Revealing sub-µm and µm-scale textures in H₂O ice at megabar pressures by time-domain Brillouin scattering

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The time-domain Brillouin scattering technique, also known as picosecond ultrasonic interferometry, allows monitoring of the propagation of coherent acoustic pulses, having lengths ranging from nanometres to fractions of a micrometre, in samples with dimension of less than a micrometre to tens of micrometres. In this study, we applied this technique to depth-profiling of a polycrystalline aggregate of ice compressed in a diamond anvil cell to megabar pressures. The method allowed examination of the characteristic dimensions of ice texturing in the direction normal to the diamond anvil surfaces with sub-micrometre spatial resolution via time-resolved measurements of the propagation velocity of the acoustic pulses travelling in the compressed sample. The achieved imaging of ice in depth and in one of the lateral directions indicates the feasibility of three-dimensional imaging and quantitative characterisation of the acoustical, optical and acousto-optical properties of transparent polycrystalline aggregates in a diamond anvil cell with tens of nanometres in-depth resolution and a lateral spatial resolution controlled by pump laser pulses focusing, which could approach hundreds of nanometres.

Knowledge of the pressure dependences of sound velocities and elastic moduli of liquids and solids at megabar pressures and the evolution of the texture of polycrystalline samples under compression is of extreme importance for a few branches of the natural sciences, such as condensed-matter physics, physics of the Earth and planetology, as well as for the monitoring and prediction of earthquakes and tsunamis and for nuclear weapons test control. Experimental information on high-pressure material parameters, which can be measured at P > 25 GPa in laboratory conditions only using a diamond anvil cell (DAC), can be substantially influenced by spatial inhomogeneities and texture in polycrystalline aggregates. It is well known that aggregate sound velocity depends on the characteristic dimensions of the individual crystallites, which are elastically anisotropic, and that even a partial alignment of the crystallites i.e., orientational texture, biases the measured aggregate sound velocities. Both of these factors prevent precise evaluation of the elastic moduli and require the development of experimental methods for the three-dimensional imaging of microscopic samples in situ when compressed in a DAC for the purpose of characterising both their morphological and orientational/directional texture.

In the past decade, significant progress has been achieved in imaging of isolated objects and multigrain bodies using two X-ray techniques. The first one, based on the spatial variation of X-ray absorption in chemically inhomogeneous samples, allows spatial resolution better than 100 nm. The second one, based on X-ray diffraction (XRD), enables determination of grain position and orientation in a polycrystalline body with the spatial resolution approaching sub-µm level. Both methods have provided the mentioned resolution only for samples recovered from high-pressure experiments. However, compression of samples in a DAC limits the solid-angle region where the samples can be accessed by X-rays, and the weight of the DAC limits the accuracy of spatial adjustment, especially when sample rotation is needed. Degradation of spatial resolution for samples in a DAC is significant (on the order of 10 µm) when grains in polycrystalline aggregates are localised using the monochromatic XRD method. By applying the polychromatic micro-diffraction method, a somewhat better resolution of 2–5 µm in the axial sample direction (or along the incident X-ray beam) was expected. Lateral resolution on the order of 100 nm can be maintained for samples compressed in a DAC only if the resolution is defined by the size of the X-ray beam. For example, this is possible for the boundary between two homogeneous media with...
different absorption \(^{14}\) and for inhomogeneities (e.g., domains) if they are isolated or separated by distances significantly exceeding the beam size\(^2\). Very recently, Bragg coherent X-ray diffraction imaging was applied for the mapping of strains in an isolated single crystal of gold with a resolution of 30 nm, but only up to 6.4 GPa\(^4\). Despite all the progress, none of the above mentioned methods provides information on the elastic properties of the examined sample volume or of individual grains. In the present paper, we introduce an experimental method that overcomes this limitation and provides spatially resolved information (in both lateral and axial directions) on the elastic behaviour of optically transparent samples compressed in a DAC to pressures approaching 1 Mbar. This permits, in turn, \textit{in situ} examination of the texture of a chemically homogeneous polycrystalline sample, provided the sample material is elastically anisotropic.

Of the methods for the evaluation of elastic parameters of condensed media at high pressures, an important role is played by those based on the interaction of laser radiation with acoustical phonons. Application of optical radiation is particularly suited for the DAC, in which the transparency of diamond, needed for optical access to the compressed sample, is essential. In the classic frequency-domain Brillouin scattering (BS) technique, frequency shifts of monochromatic light scattered by thermal (incoherent) acoustic phonons in the sample provide information on the velocities of the longitudinal and shear sound\(^{17–19}\). In laser ultrasonic techniques, light is employed not only for the detection of acoustic phonons, as in the classic BS, but also for their generation\(^{20,21}\). The probe light is predominantly scattered not by the thermal phonons but by coherent laser-generated phonons. The laser ultrasonic technique of impulsive stimulated Brillouin scattering (ISBS)\(^22\), based on the generation of monochromatic coherent acoustic waves by laser-induced gratings, has been applied at high pressures to measure the velocities of both bulk\(^{23,24}\) and interface\(^{25,26}\) acoustic waves. Recently, the picosecond laser ultrasonic technique\(^27\), based on both generation and detection of wide-frequency-band coherent acoustic pulses by femtosecond laser pulses, was first applied at high pressures in DACs\(^{28}\). The laser ultrasonic technique based on the generation of acoustic pulses by sub-nanosecond laser pulses and their detection by a continuous laser radiation is described in Ref. 29. In Refs. 28 and 30, transient optical reflectivity signals obtained by the technique of picosecond acousto-optic interferometry\(^31\), also called time-domain Brillouin scattering (TDBS) (see Methods and Fig. 1), were reported for the first time at high pressures. In an inhomogeneous medium, the TDBS signal at each time instance contains information on the local parameters of the medium at the spatial position of the laser-generated light-scattering acoustic pulse at this time instance\(^31–33\). Below, we report the application of TDBS to the examination of water ice in a DAC at pressures of 57 and 84 GPa, revealing the characteristic features of its micro-crystallinity.

