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1 **Picosecond laser ultrasonics for imaging of transparent polycrystalline**  
2 **materials compressed to Megabar pressures**

3

4 Maju Kuriakose<sup>1</sup>, Samuel Raetz<sup>1</sup>, Nikolay Chigarev<sup>1</sup>, Sergey M. Nikitin<sup>1</sup>, Alain Bulou<sup>2</sup>,  
5 Damien Gasteau<sup>1</sup>, Vincent Tournat<sup>1</sup>, Bernard Castagnede<sup>1</sup>, Andreas Zerr<sup>3\*</sup>,  
6 and Vitalyi E. Gusev<sup>1\*</sup>

7

8 <sup>1</sup>LAUM, UMR-CNRS 6613, Université du Maine, Le Mans, France

9 <sup>2</sup>IMMM, UMR-CNRS 6283, Université du Maine, Le Mans, France

10 <sup>3</sup>LSPM, UPR-CNRS 3407, Université Paris Nord, Villetaneuse, France

11

12 **Abstract**

13

14 Picosecond laser ultrasonics is an all-optical experimental technique based on ultrafast high  
15 repetition rate lasers applied for the generation and detection of nanometric in length coherent  
16 acoustic pulses. In optically transparent materials these pulses can be detected not only on their  
17 arrival at the sample surfaces but also all along their propagation path inside the sample providing  
18 opportunity for imaging of the sample material spatial inhomogeneities traversed by the acoustic  
19 pulse. Application of this imaging technique to polycrystalline elastically anisotropic transparent  
20 materials subjected to high pressures in a diamond anvil cell revealed their significant  
21 texturing/structuring at the spatial scales exceeding dimensions of the individual crystallites.

22

23 **Keywords:** laser ultrasonics, picosecond ultrasonic interferometry, time-domain Brillouin  
24 scattering, 3D imaging, high pressures, diamond anvil cell

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32 \*Corresponding author(s): [zerr@univ-paris13.fr](mailto:zerr@univ-paris13.fr); [vitali.goussev@univ-lemans.fr](mailto:vitali.goussev@univ-lemans.fr)

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## 34 1. Introduction

35

36 Picosecond laser ultrasonics, developed since the pioneering works of H. J. Maris et al. in 1984  
37 [1], is a technique that uses ultra-short pump laser pulses to generate coherent acoustic pulses and  
38 detect them by time-delayed ultra-short probe laser pulses while they propagate through a  
39 transparent medium or while they reach surfaces/interfaces. For launching acoustic pulses into  
40 optically transparent samples the latter can be covered with thin layers of light absorbing  
41 materials and even single layer light absorbers [2]. The length of the laser-generated pulses  
42 depend in general on the duration of the pump laser pulses, pump light penetration depth in the  
43 material and/or the thickness of the light-absorbing opto-acoustic transducer. Through the  
44 minimization of these factors it is possible to generate coherent acoustic pulses with a spatial  
45 length of nanometers order, which makes them suitable for imaging purposes at nanoscale. The  
46 contrast in imaging of materials by picosecond laser ultrasonics could be of different physical  
47 origins. It could be caused either by the spatial inhomogeneity of the photoacoustic generation  
48 process (optoacoustic conversion), or by the influence of the material inhomogeneity on the  
49 propagation of the coherent acoustic pulses, or by the spatial inhomogeneity of the acousto-optic  
50 detection process, or by a combination of those: thermal, thermo-elastic and optical parameters of  
51 the sample material (the latter at the pump laser wavelength) are influencing thermoelastic  
52 optoacoustic conversion; acoustic parameters of the material (such as sound velocity and acoustic  
53 impedance) are influencing propagation of the acoustic pulses; and, finally, acoustical, optical and  
54 acousto-optical parameters of the sample material at the wavelength of the probe laser light are  
55 influencing the detection process. Accordingly, imaging with picosecond laser ultrasonics is  
56 expected to be sensitive to multiple parameters of the examined medium. Because of this and of  
57 the potential of nanometric in-depth spatial resolution, picosecond ultrasonic technique has been  
58 widely used for numerous imaging applications. The principles of these imaging techniques,  
59 which are different depending on the nature of inhomogeneity that provides the image contrast,  
60 are briefly reviewed in the following.

61 In sonar and medical ultrasound techniques, a piezo transducer is used to generate ultrasound  
62 to image acoustic inhomogeneities. The contrast in such imaging is based on the ultrasound  
63 reflections caused by acoustical inhomogeneities (spatial variations in acoustic impedance). The  
64 similar imaging can be achieved with picosecond laser ultrasonics, where laser replaces the  
65 piezoelectric transducers for the generation and detection of hypersound. For instance, the  
66 comparison in a wide frequency band of the reflection coefficient of nanoacoustic waves at the  
67 GaN/H<sub>2</sub>O interface with that at the GaN/air interface provided indication on the structuring of the

68 GaN/H<sub>2</sub>O interface at nanoscale [3]. Later, through a comparison of the hypersound reflection  
69 coefficient at an Al<sub>2</sub>O<sub>3</sub>/water and at Al<sub>2</sub>O<sub>3</sub>/air interfaces the profiles of density, modulus and  
70 viscosity of water were reconstructed at depths up to 1 nm from the interface. It was demonstrated  
71 that liquid-water density in the vicinity (few angstroms) of the Al<sub>2</sub>O<sub>3</sub>/water interface is up to five  
72 times larger than in bulk liquid-water [4]. Based on the same acoustic reflection coefficient wide-  
73 frequency-band analysis, acoustic images of single biological cells have been recently reported,  
74 allowing analysis of the cell/substrate adhesion at nanoscales [5]. In these applications, the small  
75 length of laser-generated acoustic pulses is advantageously used to improve the in-depth spatial  
76 resolution of the imaging.

