Negative-pressure-induced enhancement in a freestanding ferroelectric

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Experimental details:

Preparation: Wires used here were prepared initially as PX via a hydrothermal method\(^1\). 4 mmol Ti(OC\(_4\)H\(_9\))\(_4\) was first dissolved in 8 mL ethanol and then hydrolyzed in 8 mL deionized H\(_2\)O. After adding 20 mmol KOH, 5.2 mmol Pb(CH\(_3\)COO)\(_2\)\(_3\)H\(_2\)O, and 0.050 g polyvinyl alcohol (PVA) under stirring, the final feedstock was adjusted to 40 mL with deionized H\(_2\)O and transferred to a 50mL Teflon-lined autoclave. The hydrothermal processing was conducted at 200\(^\circ\)C for 3.5 hours. The products were washed first with deionized H\(_2\)O for several cycles and then with 10wt% H\(_2\)(CH\(_3\)COO)\(_2\) solution to remove unreacted ions and the remnant PbO. The final pure PX-phase sample was obtained by another cycle of washing with de-ionized H\(_2\)O and dried at 60\(^\circ\)C in air. The PX-phase powders have the same stoichiometry as perovskite PT but a crystalline structure with a reduced density (by 13\%). When annealed in air at 540 \(^\circ\)C for 30 min they transformed into conventional perovskite PT. The microstructural feature and the phase characteristic of the converted perovskite PT wires are shown in Supplementary Fig.1.
**Figure S1 | Structural characterization of the perovskite PT sample.**

**a,** High resolution image revealing that the monocrystallinity is not affected by the pores. **b,** Powder XRD of the PbTiO$_3$ sample obtained by annealing the fibrous PX phase shows a tetragonal perovskite structure. The red solid lines are the standard powder XRD pattern of perovskite PbTiO$_3$ (JCPDS card No. 06-0452) for reference. **c,** Raman spectra from the thinnest wire studied. The frequencies of the four most prominent peaks are given, with in parentheses the frequencies measured in a bulk PbTiO$_3$ single crystal sample at room temperature (ref.3). Some of the features are from quasimodes that appear broadened by the variable phonon propagation directions and thus do not correspond exactly to zone centre frequencies (ref.4). The wire was much smaller than the diffraction-limited focus, and the strong sapphire substrate line at 413 cm$^{-1}$ then provides a convenient calibration check. **b.** TEM image of the area with 90° domains.
Raman Spectroscopy on single wires. Raman spectroscopy was performed with a Horiba Jobin-Yvon T64000 spectrometer, excited with the 514.5 nm line from an Ar+ ion laser. Measurements were performed on single wires of 125, 250 and 650 nm diameter previously selected by scanning electron microscopy, on small bundles of large-diameter wires and on a macroscopic pile of wires. The samples were supported on sapphire substrates placed on the hearth of a Linkam variable-temperature microscope stage capable of being heated to 600 °C. The single wires were too small to be resolved in the microscope, so after imaging the field in a scanning electron microscope they were identified by larger nearby bundles of wires. The power used was reduced to avoid heating the wire, and carefully checked to establish that increasing it by factors of 2 did not affect the results.

X-ray Diffraction. The temperature-dependent XRD measurements on the multiple-wire sample were performed using a high resolution two axis X-Ray diffractometer in Bragg-Brentano geometry with the Cu-Kβ radiation (λ=1.3922 Å). The \{200\}, \{220\} and \{222\} family peaks were recorded in the temperature range between 25 °C and 640 °C with a temperature step of 10 °C. After correction of the zero shift, the lattice parameters in both tetragonal and cubic phases have been extracted.

Ferroelectric switching and piezoelectric response: The local piezoelectric and ferroelectric activity of the PT wires were examined by piezoresponse force microscopy (Cypher™, Asylum Research) with a Ti/Ir coated tip (3 N /m in force constant). Supplementary Fig. 2 shows representative result on an individual wire dispersed on a conductive Nb-doped SrTiO₃ substrate. The particular shown wire has the diameter of \(\approx 105\) nm, showing switchability of the most highly stretched wires.
Figure S2 | piezoresponse of a perovskite PT nanowire of \( \approx 105 \) nm diameter and its local switching behavior. a, A topography image of the nanowire and its measured, effective, width. b, A schematic diagram showing the effect of tip-sample convolution where the true radius of a nanowire, \( r \), is increased to an effective radius, \( r_{\text{eff}} \) and the measured, apparent, profile is given by the red dotted line. Taking into account the tip diameter of 30 nm, the true diameter of the wire shown in (a) is estimated to be 105 nm. c, d, e, & f, PFM amplitude (c) and (e) and corresponding phase images (d) and (f) for the domain structure and after positive (c) & (d) and negative (e) & (f) switching with a scanning probe. g, The fraction of each domain from phases (d) & (f) for the two different states. h & i, PFM amplitude (h) and phase (i) hysteresis loop taken at the point indicated by the red dot in (f).
Estimation of spontaneous polarization

