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Supporting information for article:

Structure–property relationships of molecular shape and orientation with compression and expansion of xylitol

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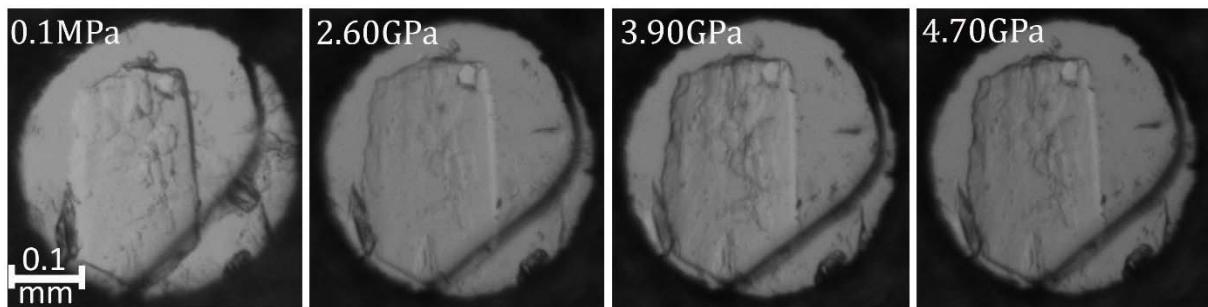


Figure S1 Single crystals of xylitol isothermally compressed in the diamond-anvil cell at 0.1 MPa–4.70 GPa. The cotton fiber used to fix crystal in the hole and several small ruby chips are mounted in the corner.

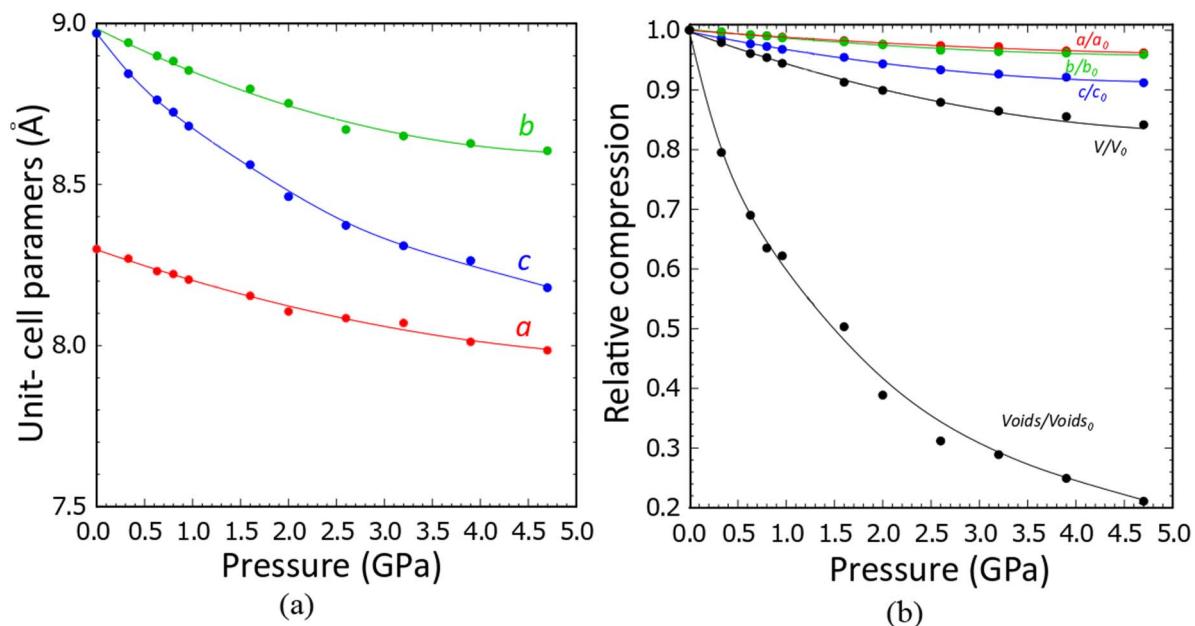


Figure S2 (a) Compression of unit cell parameters in xylitol; and (b) compression of the unit-cell dimensions and voids related to the 0.1 MPa/296 K values. The voids volume was calculated by Mercury assuming the probing-sphere radius of 0.5 Å and the step of 0.1 Å.