Classic frequency-domain BS experiments with single-crystal H\(_2\)O ice are extremely rare\(^{34,35}\) and have been reported only at relatively low pressures (below 10 GPa); experiments at higher pressures have been conducted on polycrystalline ice\(^{36–38}\). The problems in the application of the classic BS by thermal phonons in polycrystalline materials are well known\(^{19,36–38}\). The BS signal is very weak, and signal collection can take dozens of hours. The Brillouin spectral lines not only are considerably broadened\(^{36,37}\) but are also split\(^{36,38}\) because of the simultaneous contributions to the scattered light from multiple differently oriented crystallites, i.e., elastically anisotropic grains, inside the scattering volume. Detection of the broad Brillouin lines provides an opportunity to extract only the orientation-averaged, i.e., so-called aggregate, sound velocities\(^38\), whereas splitting of the Brillouin peaks requires data collection through a large number of different scattering volumes covering many randomly oriented grains, with the goal of establishing the maximum and the minimum boundaries of compressional and shear sound velocities\(^38\). The experiments with cubic polycrystalline ices are further complicated by their optical isotropy\(^39\), which makes it impossible to visualise/characterise the grain distribution, i.e., the polycrystalline aggregate texture, by birefringence, which could be very useful in the case of grains without inversion symmetry\(^40,41\). The in-depth spatial resolution in the classic BS microscopy\(^42\) applied to three-dimensional imaging\(^43\) currently exceeds tens of micrometres.

Here, we report experimental “visualisation” of the texture in a polycrystalline aggregate of H\(_2\)O ice compressed in a DAC to pressures approaching 1 Mbar by TDBS. The demonstrated two-dimensional, in-depth and lateral, imaging of the texture in cubic, i.e., optically isotropic, ice is due mostly to the contrast provided by differences in sound wave velocities inside the differently oriented crystallites/domains relative to the propagation direction of the acoustic and probe-laser pulses. When a coherent acoustic pulse of nanometre to sub-micrometre spatial length and of lateral dimension controlled by pump laser focusing propagates inside the sample, we resolve in time/space with previously inaccessible precision sound velocities corresponding to the particular orientations of the spatial domains, in which the coherent acoustic pulse is currently localized.

### Results

The TDBS experiments on samples compressed in a DAC were conducted using the pump/probe configuration for transient reflectivity optical measurements presented in Fig. 1(a) (see Methods).

#### Experimental signals and their processing

Typical transient reflectivity signals recorded in the experiments at 57 and 84 GPa, where water ice appears most likely in phase X with ordered positions of protons\(^44,45\), are presented in Fig. 1(c). Here, the temporal window spans the delay times necessary for one-way propagation of the photo-generated coherent acoustic pulse from the iron opto-acoustic generator to the ice/diamond interface (see Fig. 1(b)). The arrival times of the acoustic echoes at the ice/diamond interface, indicated by arrows in Fig. 1(c), manifest themselves as an abrupt diminishing in the amplitude of the Brillouin oscillation at 880 ps and 1134 ps for 84 GPa and 57 GPa, respectively. Fig. 1(c) and, especially, the insert in Fig. 2(a) clearly show, even without any signal processing, that the transmission of the acoustic pulse across the ice/diamond interface is additionally accompanied by an abrupt increase in the frequency of the oscillating part of the transient reflectivity. These observations are in accordance with the estimated weak reflection, less than 15% in amplitude, of acoustic waves from the ice/diamond interface, the lower photo-elastic (acousto-optic) constants of diamond in comparison with those of ice at the optical probe wavelength, the larger Brillouin frequency shifts in diamond than in ice measured by the classic BS at similar pressures\(^46\) and the decrease in the acoustic pulse spectral amplitude with increasing frequency. This arrival time is known to provide information on the acoustic velocity averaged over the path of the coherent acoustic pulse and on the sample thickness\(^47–49\) (see Methods).

The non-monotonous variations in time of the Brillouin oscillation amplitude before the arrival of the coherent acoustic pulse at the ice/diamond interface, which are observable in Figs. 1(c), 2(a) and 2(b) without any signal processing, are a strong indication of the samples’ spatial inhomogeneity, i.e., polycrystallinity and texturing. These variations cannot be attributed to the beatings of TDBS signals of different frequencies and are manifestations of texturing in the distribution of both photo-elastically (acousto-optically) and elastically anisotropic sub-μm grains composing the ice aggregate (see Section on the amplitude of the TDBS signal).