The spontaneous polarization ($P_s$) in $d = 116$ nm nanowire, was estimated based on a high-resolution high-angle annular-dark-field (HAADF) image following the linear relationship between $P_s$ and the relative displacements of the B-site cations in displacive ferroelectrics $^5$, similarly to e.g., Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ $^6$ and BiFeO$_3$ $^7$. The high-resolution STEM image was obtained on a probe-corrected FEI Titan-80-300 microscope with an operating voltage of 300 kV. The image with indication of column types is shown in Supplementary Fig. 3(a). By measuring the positions of Pb and Ti columns, the relative shift of Ti, $\delta z$, with respect to centers of the nearest four Pb columns are calculated and counted, with its mean value located at $\delta z = 0.0327$ nm. The bulk $\delta z_0$ value of PbTiO$_3$ from XRD refinements is $0.0162$ nm $^8$, leading to $P_s$ value for the bulk of $P_{s0} = \kappa \delta z = 81.6 \mu$C/cm$^2$ ($\kappa = 2500$ nm$^{-1}$C/cm$^2$) $^5$. The polarization in the nanowire is $P_s = (\delta z / \delta z_0)P_{s0} = 164.5$ $\mu$C/cm$^2$.

![Figure S3](image_url)

**Figure S3** | **a**. HAADF image of $d = 116$ nm nanowire along [100] zone axis. The column types are denoted on the magnified inset: red-Pb, blue-Ti. Orientation of the $P_s$ is denoted by the red arrow. **b** Illustration of atom positions in a perovskite unit.
cell (red-Pb, blue-Ti, olive-O). \( \delta \) denotes the displacements of Ti with respect to center of the nearest four Pb columns. The mean value of \( \delta \) in 116 nm nanowire is 0.0327 nm as measured from (a) while its bulk value in PbTiO\(_3\) is 0.0162 nm.

![Distribution profile of perovskite PbTiO\(_3\) wires as a function of diameters](image)

Figure S4 | Distribution profile of perovskite PbTiO\(_3\) wires as a function of diameters. The data were extracted from the SEM images each typically containing 20-150 nanowires. The sample for the SEM imaging was without any pretreatment like centrifugation or ultrasonic bathing. The volume-average diameter mentioned in the main text was determined with the observation that the average wire length was approximately proportional to the diameter, resulting in a volume-weighted average of about 220-270 nm.

**Thermodynamic calculations**

The Landau-Ginzburg-Devonshire (LGD) free energy of PbTiO\(_3\) is expanded as follows,
\[ G = \alpha_1(R_1^2 + P_2^2 + P_3^2) + \alpha_{11}(R_1^4 + P_2^4 + P_3^4) + \alpha_{12}(R_1^2P_2^2 - P_2^2P_3^2 + P_3^2R_1^2) + \alpha_{111}(R_1^6 + P_2^6 + P_3^6) + \alpha_{121}(P_2^2 + P_3^2) + P_2^4(R_1^2 + P_3^2) + P_3^4(R_1^2 + P_2^2) \]
\[ + \alpha_{123}(R_1^2P_2^2P_3^2) - Q_{11}(\sigma_1R_1^2 + \sigma_2P_2^2 + \sigma_3P_3^2) \]
\[ - Q_{12}[\sigma_1(P_2^2 + P_3^2) + \sigma_2(R_1^2 + P_3^2) + \sigma_3(R_1^2 + P_2^2)] + Q_{14}(R_4P_3 + \sigma_5P_3 + \sigma_6P_3) \]
\[ - \frac{1}{2}s_{11}(\sigma_1^2 + \sigma_2^2 + \sigma_3^2) - s_{12}(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_3\sigma_2) - \frac{1}{2}s_{44}(\sigma_4^2 + \sigma_5^2 + \sigma_6^2) + \frac{1}{2}s_{11}(\sigma_1^2 + \sigma_2^2 + \sigma_3^2) \]
\[ = 2(Q_{11} + 2Q_{12})\sigma_0C \]  