Table S1 Experimental and crystal data for xylitol.

| | | | | | | |
|--|--------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| $C_5H_{12}O_5$ | High-density phase | | | | | |
| Pressure (GPa) | 0.0001(2) | 0.33(2) | 0.63(2) | 0.8(2) | 0.96(2) | 1.60(2) |
| Temperature (K) | 296(2) | | | | | |
| Formula weight | 152.15 | | | | | |
| Crystal color | colorless | | | | | |
| Crystal size (mm) | 0.15×0.1×0.11 | | | | | |
| Crystal system | Orthorhombic | | | | | |
| Space group | $P2_12_12_1$ | | | | | |
| Unit cell (Å) <i>a</i> | 8.2993(3) | 8.2694(3) | 8.2305(2) | 8.2213(4) | 8.204(2) | 8.1540(5) |
| <i>b</i> | 8.9697(4) | 8.9403(12) | 8.8992(11) | 8.883(2) | 8.854(2) | 8.7964(16) |
| <i>c</i> | 8.9693(4) | 8.8438(9) | 8.7624(8) | 8.7242(17) | 8.6809(7) | 8.5610(19) |
| Volume (Å ³) | 667.69(5) | 653.83(11) | 641.80(10) | 637.1(2) | 630.6(2) | 614.04(18) |
| <i>Z</i> | 4 | 4 | 4 | 4 | 4 | 4 |
| Density (g/cm ³) | 1.514 | 1.546 | 1.575 | 1.586 | 1.603 | 1.646 |
| Wavelength MoKα (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Absorption (mm ⁻¹) | 0.136 | 0.139 | 0.142 | 0.143 | 0.144 | 0.148 |
| F(000) | 328 | 328.0 | 328.0 | 328.0 | 328.0 | 328 |
| 2θ max (°) | 53.76 | 53.516 | 52.352 | 52.018 | 54.566 | 54.034 |
| Index ranges <i>h</i> _{min} / <i>h</i> _{max} | -10/3 | -9/10 | -10/10 | -9/9 | -7 / 7 | -10/10 |
| <i>k</i> _{min} / <i>k</i> _{max} | -5/11 | -7/7 | -7/7 | -6/6 | -8 / 8 | -8/8 |
| <i>l</i> _{min} / <i>l</i> _{max} | -5/11 | -8/8 | -8/8 | -7/7 | -11 / 11 | -7/7 |
| Refl. Collected | 1283 | 2431 | 2149 | 305 | 2619 | 2583 |
| Completeness (%) | 77 | 44 | 39 | 24 | 37 | 41 |
| Refl. observed (<i>I</i> >4σ _{<i>I</i>}) | 1011 | 547 | 482 | 280 | 467 | 502 |
| <i>R</i> (int) | 0.0139 | 0.0197 | 0.0203 | 0.0066 | 0.0645 | 0.0588 |
| Data/restraints/parameters | 1011/0/96 | 547/0/94 | 482/0/96 | 280/20/96 | 467/7/94 | 502/14/96 |
| Goodness-of-fit on F ² | 1.064 | 1.122 | 1.127 | 1.208 | 1.087 | 1.090 |
| Final <i>R</i> ₁ (<i>I</i> >2σ _{<i>I</i>}) | 0.0328/ 0.0754 | 0.0241/ 0.0538 | 0.0236/ 0.0575 | 0.0227/ 0.0509 | 0.0339/ 0.0681 | 0.0395 /0.0583 |
| <i>R</i> ₁ /w <i>R</i> ₂ (all data) | 0.0369/ 0.0788 | 0.0282/ 0.0566 | 0.0263/ 0.0596 | 0.0235/ 0.0514 | 0.0512/ 0.0765 | 0.0568 /0.0634 |

Table S1 (Continued) Experimental and crystal data of xylitol.