Further indication of the spatial inhomogeneities could be the variations with the delay time of the frequency of the Brillouin oscillation\(^11–13\). For the bulk of the ice X sample, this can be revealed by a Fourier transform performed inside an appropriately chosen time window after subtraction from the total time-resolved reflectivity...
Figure 1 | Time-domain Brillouin scattering in a diamond anvil cell. TDBS is an optical pump–probe technique in which the pump laser pulse generates a light-absorbing opto-acoustic transducer a picosecond acoustic pulse that propagates through an optically transparent sample contacting the transducer while the probe laser pulse monitors the propagation of the acoustic pulse ((a) and (b)). The probe laser pulse, delayed in time relative to the pump laser pulse ((a) and (b)), preferentially interacts with those coherent GHz phonons of the acoustic pulse spectrum that satisfy the conservation of momentum in photon–phonon photo-elastic interactions31,45. Weak light pulses scattered by the acoustic pulse interfere at the photo-detector with the probe light pulses of significantly higher amplitude reflected from various surfaces/interfaces of the set-up. The modification of the optical reflectivity is proportional, in leading order, to the product of these two scattered light fields. Thus, a heterodyning of a weak field against a strong one is achieved. The transient reflectivity signal varies with time because the relative phase of the light scattered by the propagating acoustic pulse and reflected by immobile surfaces/interfaces continuously changes with time due to the variation in the spatial position of the propagating acoustic pulse. If the acoustic pulse propagates at a constant velocity, the amplitude of the signal changes in time in a sinusoidal manner at a GHz frequency precisely equal to the Brillouin frequency. Thus, measuring the period/frequency of this time-domain Brillouin oscillation provides information on the velocity of the acoustic wave in the sample. (a): Schematic presentation of the experimental setup. (b): Sample in a DAC with qualitative presentation of some of the probe optical rays contributing to the TDBS detection. For the characteristic dimensions of the ice sample and of the opto-acoustic transducer noted in (b), see Methods. (c): Transient reflectivity signals detected in the ice samples compressed in a DAC to 57 and 84 GPa as a function of the delay time between the probe and the pump laser pulses. Arrows indicate the times for the first arrival of the photo-generated acoustic pulse at the interface of ice and the diamond anvil.

signal of the time-varying thermo-reflectance contribution caused by sample heating32,33. This signal processing leads to the TDBS signal, which is due to the interaction of the probe light with the photo-generated acoustic pulse only (Fig. 2(b)). The plots in the insert of Fig. 2(b), as well as all other FFT plots calculated in this work, were clearly dominated by a single strong peak related to the Brillouin frequency of the longitudinal sound wave. The ±10% deviations of the Brillouin frequencies from their average, revealed here (insert in Fig. 2(b)), clearly indicate the presence of spatial elastic inhomogeneities in the ice sample due to polycrystallinity/texturing.

Performing a Fourier transform in a continuously moving smoothed time window of appropriately chosen duration and taking the frequency of the maximum in the spectra makes it possible to extract the temporal-profile of the dominant Brillouin frequency along the particular path of the coherent acoustic pulse propagation. Changing the time-window size allows different degrees of averaging along the sound propagation direction. The resolution of such in-depth profiling of the spatially inhomogeneous media using TDBS is known to be limited either by the spatial length of the coherent acoustic pulse or by restrictions introduced by specific signal processing techniques32,33. In our experiments, the duration of the emitted longitudinal acoustic pulse is controlled by a pump laser pulse duration of 1.9 ps, and its width in ice near the opto-acoustic generator is approximately 30 nm at 84 GPa (see Supplementary Note 1). The observed abrupt changes in the amplitude and frequency of the Brillouin oscillations upon the arrival of the acoustic pulse at the ice/diamond interface (Fig. 2 (a)) indicate that, although this pulse could be broadened by bulk high-frequency absorption and scattering, the duration of the acoustic pulse does not exceed the Brillouin period of approximately 15 ps, corresponding to a spatial scale of approximately 0.23 μm at 84 GPa. For the Fourier transforms in the present study, we used the windows whose FWHM exceed the Brillouin periods. Thus, we achieved depth-profiling with the same in-depth spatial resolution (controlled by the duration of the moving Fourier transform window) throughout the whole sample thickness via the simplest signal processing technique. In-depth spatial resolution controlled by the acoustic pulse duration, achievable by advanced methods of signal processing32,33, is beyond the scope of the present report. In Fig. 2(c), we present the temporal profile of the Brillouin frequency for the TDBS signal shown in Fig. 2(b) obtained with the moving rectangular time window of 100 ps, corresponding to an in-depth spatial resolution of approximately 1.5 μm.

In our polycrystalline ice sample, the photo-generated coherent acoustic pulse, which is initially launched normal to the Fe/ice interface and propagates parallel to the direction of the probe laser beam, could be refracted when crossing such plane interfaces between the grains, which are not parallel to the Fe/ice interface. Thus, in general, the coherent acoustic pulse propagates non-collinearly to the probe light. In this case, evaluation of the momentum-conservation triangle composed of the wave vectors of an acoustic phonon and of the
incident and the scattered probe light photons leads to the following solution for the Brillouin frequency $f_B$ (see Refs. 32, 45):

$$f_B \approx \frac{2nu \cos \theta}{\lambda_0}$$  \hspace{1cm} (1)