where \( P_i \) and \( \sigma \) are the polarization and stress components; \( \alpha \) with subscript index are expansion coefficients; \( s_{ij} \) is the elastic compliance coefficient; and \( Q_{ij} \) is the electrostrictive coefficient. \( \alpha_1 \) has a temperature dependence of \( \alpha_1 = (T - T_0)/(2\varepsilon_0 C) \), in which \( T_0 \) is the Curie-Weiss temperature, \( \varepsilon_0 \) is the vacuum permittivity, and \( C \) is the Curie-Weiss constant.

For the tetragonal phase PbTiO\(_3\) with hydrostatic stress \( \sigma \), \( P_1 = P_2 = 0 \), \( P_3 \neq 0 \), \( \sigma_1 = \sigma_2 = \sigma_3 = \sigma \), and \( \sigma_4 = \sigma_5 = \sigma_6 = 0 \). The introduction of the stress only renormalizes the \( T_0 \), and the shift of the Curie temperature \( \Delta T_C \) can thus be obtained as

\[ \Delta T_C = 2(Q_{11} + 2Q_{12})\sigma_0C \]  

The lattice parameters with respect to the polarization and the hydrostatic stress are deduced through,
\[ u_1 = u_2 = (a - a_0)/a_0 = -\partial G/\partial \sigma_1, \quad u_3 = (c - a_0)/a_0 = -\partial G/\partial \sigma_3 \]
\[ c = a_0\left(1 + Q_{11}P_3^2 + (s_{11} + 2s_{12})\sigma\right) \]
\[ a = a_0\left(1 + Q_{12}P_3^2 + (s_{11} + 2s_{12})\sigma\right) \]  

where \( a_0 \) is the stress-free cubic cell length (extrapolated when the equilibrium structure is in the ferroelectric phase\(^9\)). At the equilibrium state, \( P_3 \) is obtained by minimizing the free energy \( G \) with respect to its value. The thermal expansion effect has been contained in the temperature dependent \( a_0 \).
For PbTiO$_3$, $Q_{12}<0$ and $Q_{11}>0$. As hydrostatic tensile stress ($\sigma>0$) is imposed, the spontaneous polarization will be increased, thus as seen from equation (3), in the ferroelectric tetragonal phase, the $c$ axis will have a definite increase due to the enhancing role of both $P_{\sigma,T}$ and $\sigma$ terms. In parallel, the $a$ axis will change much less drastically since the effects of $P_{\sigma,T}$ and $\sigma$ terms tend to cancel out each other. This feature is clearly shown in the measured lattice constants of the multiple-wire sample (Fig. 3a).

Equations (2) and (3) are precise only in low pressure and higher-order terms in the LGD expansion are needed for high pressure. However, as seen from Fig. 3c, the deviation of the ab-initio results from the LGD results starts only above 3 GPa.

It is noted that although inhomogeneity of stress might be expected in highly stressed wires as indicated in Fig. 4e, the signal in the XRD measurement on the multiple-wire sample (Fig. 3a and 3b) is mainly from 220-270nm thick wires, in which the built-in stress is the residual stress after relaxation due to the formation of a big central void or cracks. It is expected that the stress heterogeneity is much reduced after relaxation and thus it is reasonable to use uniform hydrostatic stress as effective stress in the LGD simulation.

**Ab-initio calculations**

To study the behavior of PT under negative pressure we use the Quantum ESPRESSO (QE)$^{10}$ ab initio package. For the structural full relaxation calculations, we exploit PWscf code, which is a set of programs for electronic structure calculations within density functional theory (DFT). The PWscf calculations are made within the generalized gradient approximation (GGA) with PBE exchange-correlation functional.
with ultrasoft pseudopotential from PSLibrary 0.3.1. We use an automatically generated uniform Monkhorst-Pack 10x10x10 grid of k-points, and the kinetic energy cutoff for wavefunctions is 80Ry. The atomic positions are allowed to relax until the forces on atoms are smaller than 10\(^{-5}\) Ry/bohr (0.3 meV/A). We perform variable-cell full relaxation calculations of structural parameters of tetragonal PT as a function of external hydrostatic pressure. It is achieved by iterating until the Hellmann-Feynman forces on the atoms are zero, and the Hellmann-Feynman stress tensor matches the one corresponding to the imposed external pressure. The lattice vectors are considered optimized if the residual stress difference is within 2 MPa.