| | | | | | |
|---|--------------------|-------------------|-------------------|-------------------|-------------------|
| $C_5H_{12}O_5$ | High-density phase | | | | |
| Pressure (GPa) | 2.00(2) | 2.60(2) | 3.20(2) | 3.90(2) | 4.70(2) |
| Temperature (K) | 296(2) | | | | |
| Formula weight | 152.15 | | | | |
| Crystal color | Colorless | | | | |
| Crystal size (mm) | 0.15×0.1×0.11 | | | | |
| Crystal system | Orthorhombic | | | | |
| Space group | $P2_12_12_1$ | | | | |
| Unit cell (\AA) <i>a</i> | 8.105(9) | 8.0845(8) | 8.0696(15) | 8.0108(4) | 7.9846(14) |
| <i>b</i> | 8.752(6) | 8.67(2) | 8.65(5) | 8.6270(5) | 8.6043(11) |
| <i>c</i> | 8.462(2) | 8.3725(11) | 8.309(2) | 8.263(8) | 8.179(12) |
| Volume (\AA^3) | 600.3(8) | 586.9(14) | 580(3) | 571.0(6) | 561.9(9) |
| <i>Z</i> | 4 | 4 | 4 | 4 | 4 |
| Density (g/cm ³) | 1.684 | 1.722 | 1.742 | 1.770 | 1.798 |
| Wavelength MoK α (\AA) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Absorption (mm ⁻¹) | 0.152 | 0.155 | 0.157 | 0.159 | 0.162 |
| F(000) | 328 | 328 | 328 | 328 | 328 |
| 2 θ max (°) | 53.55 | 54.934 | 53.772 | 53.904 | 55.294 |
| Index ranges h_{\min}/h_{\max} | -7/7 | -10/10 | -9/10 | -10/9 | -10/10 |
| k_{\min}/k_{\max} | -8/8 | -2/2 | -2/2 | -10/10 | -10/10 |
| l_{\min}/l_{\max} | -10/10 | -10/10 | -10/10 | -2/2 | -2/2 |
| Refl. Collected | 2462 | 2371 | 2087 | 2081 | 2216 |
| Completeness (%) | 34 | 24 | 24 | 28 | 27 |
| Refl. observed ($I > 4\sigma_I$) | 391 | 283 | 275 | 303 | 290 |
| <i>R</i> (int) | 0.1200 | 0.0732 | 0.0876 | 0.0483 | 0.2099 |
| Data/restraints/parameters | 391/60/95 | 283/80/94 | 275/73/93 | 303/60/96 | 290/86/95 |
| Goodness-of-fit on F ² | 1.036 | 1.215 | 1.164 | 1.055 | 1.014 |
| Final <i>R</i> ₁ ($I > 2\sigma_I$) | 0.0544 /0.1187 | 0.0409 /0.0726 | 0.0520 /0.1061 | 0.0259 /0.0411 | 0.0547 /0.0696 |
| <i>R</i> ₁ /w <i>R</i> ₂ (all data) | 0.1025 /0.1382 | 0.0811 /0.0879 | 0.0965 /0.1243 | 0.0464 /0.0464 | 0.1268 /0.0827 |

Table S2 The Assignments of the unit-cell dimensions of xylitol crystal in the literatures as well as conditions of temperature (T) and pressure (P) of the measurements

| Authors | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | <i>T</i> (K)/ <i>p</i> (GPa) | References |
|-----------------------------------|--------------|--------------|--------------|------------------------------|---|
| Kim & Jefferey | 8.291(2) | 8.970(2) | 8.970(5) | RT ¹ /0.0001 | <i>Acta Cryst.</i> 1969 , 25, 2607-2613, |
| Madsen <i>et al.</i> ² | 8.262(2) | 8.918(1) | 8.895(1) | 101 / 0.0001 | <i>J. Phys. Chem. A</i> 2011 , 26, 7794-7804 |
| Madsen <i>et al.</i> ² | 8.262(5) | 8.923(2) | 8.900(2) | 122 /0.0001 | <i>J. Phys. Chem. A</i> 2011 , 26, 7794-7804 |
| Madsen <i>et al.</i> ² | 8.274(2) | 8.9241(10) | 8.9073(11) | 141 /0.0001 | <i>J. Phys. Chem. A</i> 2011 , 26, 7794-7804 |
| Madsen <i>et al.</i> ² | 8.279(2) | 8.934(2) | 8.925(2) | 181 /0.0001 | <i>J. Phys. Chem. A</i> 2011 , 26, 7794-7804 |
| Safari & Katrusiak ³ | 8.2993(3) | 8.9697(4) | 8.9693(4) | 296/0.0001 | This work |
| Safari & Katrusiak | 8.2694(3) | 8.9403(12) | 8.8438(9) | 296/0.33 | This work |
| Safari & Katrusiak | 8.2305(2) | 8.8992(11) | 8.7624(8) | 296/0.63 | This work |
| Safari & Katrusiak | 8.2213(4) | 8.883(2) | 8.7242(17) | 296/0.80 | This work |
| Safari & Katrusiak | 8.204(2) | 8.854(2) | 8.6809(7) | 296/0.96 | This work |
| Safari & Katrusiak | 8.1540(5) | 8.7964(16) | 8.5610(19) | 296/1.60 | This work |
| Safari & Katrusiak | 8.105(9) | 8.752(6) | 8.462(2) | 296/2.00 | This work |
| Safari & Katrusiak | 8.0845(8) | 8.67(2) | 8.3725(11) | 296/2.60 | This work |
| Safari & Katrusiak | 8.0696(15) | 8.65(5) | 8.309(2) | 296/3.20 | This work |
| Safari & Katrusiak | 8.0108(4) | 8.6270(5) | 8.263(8) | 296/3.90 | This work |
| Safari & Katrusiak | 7.9846(14) | 8.6043(11) | 8.179(12) | 296/4.70 | This work |

¹ RT – room temperature, as described by the authors.