Here, $u$ denotes the speed of the acoustic wave along a particular direction of its propagation in elastically anisotropic media, $\lambda_0$ is the wavelength of the probe light in vacuum, $n$ is the optical refractive index of the media for the probe light, and $\theta$ is the angle between the propagation directions of the probe light and the sound. In general, three factors in equation (1), i.e., $\theta$, $n$ and $u$, could be responsible for different values of the Brillouin frequency when the coherent acoustic pulse travels along its propagation path. We estimated theoretically and confirmed by additional experiments that variations of the refractive index play a negligible role in comparison with those of sound velocity (see Section on the induced optical anisotropy). In Section on the acoustic refraction and diffraction, we demonstrate theoretically that variations caused by the acoustic beam refractions could also be neglected in the first approximation. Thus, in the following analysis, we assume that the experimentally revealed variations in the Brillouin frequency are due to the variations of the sound velocity only, i.e., that they are dominantly caused by the different orientations of elastically anisotropic crystallites or groups of crystallites in the polycrystalline ice aggregate. As an example, assuming in equation (1) that $\theta = 0$ and taking the refractive index of the ice from the literature\textsuperscript{39}, it is a straightforward process to obtain from the dependence in Fig. 2(c) the dependence of the acoustic velocity in ice first on time and then on the in-depth coordinate (Fig. 2(d)). The experimentally observed spatial inhomogeneity of the polycrystalline aggregates of ice X (Fig. 2(d)) can be more deeply characterised in two-dimensional imaging experiments, performing such TDBS measurements at several consecutive spatial positions along a lateral sample coordinate. In Fig. 3, to reveal large-scale
in the ice X aggregate, we show the Brillouin frequency distribution obtained with the in-depth spatial resolution of approximately 1 µm. The resolution is determined by a 67 ps FWHM duration of the Hanning temporal window chosen for the Fourier transform (see Methods). Fig. 3(b) and 3(d) show the time-resolved profiles of the Brillouin frequency, which we hereafter call "images", obtained for the ice sample at 84 GPa and 57 GPa, respectively, by its displacement in a lateral direction.

The results presented in Fig. 3 clearly demonstrate the ability of the TDBS technique to reveal texturing of transparent polycrystalline aggregates such as our ice sample with a spatial scale better than 1 µm.

The characteristic dimension of the individual crystallites in the ice X aggregate estimated from our XRD measurements at the considered pressures of 57–84 GPa is 0.45 µm (see Methods). To check the sensitivity of the TDBS technique to in-depth inhomogeneities at a sub-micrometre scale, we processed the signals in a moving Hanning temporal window of 17 ps FWHM duration, approximately corresponding to a single period of the Brillouin oscillation at 84 GPa. The expected spatial resolution of approximately 0.26 µm is still controlled by the duration of the moving window. The results of the processing of the TDBS signals (Fig. 3(a)) in the delay time interval from 100 ps to 400 ps are presented in Fig. 4, which shows strong variations of the BS frequency (up to ±26% for the maximal-to-minimal velocity variation, and up to ±10% for adjacent maxima and minima) and, accordingly, of the longitudinal sound velocity by moving in depth (corresponding to the delay-time axis). From theoretical calculations for ice X, the maximal-minimal velocity variation approaches, within a single crystal, ±16%, thus indicating that ice X should be strongly anisotropic. However, the degree of anisotropy appears to be difficult to calculate theoretically, and no experimental information, except the present work, is available. The characteristic spatial (in-depth) scale of the BS frequency variations is 0.26–0.6 µm. We should bear in mind the relatively large cross section of ~10 µm² of the opto-acoustically tested volume and the small size of the ice crystallites of ~0.45 µm, implying that the recorded BS signal (at any delay time) is averaged in both lateral directions over approximately 50 individual crystallites. A large change in the BS frequency by moving in depth to the next layer of grains (increase or decrease of the delay time by 20–30 ps) suggests a significant degree of crystallographic ordering in each of the layers but also a significant difference in the average crystallographic orientation of the adjacent ordered layers. This could be considered as a strong indication of sample texturing parallel to or inclined with respect to the anvil culets. However, we do not recognise any pattern by shifting our sample in a lateral direction (Fig. 4(a) and (b)), even though the step size of 1 µm implies a partial overlapping of the examined volumes of the adjacent depth profiles of the BS frequency. No pattern can also be recognised when the time-axes in Fig. 4 (a) and (b) are recalculated into in-depth coordinate axes. This observation excludes the above discussed possibility of sample texturing parallel to the diamond anvils, at least on the scale significantly larger than 1 µm, in the lateral directions. The only possible model that we can currently suggest is a sample that consists of or contains orientationally (or elastically) homogeneous mesoscopic crystallite groups in the form of lamellae, discs, or lenses having a lateral size of approximately 1 µm and a thickness of 0.3–0.6 µm. Formation of such elastically homogeneous crystallite groups having only one distinct direction appears possible because in two crystallographic directions, [110] and [111], the sound velocities in ice X are predicted to be similar (only approximately ±3% different) and significantly higher than in the [100] direction (±16%). The physical behaviour of ice X at the pressures of our experiment is also predicted to be anisotropic and dominated by only one slip system, namely, , <111> [110] .

