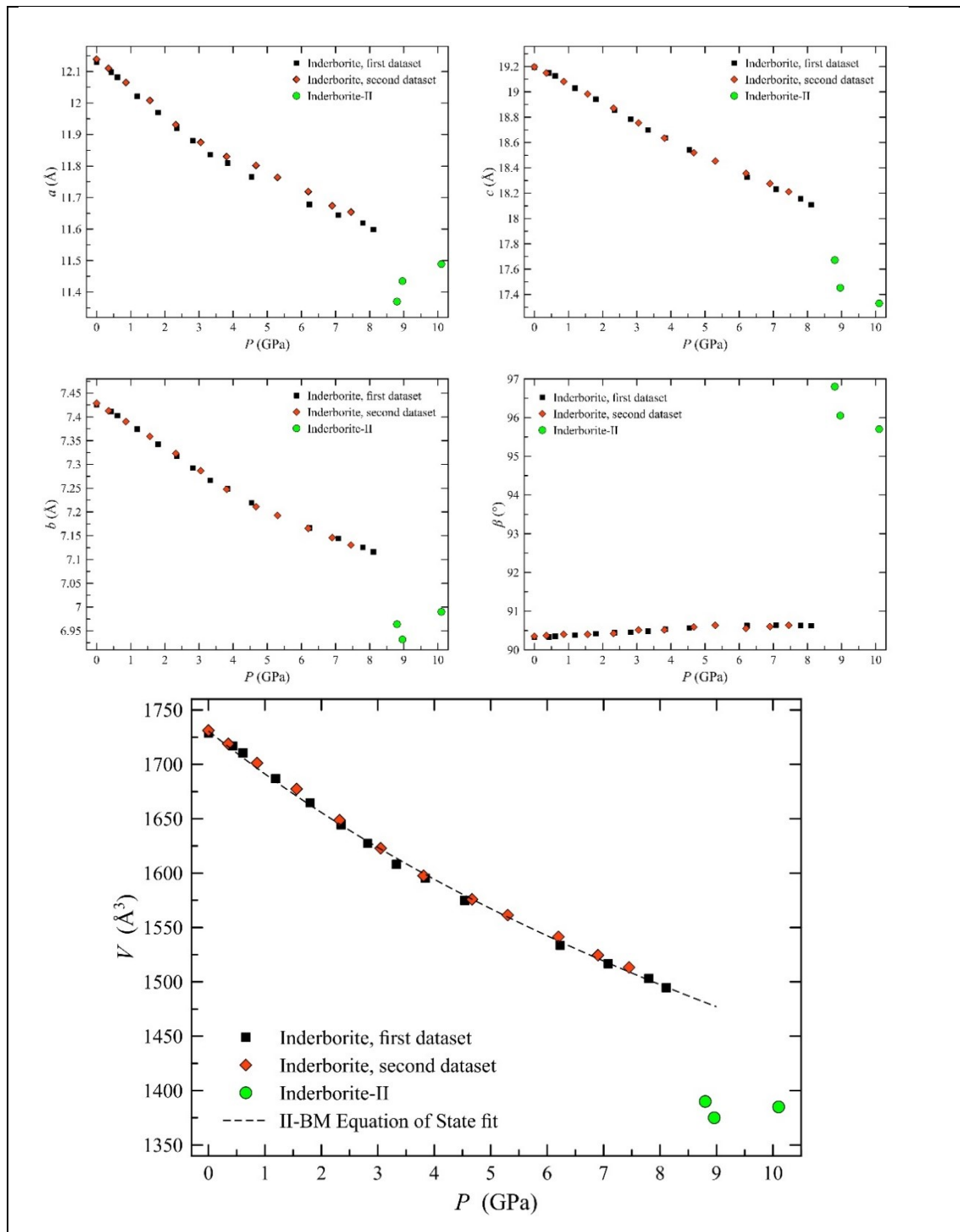


Figure 3: Reconstruction, based on the experimental data, of the $0kl^*$, $hk0^*$ and $h0l^*$ reciprocal lattice planes of inderborite- (left side) and inderborite-II (right side). Above the phase transition, the number of observed reflections dropped dramatically.