² Parameters *b* and *c* are reversed by Madsen *et al.* with respect to these in the paper by Kim & Jefferey (1969), in this table the Madsen's *et al.* assignment is repeated and marked in red.

³In this work parameters *b* and *c* are assigned following Kim & Jefferey (1969).

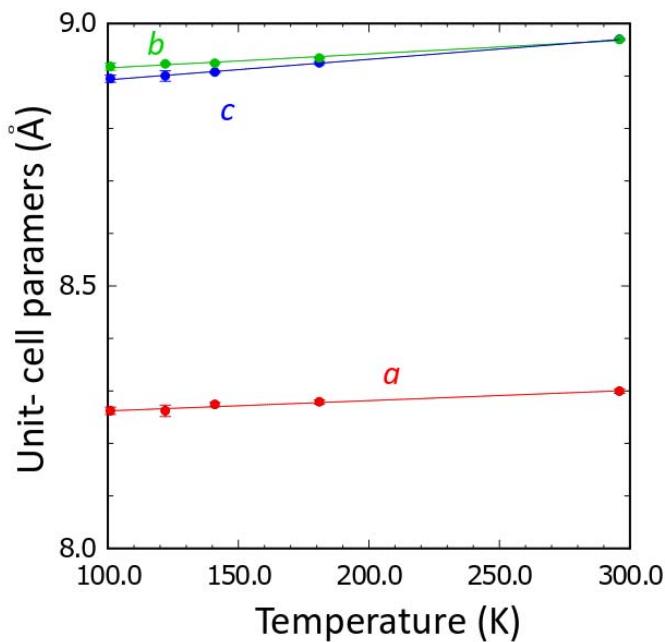


Figure S3 Unit cell parameters of xylitol as a function of temperature in the 100–180 K range (Madsen *et al.*, 2011) and at 296°K (this work).

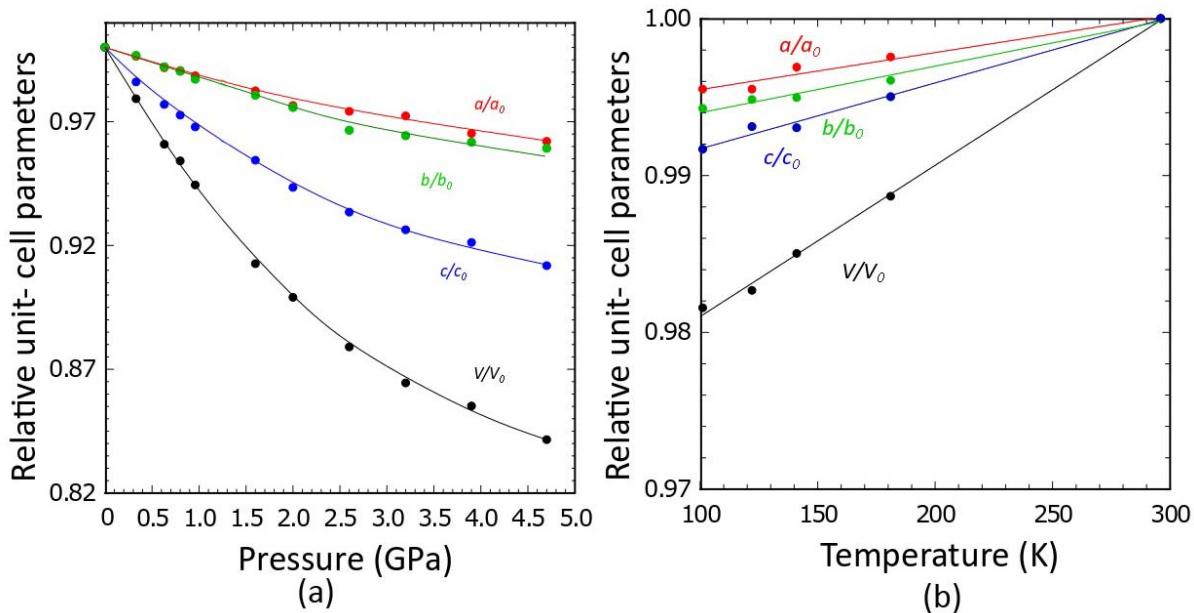


Figure S4 (a) Compression; and (b) thermal expansion of the unit-cell dimensions of xylitol related to the 0.1 MPa/296 K values.