Finally, the particular lens-shaped or lamellar objects inside a polycrystalline sample compressed in a DAC have been reported in the literature for other solids, e.g., by Burnley et al. In the suggested texture model, the signal generated in the spot of ~10 µm² stems from only 10–13 mesoscopic groups, where each of the groups is elastically homogeneous (at least in the direction of the sound propagation), but the groups could be oriented differently with respect to one another. In another model, a smaller number

Figure 3 Revealing µm-scale texture in a polycrystalline H2O ice aggregate at megabar pressures via two-dimensional imaging by the time-domain Brillouin scattering technique with an in-depth spatial resolution of ~1 µm. (a): TDBS signals in H2O ice at 84 GPa, obtained by displacing the sample relative to the co-focused pump and probe laser beams in a lateral direction, i.e., parallel to the ice/diamond interface, by 1 µm steps. The spatial in-depth distance of 1 µm corresponds here to an ~66 ps delay time. (b): Two-dimensional images of the Brillouin frequency magnitude obtained by processing the signals in (a). (c) TDBS signals in H2O ice at 57 GPa, obtained by displacing the sample in the lateral direction by 2 µm steps. The spatial in-depth distance of 1 µm corresponds here to an ~75 ps delay time. (d): Two-dimensional images of the Brillouin frequency magnitude obtained by processing the signals in (c). The isometric representation of the TDBS signals and of the temporal dependences allows better recognition of their changes with position on the sample. In (b) and (d), the signal amplitude is correlated with the symbol colour: the darker the symbol is, the higher is the maximum amplitude of the Brillouin signal, and vice versa. Image (b) reveals a clear, large-scale layering of the ice aggregate at 84 GPa in the direction normal to the diamond anvil culets. The thickness of the layers in this large-scale texture is approximately 3–5 µm. The image (d) of ice at 57 GPa reveals two regions separated laterally, which exhibit a much less pronounced in-depth layering than at 84 GPa. Visually, the lateral separation in (d) occurs in the middle of the laterally scanned region. In addition, smaller scale inhomogeneities, with a thickness of approximately 1 µm, controlled by the intentionally reduced spatial resolution, are observed at some depth positions at both pressures.
of such groups could be embedded in a disordered polycrystalline matrix. In both cases, a high degree of averaging of the total Brillouin frequency is less probable owing to the small number of differently oriented mesoscopic groups. Consequently, large shifts in the frequency by moving through the sample are feasible. We emphasise that the adjacent maxima and minima in Figure 4 (for the 17 ps window) typically show variations on the order of 610%, which are significantly below the maximal variation of 626%. The estimated number of the mesoscopic objects of approximately 10 would be consistent with such variations. Thus, the measurement with a small time window of 17 ps could have revealed some degree of texturing of our ice sample compressed to 84 GPa at sub-m scale. However, the ordered/coherent regions are small and do not extend in lateral directions significantly more than 1 µm. Note that the characteristic direction of texturing, parallel to the diamond culets, recognised on the large scale in Figs. 3(b) and 4(c) and on the short scale in Fig. 4, appears to be plausible if we consider the geometry of the sample and the uniaxial compression of the sample confined in the gasket.

Confirmation by TDBS scattering of the sub-µm size of individual crystallites provides us the opportunity to make a general statement that the averaging in our present experiments is due not only to the large number of crystallites scattering probe light in the tested volume but also to the strong diffraction of the light inside the scattered probe beam on its way to the detector. Actually, for the wavelength of the probe light of approximately 0.44 m in ice X at 84 GPa, a part of the probe laser beam scattered in a grain with a diameter not exceeding 0.45 m will diffract at distances shorter than 0.6 µm. We estimate here the diffraction length by the ratio of the surface area of the scatterer to the probe laser wavelength in the...
compressed sample. Consequently, the corrugations of the probe wave front caused by its scattering at the corrugated front of the coherent acoustic pulse propagating simultaneously in multiple crystallites is effectively smoothed by the diffraction at a sub-μm scale. Thus, the detected signal provides information on the phase variation of the smoothed front of the scattered probe light and, consequently, on the diffraction-averaged Brillouin frequency.

The above presented results show that a three dimensional imaging of the texture of a sample compressed in a DAC is feasible. Below we demonstrate that the influence on the obtained images of the optical anisotropy and of the off-axis propagation of acoustic waves can be disregarded.

On the induced optical anisotropy. In optically anisotropic grains, the light experiences double or triple refraction and the optical rays, characterised by different refractive indexes, propagate after refraction with different velocities, which, in addition, depend on the direction of rays propagation relative to crystallographic axes. However, the ice phases VII and X examined here are cubic and thus optically isotropic. Consequently, variations of the refractive index n could be caused in our samples only by anisotropy induced by nonhydrostatic stress component, i.e., due to uniaxial loading. Our order of magnitude estimates (see Supplementary Note 2) demonstrate that induced optical anisotropy could cause variations of the refractive index of Δn/Δn ≈ 5·10⁻⁴, which are negligible in our experiments. Here, chevrons (…) denote average values. However, in view of the complexity of the phenomena of stress-induced anisotropy and the lack of data on the photo-elastic tensors of the H₂O ices VII and X, we conducted additional test experiments with variable linear polarisation of the probe beam. The results presented in Fig. 5 confirm that optical anisotropy is induced in our system, but it is weak, and thus the variations of the refractive index in equation (1) could be disregarded.