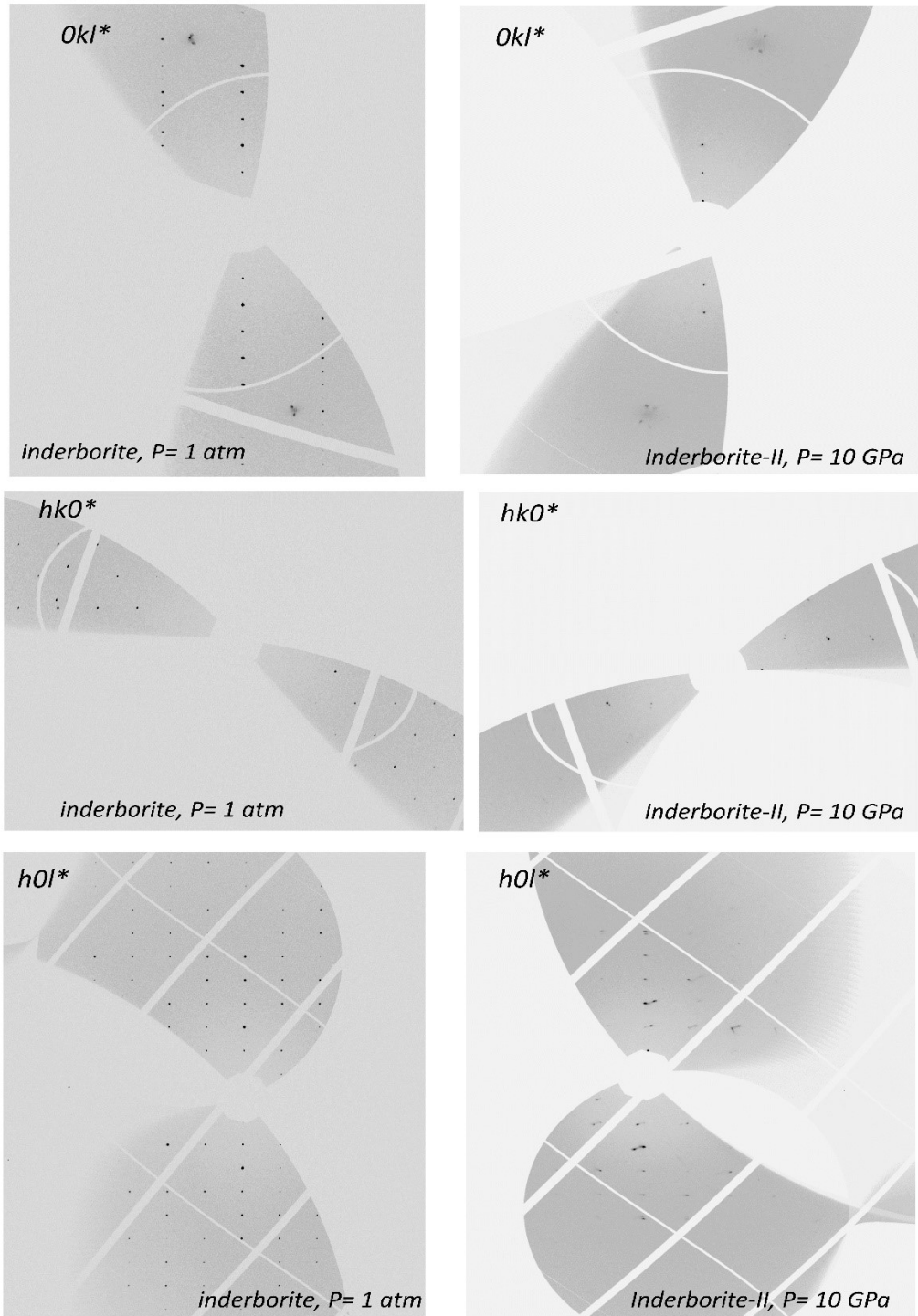


Table 2: Evolution, with pressure, of some relevant interatomic angles (in °) and distances (in Å) in inderborite structure [Δ defined as (O-O)_{0.0001GPa} – (O-O)_{P8.11(5)GPa}].

<i>P</i> (GPa)	O2-O3-O6	O1-O6-O4	O6-O1-O8	O8···O11···O9	O6···O7···O3	O5···O10···O4
0.0001	89.8(1)	165.7(1)	125.6(1)	132.2(2)	67.3(3)	121.2(4)
0.43(5)	89.3(1)	166.6(2)	125.0(1)	132.6(2)	67.3(1)	121.1(2)
0.61(5)	88.8(1)	166.8(2)	124.8(1)	132.2(3)	67.4(1)	121.1(2)
1.19(5)	88.3(1)	167.0(2)	124.7(1)	132.1(2)	67.5(1)	121.2(2)
1.80(5)	87.7(1)	167.4(2)	124.4(1)	131.6(3)	67.4(1)	121.2(2)
2.35(5)	86.9(1)	167.9(2)	124.2(1)	131.1(3)	67.9(1)	120.9(2)
2.82(5)	86.7(1)	168.2(2)	123.8(1)	131.1(3)	67.8(1)	121.2(2)
3.33(5)	86.0(1)	168.6(2)	123.5(1)	130.4(3)	68.1(1)	121.1(2)
3.84(5)	85.5(1)	169.0(2)	122.9(1)	130.3(3)	68.2(1)	121.1(2)
4.54(5)	85.0(1)	169.5(2)	122.4(1)	129.6(3)	68.2(1)	121.0(2)
6.23(5)	83.5(2)	170.7(2)	120.6(2)	128.0(3)	68.5(2)	121.0(3)
7.08(5)	82.7(2)	171.4(3)	120.2(2)	127.3(3)	68.6(2)	120.9(3)
7.80(5)	82.2(2)	172.0(3)	119.1(2)	126.8(3)	69.0(2)	120.9(3)
8.11(5)	82.0(2)	172.3(3)	118.6(2)	126.7(3)	69.2(2)	121.2(3)
Δ total	-7.8(3) °	-6.6(4) °	7.0(3) °	5.5(5)	-1.9(5)°	0.0(7) °

<i>P</i> (GPa)	O6···O7	O3···O7	O5···O10	O10···O4	O8···O11	O11···O9
0.0001	2.62(2)	2.867(9)	2.733(8)	2.79(2)	2.92(2)	3.10(2)
0.43(5)	2.639(4)	2.861(5)	2.723(6)	2.787(4)	2.898(5)	3.076(6)
0.61(5)	2.633(4)	2.859(5)	2.723(6)	2.779(4)	2.888(5)	3.083(6)
1.19(5)	2.611(4)	2.840(5)	2.713(6)	2.756(4)	2.862(5)	3.052(6)
1.80(5)	2.592(4)	2.820(5)	2.699(6)	2.732(4)	2.842(5)	3.034(6)
2.35(5)	2.576(4)	2.806(5)	2.692(6)	2.713(4)	2.824(5)	3.010(6)
2.82(5)	2.564(4)	2.789(5)	2.685(6)	2.697(4)	2.806(5)	2.982(6)
3.33(5)	2.550(4)	2.771(6)	2.669(6)	2.682(4)	2.797(5)	2.947(6)
3.84(5)	2.543(4)	2.773(6)	2.666(7)	2.671(4)	2.781(5)	2.926(7)
4.54(5)	2.529(4)	2.757(6)	2.658(6)	2.653(4)	2.770(5)	2.898(6)
6.23(5)	2.506(6)	2.719(7)	2.649(7)	2.613(6)	2.722(6)	2.873(7)
7.08(5)	2.501(6)	2.699(7)	2.646(8)	2.594(6)	2.712(6)	2.866(7)
7.80(5)	2.493(6)	2.677(7)	2.649(8)	2.579(6)	2.694(6)	2.866(7)
8.11(5)	2.487(6)	2.674(7)	2.638(8)	2.574(6)	2.684(6)	2.856(7)
Δ total	0.13(3)	0.19(2)	0.10(2)	0.22(3)	0.24(3)Å	0.24(3)Å