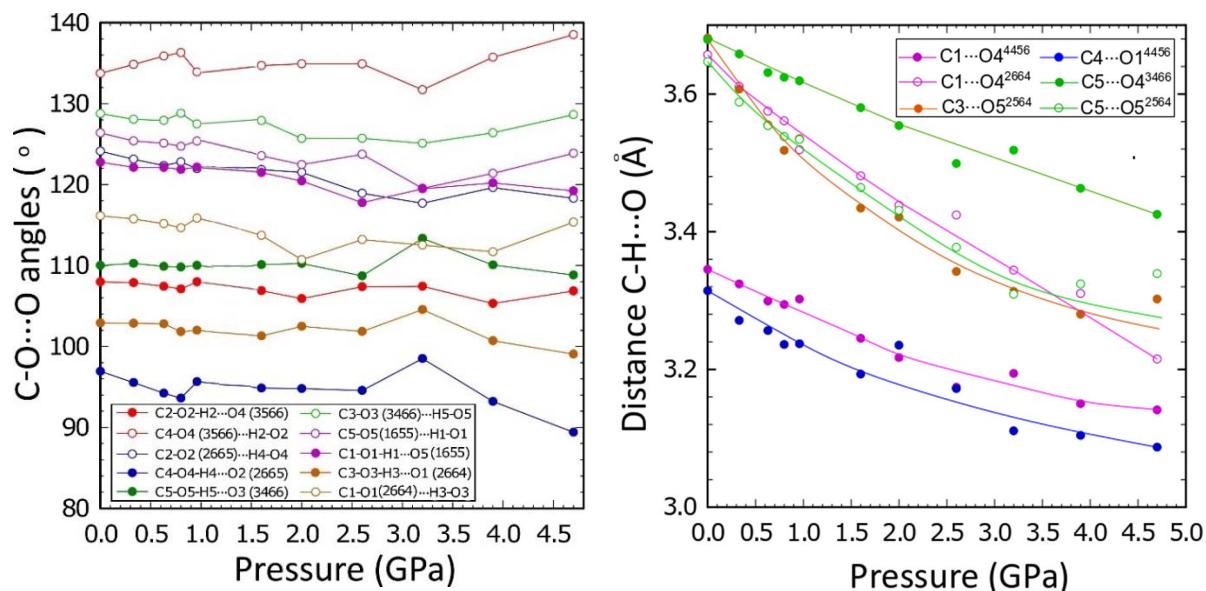


Figure S5 The C- O···O angles and C···O distances in xylitol as function of pressure up to 4.70 GPa. The lines joining the points are for guiding the eye only.