On acoustic refraction and diffraction. The maximal expected deviations in the direction of the coherent acoustic pulse propagation are estimated using acoustic ray theory in Supplementary Note 3. These estimates predict that the dominant cause of the relative variations of the Brillouin frequency, |ΔfB|/fB, in our experiments is the sound velocity variations, |Δυ/υ| ≪ |ΔfB|/fB ≲ 0.2, and the dependence on cos θ in equation (1) can be disregarded in the first approximation because Δ(cos θ)/cos θ ≲ 0.04.

In our opinion, there is an additional and more important factor, specific to micro-crystalline samples, that could significantly diminish the maximum effective angles that should be used in the estimates based on equation (1). In fact, when the acoustic pulse crosses a layer of differently oriented crystallites, distributed laterally, the phase front of the acoustic pulse has a tendency to corrugate because of the difference in the magnitudes and the directions of the sound velocity in different crystallites. However, this tendency is strongly suppressed by the diffraction phenomena smoothing the amplitude and phase differences between the different parts of the acoustic beam. The shortest (30 nm) acoustic pulse, realised in our experiments in the vicinity of the Fe opto-acoustic generator (see Supplementary Note 1), corresponds to the characteristic acoustic wavelength of 0.2 μm (in ice X at 84 GPa). Consequently, the lateral corrugations of the acoustic pulse, which could accumulate in its refraction inside the crystallites with dimensions below 0.45 μm, are continuously washed out by diffraction at distances below 1.2 μm. Thus, while the diffraction of the total acoustic beam plays a negligible role in our experiments, the diffraction inside the acoustic beam supports the propagation of all parts of the beam quasi-collinear to the DAC axis.

On the amplitude of the TDBS signal. The discussion in Supplementary Note 4 indicates that non-monotonous variations of the TDBS signal amplitude in time in our experiments (see Figs. 1 (c) and 3 (a) and (c), for example) are not the manifestation of beatings/interference among different frequency components of the signal but instead are the second (in addition to the Brillouin frequency variation in time) direct manifestation of the misorientation of grains or groups of grains in the examined polycrystalline H₂O ice aggregates. Actually, cubic crystallites of ice are optically isotropic but anisotropic photo-elastically (acousto-optically). The magnitude of the effective photo-elastic constant, which couples collinearly propagating sound and light, depends on the direction of their propagation inside individual crystallites. The amplitude of the TDBS oscillation is expected to be different in the differently oriented crystallites relative to the sample normal. Fig. 6 compares the measured variations of the amplitude and frequency, revealing their coherent dynamics at the sub-μm spatial scale; the variations of the amplitude and the frequency are mostly occurring in anti-phase. These experimental observations strongly indicate that the physical origin of both is in the orientational texture of the crystallites in our sample.

Because the amplitude A of the Brillouin oscillation is directly proportional to the effective photo-elastic constant and inversely proportional to the sound velocity, (A ∝ ρn⁻¹(ωp)⁻¹/₂, where p and ρ denote the photo-elastic constant and density, respectively), it could be expected that the photo-elastic anisotropy provides a dominant contribution in comparison with the elastic anisotropy to the non-monotonous variations of the amplitude of the Brillouin oscillations in polycrystalline aggregates. Our estimates, using the data in Fig. 6, demonstrate that the magnitude of the Brillouin oscillation in the examined W phase (X) has a maximum value of 5·10⁻⁴, which is negligible in our experiments. Here, chevrons (…) denote average values. However, in view of the complexity of the phenomena of stress-induced anisotropy and the lack of data on the photo-elastic tensors of the H₂O ices, we conducted additional test experiments with variable linear polarisation of the probe beam. The results presented in Fig. 5 confirm that optical anisotropy is induced in our system, but it is weak, and thus the variations of the refractive index in equation (1) could be disregarded.
In this work, we were able to approach a high in-depth resolution of approximately 0.45 μm, the lateral surface area tested by overlapping the probe laser beam and the coherent acoustic beam is approximately 10 μm² and the wavelength of the probe laser light when propagating in ice at Mbar pressures is approximately 0.44 μm. Thus, it is difficult to access in the present sample and experiment geometry, at any position in the sample, the extreme sound velocity values, corresponding to the specific directions in a single crystal of ice X. The highest sound velocity observed in the present work by scanning through the sample will be lower than the maximal possible sound velocity in a single-crystal ice X (along the [111] direction of a cubic crystal). Similarly, the lowest sound velocity detected here represents the upper bound for the lowest possible sound velocity in a single-crystal ice X (along the [100] direction of a cubic crystal). One way to approach the limiting sound velocity values would be to use coarse powder or single crystals as starting samples. The grains could fracture under pressure due to nonhydrostatic loading or after phase transitions, but the fragments could remain sufficiently large to deliver to the detector the TDBS signals corresponding to individual grains. In the particular case of water, single crystals of ice VI and VII can be easily obtained via a slow compression at approximately 1 GPa when crossing the melting curve, e.g., as described in Refs. 35 and 55. Another way involves a significant improvement in the lateral resolution of the experimental set-up below 0.45 μm by application of advanced focusing methods56. Combined with the already available high in-depth resolution, the improved lateral resolution would enable determination of the limit values of sound velocities as well as a 3D visualisation of a transparent polycrystalline aggregate microstructure (from grain to grain) at megabar pressures.