Table 3: Refined elastic parameters of the inderborite unit-cell and of the coordination polyhedrons, based on the isothermal II-BM Equation of State fit (*fixed parameter).

	V_0, x_0 (Å ³ , Å)	K_{V_0, x_0} (GPa)	K'	β_{V_0, x_0} (GPa ⁻¹)
V	1731(1)	41(1)	4*	0.0244(6)
a	12.129(2)	44.6(6)	4*	0.0075(3)
b	7.4255(6)	47.5(4)	4*	0.0070(2)
c	19.195(2)	34.6(4)	4*	0.0096(3)
Ca-φ₈	26.1(7)	53(4)	4*	0.019(1)
Mg-φ₆	12.27(5)	81(8)	4*	0.012(1)
B1-φ₄	1.628(3)	260(30)	4*	0.0038(5)
B2-φ₄	1.643(3)	170(12)	4*	0.0059(4)

4. Results

4.1 Elastic behaviour

The linear elastic parameters, listed in Table 3, suggest that inderborite is a rather isotropic mineral, which deforms almost equally along the **principal** crystallographic directions. However, as **expected** in monoclinic crystals, the unit-cell angle β is free to vary with pressure, meaning that the linear bulk moduli along the principal crystallographic directions (listed in Table 3) do not actually describe the compressional anisotropy. To overcome this problem, the Eulerian finite strain analysis was performed with the *Win_Strain* software (Angel, 2011). The geometrical relationships between the unit-strain ellipsoid and the crystallographic axes of inderborite can be described by the following matrix (with $\varepsilon_1 > \varepsilon_2 > \varepsilon_3$):

$$\begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{pmatrix} \prec \begin{pmatrix} 79.8^\circ & 90^\circ & 10.8^\circ \\ 169.8^\circ & 90^\circ & 79.2^\circ \\ 90.0^\circ & 180^\circ & 90.0^\circ \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

for inderborite, between 0.0001 and 8.11(5) GPa, $\varepsilon_1:\varepsilon_2:\varepsilon_3 = 1.4:1.05:1$ ($\varepsilon_1=0.00723(5)$ GPa⁻¹; $\varepsilon_2=0.00546(3)$ GPa⁻¹; $\varepsilon_3=0.00524(4)$ GPa⁻¹). Inderborite response to compression is only moderately anisotropic, with the major direction (ε_1) of compression describing an angle of only 10° with the *c* axis. This finding is surprisingly if compared to other hydrous borates, such as meyerhofferite ($\varepsilon_1:\varepsilon_2:\varepsilon_3 = 5.8:4.7:1$) or inyoite ($\varepsilon_1:\varepsilon_2:\varepsilon_3= 3.5:2.1:1$) (Comboni *et al.*, 2020a, 2022b). Regarding the high-pressure polymorph, the poor quality of the diffraction data did not allow any robust calculation, as discussed in the Section 3. However, the previous matrix, showing the unit-strain ellipsoid calculated between 0.0001 and 8.11(5) GPa, does not describe the *P*-induced evolution of the strain ellipsoid itself, which undergoes a significant change as pressure increases. Initially, between 0.0001 and 2.35(5) GPa, the unit-strain ellipsoid is described by the following matrix:

$$\begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{pmatrix} \angle \begin{pmatrix} 49.6^\circ & 90^\circ & 40.9^\circ \\ 40.4^\circ & 90^\circ & 130.9^\circ \\ 90.0^\circ & 0^\circ & 90.0^\circ \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

with $\varepsilon_1:\varepsilon_2:\varepsilon_3 = 1.3:1.1:1$ ($\varepsilon_1=0.0079(2)$ GPa⁻¹; $\varepsilon_2=0.0070(2)$ GPa⁻¹; $\varepsilon_3=0.0062(1)$ GPa⁻¹). Therefore, in the initial stage of compression, ε_1 and ε_2 lie on the *ac* plane, whereas ε_3 is parallel to *b*. However, as pressure increases, ε_1 , ε_2 and ε_3 deviate from the original orientation and, between 6.23(5) and 8.11(5) GPa, the unit-strain ellipsoid matrix changes to:

$$\begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \end{pmatrix} \angle \begin{pmatrix} 90.9^\circ & 90^\circ & 0.3^\circ \\ 90.0^\circ & 180^\circ & 90.0^\circ \\ 0.9^\circ & 90^\circ & 89.7^\circ \end{pmatrix} \cdot \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

with $\varepsilon_1:\varepsilon_2:\varepsilon_3 = 1.7:1:1$ ($\varepsilon_1=0.0063(2)$ GPa⁻¹; $\varepsilon_2=0.0037(6)$ GPa⁻¹; $\varepsilon_3=0.0036(5)$ GPa⁻¹). Close to the phase transition, magnitude and orientation of the unit-strain ellipsoid differ from the earlier stages of compression, being ε_1 almost parallel to *c*, ε_3 almost parallel to *a*, and ε_2 parallel to *b*.