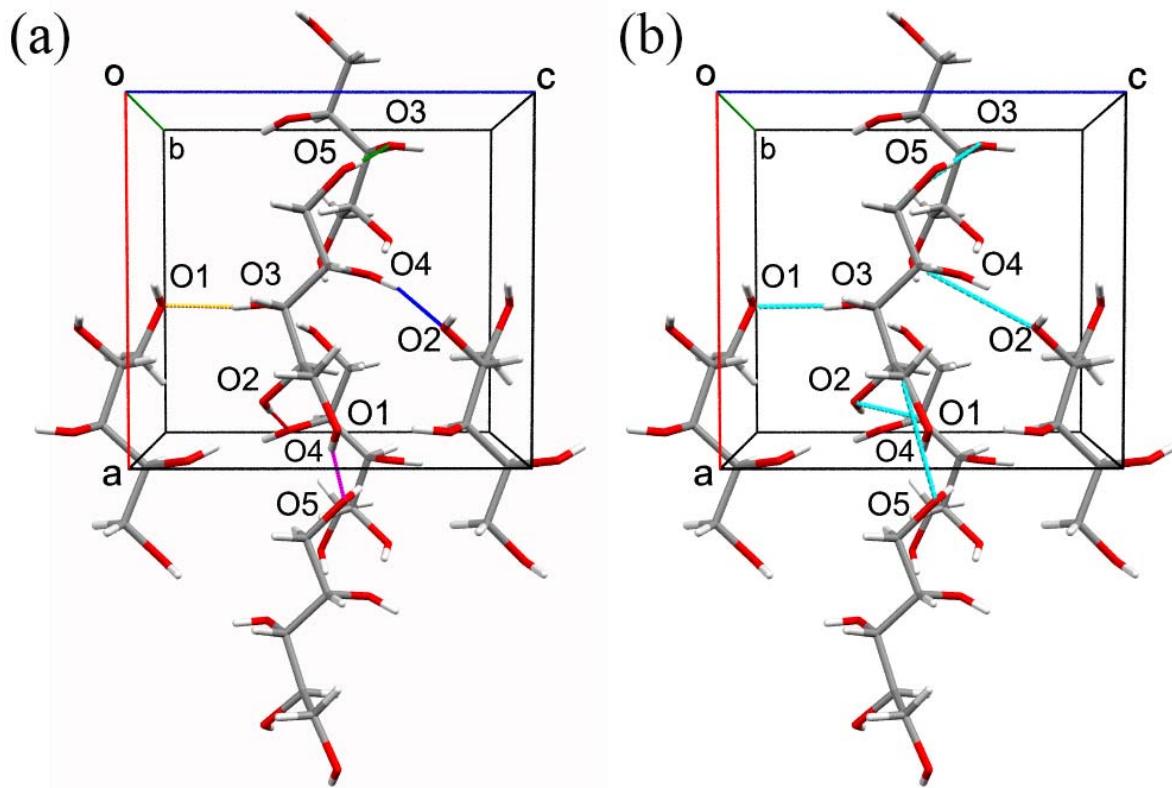


Figure S6 (a) The OH···O hydrogen bonds in xylitol crystal indicated by different colours corresponding to those used for plotting their distances in Figure 3; and (b) CH···O contacts marked in cyan.

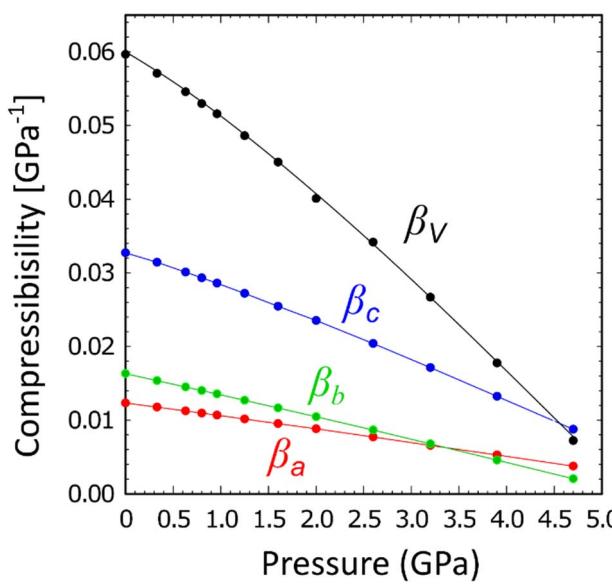


Figure S7 Volume and linear compressibility coefficients β of the unit-cell parameters of xylitol.

Table S3 The Compressibility parameters of unit-cell parameters of xylitol (a , b , c , and volume V), calculated as $\beta_x = -1/x \partial x / \partial p$, where x is a given parameter.

| Pressure (GPa) | $\beta_a (\text{GPa}^{-1})$ | $\beta_b (\text{GPa}^{-1})$ | $\beta_c (\text{GPa}^{-1})$ | $\beta_V (\text{GPa}^{-1})$ |
|----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 0.0001 | 0.0123 | 0.0163 | 0.0327 | 0.05965 |
| 0.33 | 0.0118 | 0.0154 | 0.0314 | 0.057077 |
| 0.63 | 0.0113 | 0.0145 | 0.0301 | 0.05458 |
| 0.80 | 0.0110 | 0.0140 | 0.0293 | 0.052961 |
| 0.96 | 0.0107 | 0.0136 | 0.0286 | 0.05157 |
| 1.60 | 9.5364×10^{-3} | 0.0117 | 0.0255 | 0.04508 |
| 2.00 | 8.8340×10^{-3} | 0.0105 | 0.0235 | 0.040075 |
| 2.60 | 7.7135×10^{-3} | 8.6600×10^{-3} | 0.0204 | 0.034146 |
| 3.20 | 6.5827×10^{-3} | 6.7880×10^{-3} | 0.0171 | 0.02667 |
| 3.90 | 5.2853×10^{-3} | 4.5832×10^{-3} | 0.0132 | 0.01776 |
| 4.70 | 3.7597×10^{-3} | 2.0478×10^{-3} | 8.7614×10^{-3} | 0.007219 |

Table S4 Linear functions fitted to the experimentally obtained pressure dependences of unit-cell volume V and parameters a , b , c of xylitol used for the calculation of the differential part of compressibility parameter $\beta_x = -1/x\partial x/\partial p$.

| | Compressibility |
|--------|---|
| $a(p)$ | $\beta_a = -\frac{1}{a}(0.0077p^2 - 0.1024p + 8.2977)$ ($R= 0.9959$) |
| $b(p)$ | $\beta_b = -\frac{1}{b}(0.0137p^2 - 0.1464p + 8.9844)$ ($R= 0.9961$) |
| $c(p)$ | $\beta_c = -\frac{1}{c}(0.0236p^2 - 0.2935p + 8.9457)$ ($R= 0.9983$) |
| $V(p)$ | $\beta_V = -\frac{1}{V}(3.8058p^2 - 39.8309p + 666.5427)$ ($R= 0.9991$) |