Polarization is calculated by the Born charges of cubic PT \((Z_{Pb}=3.6, Z_{Ti}=4.7, Z_{O1}=Z_{O2}=-2.0, Z_{O3}=-4.1)\) multiplied by atomic displacements. The calculations of phonon spectrum and Born charges are done using Density Functional Perturbation Theory (DFPT) as implemented in the PHonon code. The threshold for self-consistency is 10\(^{-16}\) Ry. The dielectric constants \(\varepsilon_3\) (parallel to polarization) and \(\varepsilon_1\) (perpendicular to polarization), Supplementary Fig. 5, are recalculated from phonon frequencies at gamma point of E(1TO) and A(1TO) modes respectively, using formula\(^{12}\):

\[
\omega^2(0) = \frac{4}{\varepsilon},
\]

where \(\sqrt{\lambda} = 4.7 \times 10^{13}\) Hz for PT.

The above calculation of permittivity indicates whether the material retains its ferroelectricity under negative pressure: An essential feature of a ferroelectric, tightly related to its switchability, is its lattice softness in the polar phase, resulting in enhanced values of the dielectric permittivity. In contrast, in linear pyroelectrics such enhancement is absent. Thus, a credible test for the ferroelectricity would be to monitor the dielectric permittivity under increasing negative pressure. The performed
ab initio calculations of the dielectric permittivity as a function of negative pressure (Supplementary Fig. 5) show no significant variation of this parameter. Based on this we conclude that lead titanate keeps the lattice softness and should keep its ferroelectricity under negative pressures.

Figure S5 | Dependence of relative dielectric constant on applied hydrostatic pressure obtained with ab initio calculations. The dielectric constants $\varepsilon_3$ (parallel to polarization) and $\varepsilon_1$ (perpendicular to polarization) are recalculated from phonon frequencies at gamma point of E(1TO) and A(1TO) modes respectively.

Cross sectional TEM

The nanowire TEM specimens were prepared using a focused ion beam system. A probe-corrected Titan STEM 80-300, with a point resolution of 0.8 nm, was used to identify the size and distribution of pores in the nanowires. Supplementary Fig. 5 shows the high-angle-annular-dark-field (HAADF) images of the cross-sectional
specimens. Since the HAADF technique is sensitive to element distribution and specimen thickness, morphology and size of the pores in the nanowire can be directly identified. The thickness of the cross sections is estimated by analyzing the electron energy loss spectra collected on the TEM, the mean free path of electrons used for the estimation is $\lambda = 100$ nm. From the morphology of the samples, it can be seen that the thinner wires with fewer pores have a round cross section. With increasing of the diameter, the cross section of the wires transforms from a round to a rectangular shape. The most evident effect of negative pressure appears in the wire with diameter $d = 116$ nm, where the flat surfaces, i.e., the edges of the cross section, strongly bent towards the wire center. In other wires, such bending behavior is less evident but indication of the negative pressure effect can still be seen from the wire with diameters of $d = 68$ nm, $97$ nm, $157$ nm and $210$ nm. In addition, it can be seen that larger pores with sizes above $20$ nm appear in wires with large diameter.
Figure S6 | High-angle-annular-dark-field (HAADF) images of cross-sections of nanowires with different thicknesses.
**Figure S7 | A tomogram of a perovskite PbTiO$_3$ wire with a thickness about 550 nm.** The image was obtained by FIB (focused ion beam)-milling-assisted SEM, showing the cracks in the center. The spot-like features in the cross-section are the tiny pores inside the wire.

**Description and results of simulation**

In the qualitative scenario formulated in the main text for the formation of the negative pressure at the PX/perovskite phase transition in a nanowire, the following principle features can be singled out: (i) the negative pressure in nanowires forms as a result of the layer-by-layer phase transition between the two phases, which is accompanied with the plastic deformation and a volume reduction of 13%, (ii) the negative pressure increases with increasing diameter of the nanowire, (iii) the PX/perovskite phase transition is triggered by catalytic oxygen which is supplied by diffusion from the surface of the nanowire, (iv) the negative pressure is controlled by the relation between the width of the phase front for the PX/perovskite phase transition and the wire diameter. Here we simulate this scenario. Specifically, we will show that a phase transition of this kind (with a strong volume reduction and plastic deformation) once triggered by a species provided by diffusion from the surface of the wire will be accompanied by negative pressure formation, increasing as a function of the wire diameter.