4.2 Structure evolution

Referring to the first dataset (Table 1), between ambient pressure and 8.11(5) GPa, the length of the unit-cell edges of inderborite decreases steadily by about 4.3% for the a and b unit-cell edges and by about 3.3% along the c edge. The unit-cell volume decreases monotonically by about 13.5% and the β angle steadily increases by about 3.3% (see Table 1). Similar values (*i.e.*, within 3σ) were observed for the second dataset. Up to 8.11(5) GPa, the crystal structure of inderborite deforms steadily with no significant changes. Between 8.11(5) and 8.80(5) GPa, inderborite undergoes a phase transition to its high-pressure polymorph, inderborite-II. This phase transition is rather disruptive, and data were collected only up to 10.10(5) GPa, as the number and intensity of the observed reflections (*i.e.*, with $F_o^2 > 3\sigma(F_o^2)$) significantly decreased after the phase transition (down to about 60). The phase transition is marked by a sharp volume decrease, typical of first-order phase transformations. Upon decompression, the crystal structure of inderborite does not revert to its ambient pressure polymorph, indicating that the transition is irreversible (at least at the time scale of our experiment).

5.0 Discussion

The high-quality structural refinements of inderborite with pressure allowed a full description of the main deformation mechanisms able to accommodate the effect of compression. The bulk modulus (K_{V0}) of the $B\phi_4$ tetrahedra, based on the isothermal Birch-Murnaghan Equation of State fit (Table 3), is more than five times higher than that of the inderborite unit-cell. This suggests that the boron tetrahedrons act as incompressible units, as expected at low-mid pressures (Table 3 and S1). The same behaviour has been observed in all the hydrated borates studied so far at high pressure (*e.g.*, ulexite, jadarite, kernite; Comboni *et al.*, 2020b, 2021b, 2022a) and in other

minerals as well (*e.g.*, reedmergnerite, londonite, barium metaborates, Gatta *et al.*, 2011; Bekker *et al.*, 2022; Gorelova *et al.*, 2022). On the other hand, the Mg ϕ_6 octahedra and Ca ϕ_8 polyhedrons are significantly softer but with an important difference. The Ca-polyhedron compresses as expected, similar to what observed in other hydrous borates crystal structures, such as meyerhofferite and inyoite, as evidenced by its bulk modulus (53(4) GPa) that is within 1 σ of the values observed in meyerhofferite and inyoite (Comboni *et al.*, 2020a, 2022b). In contrast, the Mg-polyhedron is significantly stiffer with respect to Mg-polyhedron in other structures: the calculated bulk modulus **in this study** (81(8) GPa) is 11% higher than that of the same polyhedron in kurnakovite and about 20% higher than that in inderite (67(4) GPa) (Pagliaro *et al.*, 2021; Comboni *et al.*, 2023). Although considerably stiff, the Mg- ϕ_6 polyhedron compression is highly anisotropic. In the experimental pressure range **of this study**, while the Mg–O9 and the Mg–O2 distances decreases by about 1.8 and 1.5%, Mg–O8 decreases by about 4%. This anisotropic compression, mainly affecting the Mg–O8 bond, leads to a progressive distortion of the Mg- ϕ_6 octahedron, as indicated by the progressive increase of the distortion index (σ^2) values (Table S1). Overall, when compared to the bulk modulus of inderborite, all the polyhedrons are stiffer than the overall structure (see Table 3), meaning that the structural deformation **in response to** the applied pressure must be accommodated even by other mechanisms. Indeed, tilting around the oxygen hinges between the B-, Ca- and Mg- polyhedrons can be deduced from the data in Table 2, which reports O–O–O angles that change significantly with pressure. Into details, the O2– $\widehat{O3}$ –O6, O1– $\widehat{O6}$ –O4 and O6– $\widehat{O1}$ –O8 angles, which describe the degree of tilting between the [B₃O₃(OH)₅]²⁻ polyion and the Ca- ϕ_8 octahedron, show a steady and progressive deformation as pressure increases (O2– $\widehat{O3}$ –O6, O1– $\widehat{O6}$ –O4 decrease of about 7.8(2)° and 6.6(2)°, whereas O6– $\widehat{O1}$ –O8 increases of about 7.0(2)°). The compression of the hydrogen-bonding network also accommodates part of the

pressure-induced deformation and the interstitial (“zeolitic”) H₂O molecule O11 might play a role in the destabilization of the crystal structure. This molecule is connected, via hydrogen bonding, with the O8 hydroxyl group and the O9 H₂O molecules (Figure 1, Figure S2). At ambient pressure, the interatomic angle O8···O11···O9 is 132.2(2)°, and it remains roughly **constant** only in the very first GPa of compression, decreasing progressively with increasing pressure (Table 2). This is paired with a steady decreasing of the O11···O9 and O11···O8 distances (Table 2), which decrease of about 8.4 and 7.9%. These are not the only atoms of oxygen connected *via* hydrogen bonding affected by the structure deformation. Indeed, the interatomic O6···O3···O7 angle, which is formed by the oxygen atom O7 (being part of the B2-tetrahedron), *acceptor* of two hydrogen bonds from the hydroxyl groups O3 and O6 (which belong to the Ca-polyhedron), deforms steadily as pressure increases (Table 2). As O11···O9 and O11···O8, also the interatomic distances O6···O7 and O7···O3 decreases drastically with pressure (of about 5 and 6.7%, Table 2). The H₂O molecules O10 is the *donor* of two hydrogen bonds, with O4 and O5 as *acceptors* (Figure S2), two atoms of oxygen **that** act as hinges in the [B₃O₃(OH)₅]²⁻ polyion. The interatomic angle O5···O10···O4 remains unchanged (within 1σ) **up to** 8.11(5), GPa but the distances between the *acceptors* (O4 and O5) and the *donor* (O10) progressively decrease of about 7.9 and 3.7%, **respectively**. Therefore, the interaction between the oxygen pairs O10···O4 and O10···O5 increases steadily with pressure. The compression of the hydrogen bond network is significantly larger with respect to the average decrease of the Ca-O, Mg-O and B-O distances (~4%, ~2%, ~1.6%, respectively), further highlighting that the main mechanisms with which the structure deforms are (i) the tilting around inter-polyhedral oxygen hinges and (ii) compression of the hydrogen bonding network. This phenomenon is analogous to what was observed in several other hydrated borate structures characterized by a pervasive hydrogen bonding network, which plays a