Table S5 Hydrogen bond contacts at 0.0001-4.70GPa range. All O-H bonds lengths have been normalized to the neutron-determined values according to Allen & Bruno in 2010.

| Angle (°) | 0.0001 | 0.33(2) | 0.63(2) | 0.80(2) | 0.96(2) | 1.60(2) |
|-----------------------|-----------|------------|------------|------------|------------|------------|
| C1-O1···H3-O3 (2664) | 116.13(3) | 115.90 (2) | 115.19(4) | 114.60(3) | 115.82(3) | 113.782) |
| C2-O2···H4-O4 (2664) | 124.15(3) | 123.04(3) | 122.36(4) | 122.73(2) | 121.89(4) | 121.90(3) |
| C3-O3-H3···O1 (2664) | 102.92(4) | 102.92(3) | 102.82(5) | 101.86(3) | 102.10(2) | 101.30(1) |
| C4-O4-H4 (2664) ···O2 | 96.91(3) | 95.54(4) | 94.26(6) | 93.68(2) | 95.68(2) | 94.92(2) |
| C2-O2-H2···O4 (4566) | 107.98(2) | 107.80(3) | 107.38(1) | 107.121(3) | 108.10 (3) | 106.96(3) |
| C5-O5-H5···O3 (4466) | 110.03(3) | 110.30 (3) | 109.88(4) | 109.76 (3) | 110.101(2) | 110.125(3) |
| C1-O1-H1 (1455) ···O5 | 122.76(2) | 122.01(3) | 122.12(5) | 121.86(2) | 122.140(4) | 121.494(1) |
| C5-O5···H1-O1(1455) | 126.38(4) | 125.31(3) | 125.109(6) | 124.68(3) | 125.28(2) | 123.62(3) |
| C3-O3 (4466) ···H5-O5 | 128.75(2) | 128.20(2) | 127.86(1) | 128.82(5) | 127.489(3) | 127.98(4) |
| C4-O4 (4566) ···H2-O2 | 133.73(3) | 135.05(3) | 135.82(4) | 136.31 (2) | 133.922(4) | 134.712(3) |

Table S5 (Continuation) Hydrogen bond contacts at 0.0001-4.70 GPa range. All O-H bonds lengths have been normalized to the neutron-determined values according to Allen & Bruno in 2010.

| Angle (°) | 2.00(2) | 2.60(2) | 3.20(2) | 3.90(2) | 4.70(2) |
|----------------------|------------|------------|------------|------------|------------|
| C1-O1···H3-O3 (2664) | 110.739(3) | 113.28(3) | 112.58(4) | 111.74(3) | 115.42(5) |
| C2-O2···H4-O4 (2664) | 121.55(2) | 118.98(3) | 117.74(4) | 119.68(2) | 118.39(2) |
| C3-O3-H3···O1 (2664) | 102.50(2) | 101.89(5) | 104.59(2) | 100.76(3) | 99.10(3) |
| C4-O4-H4 (2664)···O2 | 94.81(4) | 94.61(5) | 97.20(3) | 93.26(2) | 89.48(2) |
| C2-O2-H2···O4 (4566) | 105.93(4) | 107.42(4) | 107.49(4) | 105.35(4) | 106.93(4) |
| C5-O5-H5···O3 (4466) | 110.25(3) | 108.741(3) | 113.38(3) | 110.120(2) | 108.880(3) |
| C1-O1-H1 (1455)···O5 | 120.42(2) | 117.79(2) | 119.54(4) | 120.241(4) | 119.27(3) |
| C5-O5···H1-O1(1455) | 122.45(4) | 123.79(2) | 119.543(3) | 121.47(2) | 123.89(4) |
| C3-O3 (4466)···H5-O5 | 125.71(2) | 125.78(3) | 125.16(3) | 126.49(2) | 128.68(3) |
| C4-O4 (4566)···H2-O2 | 134.89(5) | 134.96(2) | 131.74(5) | 135.79(2) | 138.512(4) |

Table S6 Dimensions of hydrogen bonds in xylitol crystal up to 4.70 GPa.