The time-domain BS technique could have other advantages, in addition to improved spatial resolution, in comparison with the classic frequency-domain BS technique. The applicability of classic BS is substantially reduced and could even be impossible when the Brillouin spectral lines of the sample overlap with the Brillouin lines from the diamond anvils or from the pressure transmitting medium54,55, which are inevitably simultaneously detected for samples compressed in a DAC. This problem does not exist for the time-domain BS technique because the scattering of light by coherent acoustic phonons takes place in the sample only, well before the photo-generated acoustic pulse reaches the sample/diamond or sample/pressure-medium interface. Moreover, the TDBS allows direct comparison of the sound velocities and/or elastic moduli of two or more sample materials placed simultaneously in the high-pressure volume of a DAC. This comparison could be of use by establishing an absolute pressure scale at Mbar pressures.

Conclusions

The TDBS-based imaging technique described herein provides for each crystallite (or group of crystallites) in chemically homogeneous transparent aggregate usable information on its orientation (if the material is elastically anisotropic) as well as on the value of the elastic modulus along the direction of the sound propagation. This extends the basis for successful application of highly developed micromechanical models of solid deformation at Mbar pressure. Over the long term, such experiments extended to Earth’s minerals and high or low temperatures could ensure significant progress in understanding the convection of the Earth’s mantle and thus the evolution of this and other planets.

The two-dimensional imaging of the polycrystalline aggregate in-depth and in one of the lateral directions reported here indicates the feasibility of three-dimensional imaging of transparent samples compressed in a DAC with a previously inaccessible resolution of tens of nanometres in-depth. The lateral spatial resolution is controlled by the pump and the probe laser pulse focusing. In perspective, improved signal processing of such TDBS data should provide an opportunity to follow the evolution of several Brillouin frequencies in the time domain, revealing simultaneous propagation of the
coherent acoustic pulse across several mutually misoriented crystallites. In the future, TDBS experiments, conducted with both longitudinal and shear \( n \)-th coherent acoustic pulses at several angles of probe light incidence \( \theta \), could enable the determination of the spatial positions, dimensions and orientation, i.e., morphological and orientational texture, of the optical refractive index and all elastic moduli of the individual grains inside polycrystalline transparent aggregates compressed to megabar pressures.

**Methods**

**Time-domain Brillouin scattering.** In the time-domain Brillouin scattering technique, which is also called picosecond acousto-interferometry and is a particular optical pump-probe technique, the pump laser pulse generates in a light absorbing opto-acoustic medium an acoustic pulse propagating through the sample contacting the transducer. Because a typical length of the picosecond acoustic pulse is on the nanometre to sub-micrometre spatial scale, the technique is perfectly suitable for the examination of materials confined in DACs, where sample sizes are typically several tens of micrometres to a few micrometres and grains in polycrystalline samples are typically less than 1 \( \mu \)m (Fig. 1(b)). In the case of an optically transparent material, the probe laser pulse, delayed in time relative to the pump laser pulse (Fig. 1(a) and (b)), preferentially interacts with those coherent GHz phonons of the acoustic pulse spectrum that satisfy the momentum conservation law in photon-phonon photo-elastic interactions, i.e., satisfy the Bragg condition. Weak light pulses of picosecond duration, placed in Fig. 1(a), will redirect the light beams of significantly higher amplitude reflected from various surfaces and interfaces of the set-up, such as the interfaces of the sample with the diamond and of the opto-acoustic transducer with the sample (Fig. 1(b)). The detected modification of the transient optical reflectivity is proportional, in leading order, to the product of these two light fields. Thus, a heterodyning of weak field light through a strong one is achieved in picosecond ultrasonic interferometry. The measured transient reflectivity signal varies with time because the relative phase of the light scattered by the propagating acoustic pulse and reflected by immobile surfaces/interfaces continuously changes with time due to the variation in the spatial position of the propagating acoustic pulse. If the acoustic pulse propagates at a constant velocity, i.e., in a spatially homogeneous medium, the phase difference between the interfering light fields linearly changes in time and, as a consequence, the amplitude of the signal changes in time in a sinusoidal manner at a GHz frequency precisely equal to the light field linearly changes in time and, as a consequence, the amplitude of the signal changes in time in a sinusoidal manner at a GHz frequency precisely equal to the Brillouin frequency \( \omega_B \). Thus, measuring the period/frequency of this time-domain Brillouin oscillation provides information on the velocity of the acoustic wave in the sample. In the collinear scattering geometry of the TDBS experiments, the Brillouin frequency is proportional to the product of the sound velocity and the optical refractive index of the sample at the probe wavelength (see Eq. (1) in Results).

In an inhomogeneous medium, the TDBS signal at each time instance contains information on the local parameters of the medium in the spatial position of the laser-generated light-scattering acoustic pulse at this time instance \( n \). It has previously been demonstrated, although under ambient conditions, that this effect can be used for the depth-profiling of inhomogeneous transparent media with nanometre-scale resolution limited by the spatial length of the laser-generated coherent acoustic pulse \( n \). Diamond anvil cell and the samples. High pressures up to 84 GPa were generated via compression of samples between bevelled diamond anvils of Bohler-Almax design having a culet size of 300 \( \mu \)m mounted in a Bohler-Almax Plate DAC. A hole in the centre of a pre-indented stainless steel gasket represented the sample volume filled with ice, and a thin iron foil in contact with one of the anvils and the sample. The iron foil served as the opto-acoustic generator for launching coherent acoustic pulses into the ice. A magnified schematic of the sample arrangement in the DAC is presented in Fig. 1(b). The sample dimensions in the experiments conducted at 57 GPa and 84 GPa were, respectively, 103 \( \mu \)m and 90 \( \mu \)m in diameter \( D \) and 14.4 \( \mu \)m and 13.5 \( \mu \)m in thickness \( H \). The diameters of the iron opto-acoustic generators were 60 and 40 \( \mu \)m, respectively, and their thicknesses were approximately 2 \( \mu \)m at ambient pressure, in both experiments. Pressure was determined from the wavelength of the R\(_{\text{flu}}\), fluorescence line of ruby grains distributed throughout the ice sample, whose red shift with pressure was calibrated earlier \( \text{[9]} \).