We have performed a 2D plane-strain elasto-plastic modeling with the local phase of the system being described with a parameter $\varphi \in (0,1)$ where 0 stands for pure PX and 1 for pure perovskite phase. Here it is defined as $\varphi = (1 - \text{tanh}(\gamma (C - C_0)))/2$, where $\gamma$ is a constant determining the width of a phase boundary and $C$ and $C_0$ are the actual concentration of the catalytic oxygen and concentration at which
PT\textsubscript{r} occurs, respectively. The change of the phase parameter $\varphi$ introduces volume change into the tensor of a total strain through the zero-stress spontaneous-strain $\varepsilon_{0,ij} = -a \varphi(T)$ for $i=j=1,2$, when $a=0.063$ (in case of a 2D model).

The equations of the elasto-plastic model introduces below are those adopted by software Comsol Multiphysics\textsuperscript{13} from theory developed in Refs. 14, 15. In this model, the total strain $\varepsilon_t = \varepsilon - \varepsilon_0$ includes the elasto-plastic strain $\varepsilon = \frac{1}{2}(F_e^T F_e - I)$ where $F_e = FF_i^{-1}$ is a deformation gradient tensor composed of two parts: elastic $F = (I + \nabla \mathbf{u})$ and plastic $F_i = \sigma_{\text{mises}} - \sigma_{ys}$ if $F_i \leq 0$. Here $\sigma_{\text{mises}}$ is the von Mises stress and $\sigma_{ys} = \sigma_{ys0} + \frac{E_{Tiso}}{E} \epsilon_{pe}$ is a yield stress where $\sigma_{ys0}$ is an initial yield stress, $E_{Tiso}$ is an isotropic tangent modulus, $E$ is the Young’s modulus, and $\epsilon_{pe} = \frac{1}{2}(F_i^T F_i - I)$ is an effective plastic strain. We have chosen the simplest model for plasticity in order to demonstrate the fundamental mechanism. We have also tested wide range of $\sigma_{ys0}$ and $E_{Tiso}$ values while no crucial impact on qualitative behavior of the negative pressure formation was found. On the other hand, the magnitude of the built-in negative pressure is relatively strongly sensitive to the value of the Young’s modulus $E$. Even though a quantitative precision of the model was not expected, it was possible to reproduce the magnitudes of the experimental $c/a$ ratio when $E$ was assumed about two times larger than $2.37 \times 10^{11}$ Pa reported in Ref. 16 and the parameters $\sigma_{ys0}$ and $E_{Tiso}$ were used as optimization parameters to maximize the negative pressure. The qualitative characteristics of the model predictions – the negative pressure formation and its dependence on wire diameter – are robust.

PT\textsubscript{r} follows the change of concentration of the catalytic oxygen resulting from the ambient-to-wire influx. We assume a simple model for oxygen influx to the wire from
analogy with the heat surface radiation \(-D\nabla C) = e \, C^4\) where \(n\) is a surface normal vector and \(D\) is a diffusion coefficient and \(e\) is oxygen transmissibility through the surface. \(D\) and \(e\) determine the speed of oxygen influx and its distribution. The initial concentration \(C\) of the wire is set slightly above the defined phase transition point \(C_0\), i.e. \(C/C_0 = 1.0017\), to minimize calculation time before the phase transformation starts.

The concentration distribution is solved with a classical diffusion equation \(\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla C)\). The key feature of the introduced simulation is that the change of the phase parameter \(\varphi\), i.e. also the shrinkage, proceeds from the surface of the wire inward with the center of the phase boundary located at isosurface \(C=C_0\).

The PTr-induced shrinkage and the stress-strain distribution is calculated by equation: \(-\nabla \sigma = F\) where \(\sigma = \det(F)^{-1}FSF^T\). Here \(S = c_{et}\varepsilon_t\) were \(c_{et}\) is the isotropic tensor of elastic stiffness given classically by Young’s modulus \(E\) and poisons ratio \(\nu\).

The introduced model equations are solved on a square geometry with round fillets on its edges (to minimize numerical errors due to singularities). The simulation results were evaluated for a set of wire diameters from 10 to 200 nm with constants introduced in Supplementary Table 1.