| Distance (Å) | 0.0001 | 0.33(2) | 0.63(2) | 0.80(2) | 0.96(2) | 1.60 |
|----------------|------------|------------|------------|------------|------------|------------|
| O1···O5(1655) | 2.6885 (2) | 2.6770 (4) | 2.6598 (1) | 2.6448 (4) | 2.6560 (4) | 2.6180 (4) |
| O3···O1 (2664) | 2.7011 (3) | 2.6860 (4) | 2.6811(4) | 2.6910(8) | 2.6741(6) | 2.6650 (4) |
| O5···O3 (4466) | 2.7241 (2) | 2.7210 (5) | 2.7152 (5) | 2.7140 (4) | 2.6900 (2) | 2.6103 (3) |
| O2···O4 (4566) | 2.8483 (3) | 2.8220 (4) | 2.8010 (6) | 2.7970 (3) | 2.7870 (5) | 2.7592 (2) |
| O4···O2(2665) | 2.8804 (4) | 2.8706 (4) | 2.8500 (1) | 2.8420 (2) | 2.8190 (3) | 2.7940 (3) |
| H1···O5(1655) | 1.9073 (3) | 1.8880 (3) | 1.8740 (4) | 1.8610 (4) | 1.8940 (3) | 1.8280 (4) |
| H3···O1 (2664) | 1.8932 (4) | 1.8750 (3) | 1.8730 (5) | 1.8900 (2) | 1.8680 (3) | 1.8702 (3) |
| H5···O3 (4466) | 1.9045 (3) | 1.9011 (3) | 1.8960 (6) | 1.8990 (2) | 1.8870 (4) | 1.8440 (4) |
| H2···O4 (4566) | 2.0292 (2) | 2.0120 (4) | 1.9840 (1) | 1.9860 (3) | 2.0290 (3) | 1.9416 (4) |
| H4···O2(2665) | 2.0972 (3) | 2.1110 (2) | 2.0940 (4) | 2.0780 (2) | 2.0390 (4) | 2.1520 (3) |

Table S6 (continued) Dimensions of hydrogen bonds in xylitol crystal up to 4.70 GPa.

| Distance (Å) | 2.00(2) | 2.60(2) | 3.20(2) | 3.90(2) | 4.70(2) |
|--------------|------------|------------|------------|------------|------------|
| O1…O5(1655) | 2.5883 (3) | 2.5880 (3) | 2.6110 (5) | 2.5710 (3) | 2.5797 (3) |
| O3…O1 (2664) | 2.6513 (5) | 2.6291 (4) | 2.6260 (2) | 2.6300 (3) | 2.6480 (5) |
| O5…O3 (4466) | 2.6621 (2) | 2.6301 (5) | 2.6240 (5) | 2.5996 (4) | 2.5950 (5) |
| O2…O4 (4566) | 2.7428 (3) | 2.7180 (4) | 2.6900 (3) | 2.6683 (2) | 2.6482 (2) |
| O4…O2(2665) | 2.7530 (2) | 2.7510 (2) | 2.7060 (4) | 2.680 (3) | 2.6772 (3) |
| H1…O5(1655) | 1.9610 (5) | 1.8120 (4) | 1.7840 (4) | 1.7970 (3) | 1.8140 (4) |
| H3…O1 (2664) | 1.8233 (2) | 1.8197 (3) | 1.7556 (5) | 1.8520 (1) | 1.8830 (5) |
| H5…O3 (4466) | 1.8243 (3) | 1.8200 (4) | 1.8530 (3) | 1.7830 (2) | 1.7793 (5) |
| H2…O4 (4566) | 1.9660 (4) | 1.9803 (3) | 2.0160 (3) | 1.8560 (4) | 1.8410 (3) |
| H4…O2(2665) | 1.9658 (5) | 1.9153 (4) | 1.9150 (4) | 1.9280 (3) | 1.9280 (4) |

Table S7 ORTEP symmetry codes (Johnson, 1976).

| ORTEP code | Symmetry code |
|------------|--|
| 1655 | 1+x, y, z |
| 2564 | $\frac{1}{2}$ -x, 1-y, $\frac{-1}{2}$ +z |
| 2665 | $\frac{3}{2}$ -x, 1-y, $\frac{1}{2}$ +z |
| 2664 | $\frac{3}{2}$ -x, 1-y, $\frac{-1}{2}$ +z |
| 4456 | $\frac{-1}{2}$ +x, $\frac{1}{2}$ -y, 1-z |
| 4466 | $\frac{-1}{2}$ +x, $\frac{3}{2}$ -y, 1-z |
| 4566 | $\frac{1}{2}$ +x, $\frac{3}{2}$ -y, 1-z |

Madsen, A. Q., Mattson, R. & Larsen, S. (2011). *J. Phys. Chem. A*, **115**, 26, 7794–7804.

Allen, F. H. & Bruno, I. J. (2010). *Acta Crystallogr. Sect. B: Struct. Sci.* **66**, 380–386.

Johnson, C. K. (1976). Oak Ridge National Laboratory, Memphis.