paramount role in the stability of the crystalline edifice (*e.g.*, meyerhofferite, inyoite; Comboni *et al.*, 2021a, 2022b). It is likely that the combination of these two deformation mechanisms induces the changes of the orientation of the unit strain ellipsoid, ultimately affecting the elasticity and the (very moderate) anisotropy of inderborite. Figure S4 shows the evolution of the O···O distance (reported in Table 2) with pressure. It can be noted that the slopes of such trends change manifestly with pressure, so that it can be potentially correlated to the changes in the unit-strain ellipsoid **configuration**, highlighting, once again, the role of the hydrogen-bonding network on the stability of the crystal structure.

6.0 Concluding remarks

In this study, we have investigated the high-pressure behaviour of inderborite through *in-situ* single crystal X-ray diffraction, up to approximately 10 GPa. Data collected at high-pressure revealed that:

1. The ambient-condition polymorph of inderborite remains stable up to **about** 8 GPa. Between 8.11(5) and 8.80(5) GPa, inderborite undergoes a first-order phase transition. **The space group of inderborite-II, which is metrically monoclinic, remains unclear.** The phase transition (which is not reversible) is marked by a volume decrease of about 7.0 %.
2. The elastic parameters of inderborite have been determined, and the elastic behaviour has been described in detail. These data will contribute to improve the thermodynamic database of hydrous borates.
3. With increasing pressure, the volume compression is primarily accommodated by the deformation (and compression) of the hydrogen bonding network, as well as by the tilting of the Ca-, Mg- and B- polyhedrons around the bridging oxygen sites.

The pressure at which the inderborite-to-inderborite-II phase transition occurs (8.5 ± 0.40 GPa) follows the trend observed in most hydrated borates studied so far (Comboni *et al.*, 2020a, 2021b, 2022b; Pagliaro *et al.*, 2021), excluding inderite (Comboni *et al.*, 2023). This finding strengthens the **presumed** correlation between the pressure at which the phase transition occurs and the total H₂O content (in wt%, Figure S3).

The bulk modulus of inderborite ($K_{V0} = 41(1)$ GPa) is similar to the bulk modulus of quartz (~ 37 GPa) and lower than those of other aggregates used in radiation shielding concretes (*e.g.*, colemanite $K_{V0}=67(4)$; Okuno, 2005; Lotti *et al.*, 2017). Similarly to colemanite and inderite, inderborite is a Na-free borate, meaning that it cannot promote ASR reactions (*i.e.*, “alkali-silica reactions” – ASR; Thomas, 2011; Figueira *et al.*, 2019; Mohammadi *et al.*, 2020), which are known to undermine the durability of Portland cements. Considering the stability field of inderborite at high pressure and its elastic parameters, this borate can potentially be used as a B-rich aggregate in radiation- shielding materials.

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Author contributions

Daide Comboni: Conceptualization, investigation, writing – original draft; writing – review & editing. **Tommaso Battiston:** investigation **Paolo Lotti:** writing – review & editing. **Michael Hanfland:** Investigation. **G. Diego Gatta:** Conceptualization, review & editing, funding acquisition.

Declaration of interest statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request. A few CIFs (*i.e.*, crystallographic information files), containing the atomic positions at different pressure, are made available as supplementary materials.

Supplementary information

Figure S1: Normalized pressure $F = P/[3fe(1 + 2fe)^{5/2}]$ vs. Eulerian finite strain $fe = \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] / 2$ plot based on the first data set collected at high pressure.

Figure S2: Interatomic angle $\widehat{O8 \cdots O11 \cdots O9}$, $\widehat{O5 \cdots O10 \cdots O4}$, $\widehat{O6 \cdots O3 \cdots O7}$, in inderborite.

Figure S3: H₂O content vs. pressure at which the phase transition occurs in borate structures characterized by isolated polyions. A qualitative linear correlation is represented by the sky-blue shade (modified from Comboni *et al.*, 2023)

Figure S4: Evolution of the O \cdots O interatomic distances with pressure (O9, O10, O11 represent H₂O molecules, O3, O6, O7, O8 are OH⁻ groups, O4 and O5 are oxygen hinges; O3, O6, O10 and O11 are donors).

Table S1: Ca-O, Mg-O and B-O interatomic distances (in Å) in inderborite (average distance, $\langle d \rangle$, in Å; volume, V , in Å³; bond angle variance, σ^2 ; distortion index, D ; quadratic elongation $\langle \lambda \rangle$), with pressure. Data are referred to the first experimental dataset (see Table 1).