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<td>(E_{Tiso})</td>
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Supplementary Table 1 | Simulation constants

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Supplementary Fig. 7 shows a cross-section of the wire with calculated distribution of hydrostatic pressure during PTr from PX to perovskite phase. In Supplementary Fig. 7a, PTr starts forming the perovskite phase in an outer shell of the wire which results in a local shrinkage of the material inducing tensile stresses (blue) inside the outer shell. The stress results in a local plastic deformation which matches the tangential component of strains between the outer shell and the core of the wire. On the other hand, the reaction of the shrunken outer shell applies a positive pressure on the enclosed core which remains in PX phase. In Supplementary Fig. 7b, ~2/3 of the wire is transformed into perovskite phase (the regions outside the blue ring). The outermost regions, which have undergone the largest plastic deformation in the initial phase of PTr, became exposed to positive pressure applied by the less (plastically) deformed inner regions. The central part (red) remains in the PX phase and is exposed to positive pressure by the shrinking outer shell. In Supplementary Fig. 7c, the entire nanowire is transformed into the perovskite phase. The outermost regions, which underwent the largest plastic deformation during PTr, are now exposed to positive pressure and represent a rigid shell which prevents stress-free collapse of the wire core, thus forming a negative pressure.
Figure S8 | Cross-section of the 100 nm thick nanowire with calculated distribution of hydrostatic pressure $p$ during the phase transition from PX to perovskite phase. 

a, An initial stage of the phase transition. 
b, A situation when $\sim 2/3$ of the nanowire are transformed into perovskite phase (the regions outside the blue ring) while the central red part remains in the PX phase and is exposed to positive pressure. 
c, The entire nanowire is transformed into the perovskite phase where the inhomogeneous plastic deformation results in negative pressure in the central part of the nanowire.

Supplementary Fig. 9 shows negative pressure increasing with larger nanowire diameters. The negative pressure is formed in the central part of the wire covering $\sim 2/3$ of the total wire cross-section. The outer shell of the wire reacts with positive pressure. Large deviatoric stresses contributing to enhanced $c/a$ ratio by pure elastic means are created in the outer shell as well. The volume fraction of the outer shell which is exposed to the positive pressure is dependent on the exact choice of the simulation parameters, but the qualitative features of the results remain unchanged.
Figure S9 | Calculated distribution of hydrostatic pressure $p$ after the phase transformation from PX to perovskite phase shows growing magnitude with growing nanowire diameter.

The average $c/a$ ratio in the wire was calculated using the function $c/a = f(p)$ obtained by the first principles calculations in ref. 17 (Fig. 3c). Supplementary Fig. 10 shows the average $c/a$ (left axis) for wire diameters from 10 to 200 nm. Note, that the average $c/a$ from the entire wire cross-section is reduced by the small $c/a$ in the outer shell and that local maxima of $c/a$ are larger than the average.

Figure S10 | The dependence of the average $c/a$ on the wire diameter indicates the $c/a$ enhancement. Note that the $c/a$ trend is obtained by assignment of the phase field calculated stress to the first principles calculated $c/a$ in ref. 10. The zero-stress $c/a$ is set to 1.065 as determined experimentally.

Obviously, the model does not predict the sudden drop of $c/a$ seen in Fig. 1d, because it does not incorporate any stress release mechanisms like cavitation process and a finite fracture toughness. However, it is clear, that the wire cannot withstand continuous increase of the negative pressure and either pore formation or wire fracture.
must be triggered at certain threshold. This simple consideration is consistent with the experimental observations which show that wires with larger diameters (>150 nm) include a large central pore or cracked. It is known from the theory of pore formation in glasses under tensile stress\textsuperscript{18} that a large central pore is formed at specific values of negative pressure in materials which undergo volume shrinkage progressing from outside inward, and that the pore formation is followed by a rapid stress-release in the rest of the material.

In summary, we show that the $c/a$ enhancement is induced by a volume shrinkage progressing from the surface inwards due to gradual PTr. The experimental observation suggests that the enhancement is limited by pore cavitations and wire fracture.

**References**


13. Adaptation of the elasto-plastic equations from Refs 9, 10 for Comsol Multiphysics 4.3a is described in detail in Comsol’s “Nonlinear Structural Materials Module” documentation.