**Pump and probe optical setup.** The experiments on ice compressed in the DAC were performed using a typical pump/probe configuration for transient reflectivity optical measurements (Fig. 1(a)) involving a pulsed Ti:Sapphire laser with the following characteristics: 2 W average power, 808 nm wavelength and 2.7 ps FWHM duration of the laser pulses at the repetition rate of 80 MHz. This radiation was divided by a polarising cube in the pump and probe beams. The pump laser beam was modulated acoustically optically at a frequency of 161.1 kHz for the subsequent realisation of the synchronous detection of the probe laser radiation scattered by the sample. Then, it was frequency-doubled by a 1 cm-long BBO non-linear crystal to obtain 25 mW of 404 nm wavelength light pulses of 1.9 ps duration at FWHM for the generation of coherent acoustic pulses in the Fe-foil near its interface with \( \text{H}_2\text{O} \) ice. A computer-controlled rotating mirror with a two-patented moving time window of 17 ps (Fig. 4). The measurement of the transient thermo-reflectance signal, which corresponds to the coincidence in time of pulses of the pump and probe beams. Then, the pump beam was scanned in the vertical direction to obtain the transient thermo-reflectance signal as a function of the position. This function, showing the correlation of the pump and probe beams in the vertical direction, provided the width of 3 \( \mu \)m at FWHM. This indicates a 4 \( \mu \)m radius of the probe laser spot and a 4.5 \( \mu \)m FWHM of the correlation function of the two beams in the direction of the long (horizontal) axis of the pump laser elliptical focus. In addition, the DAC was mounted on a motorised XYZ stage to control the displacement of the sample in the horizontal and vertical lateral direction on the surface of the opto-acoustic generator with a precision of 0.1 \( \mu \)m. The filter (F in Fig. 1(a)) was introduced before the photo-detector to avoid its illumination by the pump radiation scattered from the sample.

**Processing of TDBS signals.** Panels (b) and (d) in Fig. 3 represent the dominant frequency of the reflectivity signals as a function of time. The dominant frequency values at these times are obtained from a spectrogram analysis of the temporal signals with a Hannig weighted window of 67 ps (64 points at a 0.9959 THz sampling frequency). For each central time of this sliding analysis window, every ~8 ps, the spectral component with the maximum amplitude is extracted. The frequency domain of this precision is interpolated with a smooth function, which provides frequency steps of 0.2 GHz. The maximum amplitude is used for the colour scale of the plotted symbols. Thus, the darker the symbol is, the larger is the maximum amplitude of the Brillouin signal, and vice versa.

**Estimates of the crystallite dimensions from X-ray diffraction data.** We collected two-dimensional XRD patterns of \( \text{H}_2\text{O} \) ice VII and ice X samples compressed in a DAC using monochromatic synchrotron radiation of the beam-line P2.02 (Pietra, HASYLAB, DESY) \( \text{[10]} \). The patterns were collected from sample areas of approximately \( 15 \times 15 \mu \)m\(^2\); the sample thickness was also approximately 15 \( \mu \)m. The samples were recorded at a synchrotron beam of diameter \( \approx 40 \mu \)m to obtain an average size of crystallites in our samples at 57–84 GPa to be \( \approx 40 \mu \)m. The crystallites of the ice layer thickness between Fe/ice of \( \approx 5 \mu \)m thickness, which are in a very good agreement with the values of the aggregate sound velocities of ice.
measured by classic BS35. We also applied the so-called envelop method to determine the C_{11} modulus in our samples. For this, we found the minimum value of the Brillouin frequency from the data detected at three different points of the samples and determined the minimal longitudinal wave velocity using n extrapolated from Ref. 39. The minimum velocity in cubic single crystals is along the [100] direction and depends only on C_{11} and the density of ice. Taking the values of densities reported in Ref. 44, we found C_{11} at 84 GPa to be 35 GPa at 56 GPa, with reasonable agreement with the values of 540 GPa and 350 GPa, respectively, extracted by classical BS35. A detailed report on the sound velocities of ice VII and X as a function of pressure will be presented in a separate paper.

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Author contributions
V.E.G., N.C., S.M.N., A.B. and B.C. designed the research. S.M.N. and A.Z. prepared the samples. S.M.N., N.C., A.Z. and A.B. contributed to the experiments. V.T., S.M.N. and D.G. performed signal processing. V.E.G., A.Z., D.G., S.M.N. and N.C. contributed to developing the theory. V.E.G., A.Z., S.M.N. and V.T. analysed and interpreted the experimental observations. V.E.G., A.Z., S.M.N. and N.C. wrote the manuscript.

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