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Table S1: Ca-O, Mg-O and B-O interatomic distances (in Å) in inderborite (average distance, $\langle d \rangle$, in Å; volume, V , in Å³; bond angle variance, σ^2 ; distortion index, D ; quadratic elongation $\langle \lambda \rangle$), with pressure. Data are referred to the first experimental dataset (see Table 1). Average $\Delta\%_{\text{Ca-O}} \sim 4\%$, $\Delta\%_{\text{Mg-O}} \sim 2\%$, $\Delta\%_{\text{B-O}} \sim 1.6\%$ [$\Delta\%$ defined as $100 \cdot (X\text{-O}_{0.0001\text{GPa}} - X\text{-O}_{P8.11(5)\text{GPa}}) / X\text{-O}_{0.0001\text{GPa}}$, where X-O is the cation-oxygen bond length].

<i>P</i> (GPa)	0.0001	0.43(5)	0.61(5)	1.19(5)	1.80(5)	2.35(5)	2.82(5)	3.33(5)	3.84(5)	4.54(5)	6.23(5)	7.08(5)	7.80(5)	8.11(5)
Ca1-O1 x2	2.394(3)	2.387(4)	2.385(4)	2.371(4)	2.356(4)	2.350(4)	2.342(4)	2.330(4)	2.327(4)	2.316(4)	2.292(5)	2.283(5)	2.280(5)	2.276(5)
Ca1-O3 x2	2.438(7)	2.437(3)	2.439(3)	2.436(3)	2.433(3)	2.438(3)	2.432(3)	2.437(3)	2.438(4)	2.435(3)	2.433(4)	2.431(4)	2.430(4)	2.423(4)
Ca1-O10 x2	2.450(8)	2.442(3)	2.441(3)	2.434(3)	2.427(3)	2.420(3)	2.415(3)	2.408(3)	2.402(3)	2.394(3)	2.382(4)	2.375(4)	2.373(4)	2.369(4)
Ca1-O6 x2	2.520(6)	2.496(4)	2.494(4)	2.471(4)	2.450(4)	2.440(4)	2.424(4)	2.409(4)	2.401(4)	2.390(4)	2.366(5)	2.350(5)	2.353(5)	2.352(5)
<Ca1-O>*	2.451	2.441	2.440	2.428	2.417	2.412	2.403	2.396	2.392	2.384	2.368	2.360	2.359	2.355
<i>V</i> (Å³)	26.23	25.89	25.87	25.50	25.15	25.01	24.75	24.52	24.39	24.15	23.67	23.41	23.44	23.30
<i>D</i>	0.014	0.012	0.011	0.012	0.012	0.013	0.013	0.014	0.013	0.014	0.017	0.018	0.018	0.017

<i>P</i> (GPa)	0.0001	0.43(5)	0.61(5)	1.19(5)	1.80(5)	2.35(5)	2.82(5)	3.33(5)	3.84(5)	4.54(5)	6.23(5)	7.08(5)	7.80(5)	8.11(5)
Mg1-O9 x2	2.091(5)	2.095(5)	2.094(5)	2.090(5)	2.089(5)	2.078(5)	2.088(6)	2.084(6)	2.087(6)	2.087(6)	2.081(6)	2.064(6)	2.060(6)	2.053(6)
Mg1-O8 x2	2.102(5)	2.103(3)	2.100(3)	2.101(3)	2.098(3)	2.096(3)	2.095(3)	2.088(3)	2.082(3)	2.048(3)	2.033(4)	2.025(4)	2.023(4)	2.019(4)
Mg1-O2 x2	2.072(8)	2.077(3)	2.076(3)	2.072(3)	2.066(3)	2.066(3)	2.063(3)	2.054(3)	2.052(3)	2.081(3)	2.068(4)	2.060(5)	2.051(5)	2.047(4)
<Mg1-O>*	2.088	2.092	2.090	2.088	2.084	2.080	2.082	2.075	2.074	2.072	2.061	2.045	2.045	2.040
<i>V</i> (Å³)	12.12	12.17	12.14	12.09	12.02	11.93	11.97	11.83	11.80	11.76	11.54	11.35	11.28	11.17
<i>D</i>	0.005	0.005	0.004	0.005	0.006	0.005	0.006	0.007	0.007	0.008	0.009	0.008	0.007	0.007
$\langle \lambda \rangle$	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.1	10.1	10.1	10.1	10.1	10.1	10.1
σ^2	52.0	66.8	69.0	86.4	104.7	125.8	140.2	167.6	188.1	211.8	257.7	283.5	298.5	309.2

<i>P</i> (GPa)	0.0001	0.43(5)	0.61(5)	1.19(5)	1.80(5)	2.35(5)	2.82(5)	3.33(5)	3.84(5)	4.54(5)	6.23(5)	7.08(5)	7.80(5)	8.11(5)
B3-O5	1.406(18)	1.364(5)	1.361(5)	1.357(5)	1.359(5)	1.361(5)	1.357(5)	1.359(5)	1.364(6)	1.364(6)	1.356(7)	1.358(7)	1.362(7)	1.365(6)
B3-O4	1.334(13)	1.369(6)	1.371(7)	1.363(7)	1.368(7)	1.377(7)	1.372(7)	1.367(7)	1.362(7)	1.362(7)	1.367(8)	1.364(9)	1.357(9)	1.358(8)
B3-O6	1.389(7)	1.366(8)	1.361(8)	1.368(8)	1.365(8)	1.357(8)	1.363(8)	1.364(8)	1.360(8)	1.360(8)	1.363(10)	1.360(10)	1.356(10)	1.339(10)
< B3-O >*	1.3764	1.3665	1.3642	1.3628	1.3642	1.3648	1.364	1.3635	1.362	1.362	1.3619	1.3609	1.358	1.3539

<i>P</i> (GPa)	0.0001	0.43(5)	0.61(5)	1.19(5)	1.80(5)	2.35(5)	2.82(5)	3.33(5)	3.84(5)	4.54(5)	6.23(5)	7.08(5)	7.80(5)	8.11(5)
B1-O1	1.42(2)	1.434(5)	1.432(5)	1.435(5)	1.435(5)	1.432(5)	1.466(8)	1.466(8)	1.434(5)	1.438(5)	1.431(6)	1.431(6)	1.434(6)	1.430(6)
B1-O4	1.498(6)	1.476(7)	1.475(8)	1.471(8)	1.468(8)	1.467(8)	1.480(6)	1.480(6)	1.472(8)	1.455(8)	1.459(9)	1.459(9)	1.468(10)	1.47(1)
B1-O2	1.493(5)	1.492(5)	1.489(5)	1.485(5)	1.486(5)	1.482(5)	1.476(5)	1.476(5)	1.473(5)	1.473(5)	1.465(6)	1.465(6)	1.452(6)	1.459(6)
B1-O3	1.483(9)	1.469(6)	1.471(6)	1.478(6)	1.480(6)	1.477(6)	1.435(5)	1.435(5)	1.470(6)	1.476(6)	1.479(7)	1.479(7)	1.475(7)	1.475(7)
< B1-O >*	1.474	1.468	1.467	1.467	1.467	1.465	1.464	1.464	1.462	1.461	1.459	1.459	1.457	1.458
<i>V</i> (Å ³)	1.640	1.620	1.616	1.618	1.618	1.609	1.608	1.608	1.603	1.596	1.591	1.591	1.587	1.590
<i>D</i>	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
< <i>λ</i> >	10.023	10.016	10.016	10.015	10.016	10.014	10.013	10.013	10.011	10.012	10.010	10.010	10.008	10.007
<i>σ</i> ²	64.701	46.040	43.795	46.909	50.335	42.762	41.931	41.931	31.850	39.810	31.542	31.542	23.173	18.264

<i>P</i> (GPa)	0.0001	0.43(5)	0.61(5)	1.19(5)	1.80(5)	2.35(5)	2.82(5)	3.33(5)	3.84(5)	4.54(5)	6.23(5)	7.08(5)	7.80(5)	8.11(5)
B2-O5	1.496(7)	1.484(7)	1.487(7)	1.482(7)	1.480(7)	1.476(7)	1.466(7)	1.464(7)	1.467(8)	1.460(7)	1.462(9)	1.467(9)	1.459(9)	1.449(6)
B2-O1	1.443(10)	1.451(6)	1.456(6)	1.453(6)	1.456(6)	1.449(6)	1.451(6)	1.456(6)	1.449(6)	1.446(6)	1.438(7)	1.438(8)	1.430(8)	1.460(9)
B2-O8	1.500(4)	1.502(4)	1.506(4)	1.504(4)	1.500(4)	1.497(4)	1.497(4)	1.492(4)	1.491(5)	1.487(4)	1.474(5)	1.470(5)	1.476(5)	1.476(5)
B2-O7	1.448(13)	1.455(5)	1.449(5)	1.452(5)	1.456(5)	1.456(5)	1.454(5)	1.452(5)	1.454(5)	1.449(5)	1.448(6)	1.449(6)	1.453(6)	1.431(8)
< B2-O >*	1.472	1.473	1.474	1.473	1.473	1.470	1.467	1.466	1.465	1.461	1.456	1.456	1.454	1.454
<i>V</i> (Å ³)	1.635	1.638	1.643	1.638	1.638	1.627	1.619	1.616	1.613	1.597	1.581	1.583	1.576	1.576
<i>D</i>	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
< <i>λ</i> >	10.010	10.006	10.007	10.007	19.919	10.007	10.007	10.006	10.007	10.008	10.009	10.009	10.010	10.008
<i>σ</i> ²	32.217	21.942	24.203	22.855	39.780	24.737	24.998	25.169	26.133	31.218	34.508	33.921	41.427	31.449

*In the *P*-range considered, the $\langle \text{Ca-O} \rangle$, $\langle \text{Mg-O} \rangle$, $\langle \text{B1-O} \rangle$, $\langle \text{B2-O} \rangle$ and $\langle \text{B3-O} \rangle$ distances decrease of about 3.9, 2.3, 1.1, 1.2 and 1.6%, respectively.

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Figure S2: Interatomic angles $\widehat{O8 \cdots O11 \cdots O9}$, $\widehat{O6 \cdots O3 \cdots O7}$, $\widehat{O5 \cdots O10 \cdots O4}$, due to the H-bond interaction in inderborite.

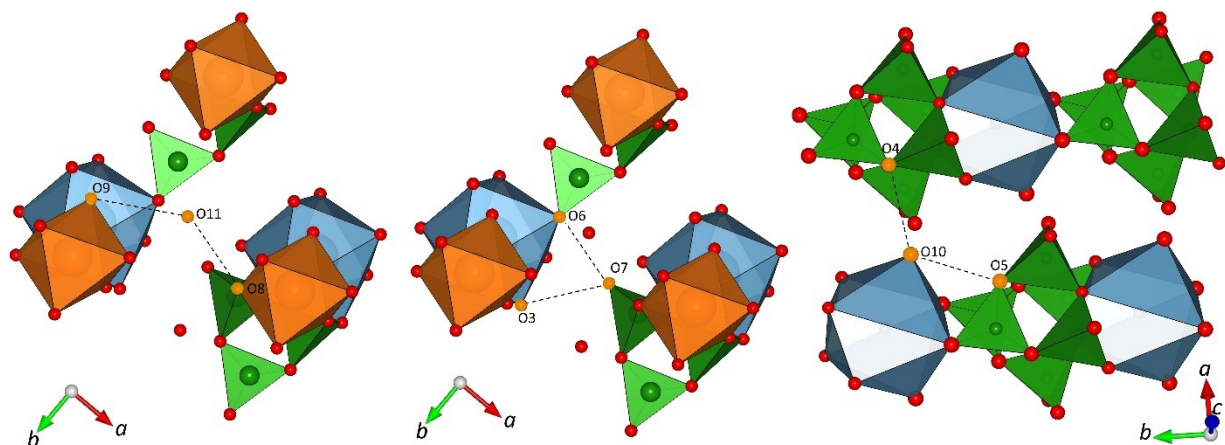


Figure S3: H₂O content vs. pressure at which the phase transition occurs in borate structures characterized by isolated polyions. A qualitative linear correlation is represented by the sky-blue shade (modified from Comboni *et al.*, 2023)

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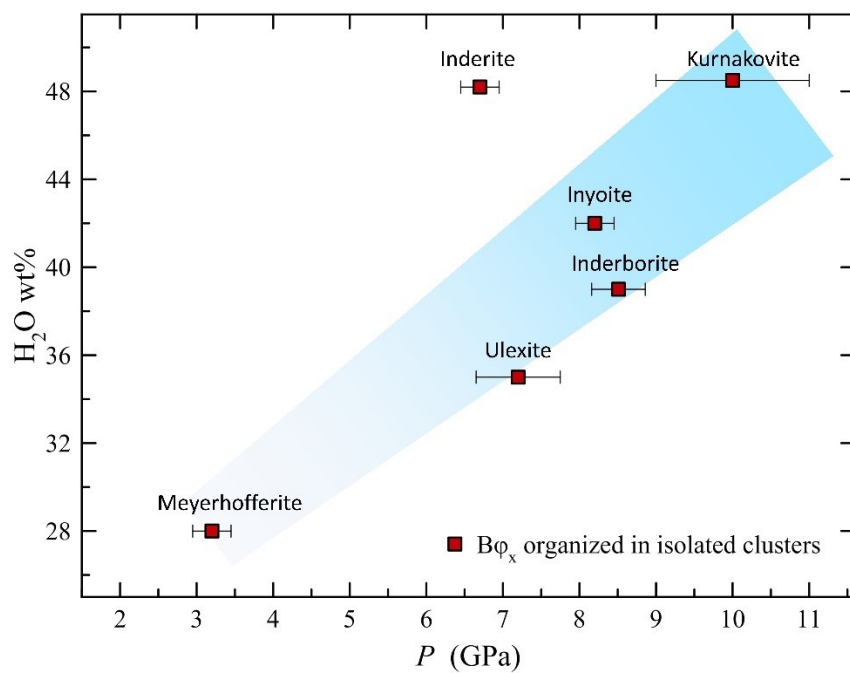
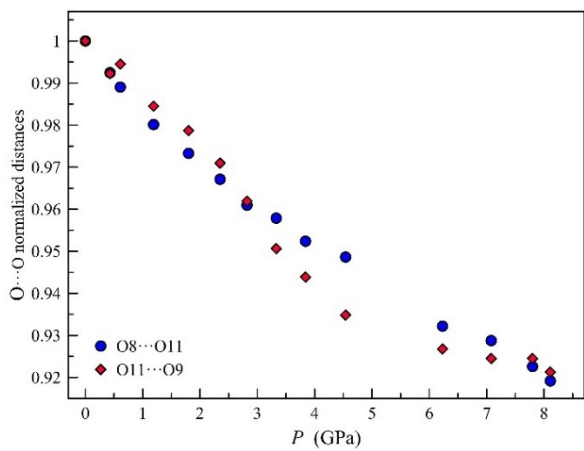
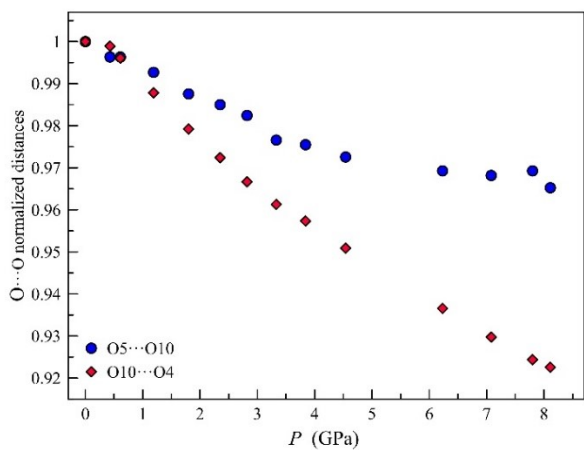
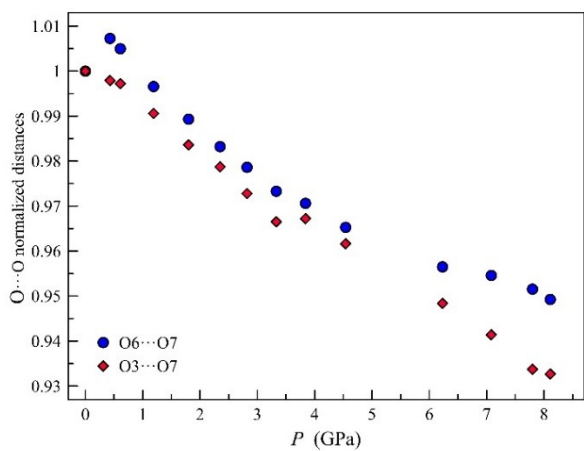


Figure S4: Evolution of the O \cdots O interatomic distances with pressure (O9, O10, O11 represent H₂O molecules, O3, O6, O7, O8 are OH⁻ groups, O4 and O5 are oxygen hinges; O3, O6, O10 and O11 are donors).

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