77 On the other hand, the so-called photoacoustic imaging [6, 7] is mostly based on the contrast  
78 due to possible spatial inhomogeneity of pump laser radiation absorption in optically  
79 transparent/diffusive multiphase media. Though this was initially developed for medical purposes  
80 [6-8] using, in particular, contrast in light absorption between blood containing vessels and tissue,  
81 the technique is also receiving a growing attention for industrial applications in solid media [9-  
82 13] where the contrast in optoacoustic conversion is due to spatial inhomogeneity in chemical  
83 composition of the samples. Regardless of its potential to produce images combining high optical  
84 contrast and high acoustic resolution, the technique has not been advanced until now to the  
85 nanoscales, although at depths shallower than 1 mm, optical-resolution photoacoustic  
86 microscopic system has been developed [8].

87 Finally, while dealing with optically transparent media, it is possible to realize imaging based  
88 on the spatial contrast in acousto-optic detection process. This imaging is sensitive to some  
89 additional parameters of the media, which cannot be probed by the two above described  
90 approaches. This type of imaging can be achieved with ultrafast lasers by the technique that is  
91 known under the name of the picosecond acoustic interferometry [14, 15] or time-resolved/time-  
92 domain Brillouin scattering. Indeed, when a laser-generated picosecond coherent acoustic pulse  
93 propagates in a medium, it induces through the acousto-optic effect a local change in the density  
94 and, accordingly, in the refractive index of the medium proportional to the acoustic strain. This  
95 causes a local reflection of the probe light for which the medium is transparent [see the paths of  
96 the pump (in blue) and probe (in red) optical rays in the sample in the left part of Fig. 1]. The  
97 name “interferometry” comes from the fact that, at the photodetector, the reflections of the probe  
98 laser beam from different stationary surfaces and interfaces of the tested sample interfere with the  
99 probe laser reflections from the moving coherent acoustic pulse. The scattering of probe in the  
100 considered case is the Brillouin scattering of light by coherent acoustic waves (coherent  
101 phonons). Similar to the Brillouin scattering by thermal incoherent phonons, the process is

102 controlled, in addition to acoustic parameters of the material (sound velocity and acoustic  
103 impedance, or equivalently material density and elastic moduli), by the optical refractive index  
104 and the acousto-optic (photo-elastic) tensor that defines efficiency of light interaction with the  
105 sound pulse. The transient signal detected in picosecond ultrasonic interferometry thus contains,  
106 at each moment of time, information on the local elastic, optical and elasto-optical properties of  
107 the tested material at the position where the ultrashort acoustic pulse is located during its  
108 propagation in the sample. The detected interference signal has commonly the form of a quasi-  
109 sinusoidal oscillation (the so-called Brillouin oscillation, see Fig. 2), where the information on the  
110 local parameters of the inhomogeneous media traversed by the coherent acoustic pulse is  
111 contained both in the amplitude and in the phase (frequency) of the oscillation [16]. This  
112 technique of picosecond ultrasonic interferometry was successfully applied for the depth profiling  
113 of material properties with nanometric spatial resolution at ambient conditions [17-19] and has  
114 been recently extended to probe material properties at megabar pressures [20]. The imaging was  
115 based on the analysis of the temporal evolution of either the Brillouin oscillation frequency [17]  
116 or the Brillouin oscillation amplitude [18], or of the both [19]. The in-depth spatial resolution of  
117 about 40 nm was achieved in low- $k$  nanoporous sub- $\mu\text{m}$  thick films [17, 19] and of about 30 nm  
118 in ion-irradiated semiconductor [18]. Three-dimensional imaging by this technique of a single  
119 biological cell, which allows average measurements of sound velocities and attenuation in the  
120 cells, was also reported [21].

121 In this paper, the information on the picosecond acoustic interferometry, the required signal  
122 processing, and on their applicability to image transparent materials compressed up to megabar  
123 pressures in a diamond anvil cell (DAC) are presented. The purposes of conducting high spatial  
124 resolution imaging at megabar pressures are to measure accurately local mechanical properties of  
125 materials under extreme conditions as well as to get spatially resolved images of texturing  
126 (ordering of nano- and micro-crystallites at the scales exceeding dimensions of individual  
127 crystallites) in compressed polycrystalline materials. Both of these purposes cannot be achieved  
128 with the classical frequency-domain Brillouin scattering technique because the latter gives access  
129 only to the parameter values averaged over the thickness of the sample that commonly exceeds  
130 several micrometers in the high-pressure experiments conducted in a DAC [22, 23].

131 Thus the sub-micrometer and even the nanometer in-depth spatial resolution that could be  
132 provided by the time-domain Brillouin scattering leads to an enhanced accuracy in determining  
133 elastic properties of compressed materials which are of extreme interest for a few branches of  
134 natural sciences such as condensed matter physics, physics of the Earth and planetology, as well  
135 as for monitoring and predicting earthquakes and tsunamis or nuclear weapons test control. This

136 motivated our efforts in the developments and the improvements of this imaging technique. In the  
137 following sections, firstly, the experimental setup together with the depth-profiling technique is  
138 described. Then the signal processing is presented and the lateral and the in-depth resolutions are  
139 discussed. Finally, some examples of imaging of H<sub>2</sub>O ice and solid argon compressed up to  
140 megabar pressures, at room temperature, are presented, compared and discussed.

141

142

## 143 **2. Experimental setup and imaging technique**

144

145 To reproduce extreme pressure conditions in laboratories, the most widely used tool is the  
146 diamond anvil cell (DAC). The device consists of two opposing diamond anvils with the culets  
147 compressing a sample in the center of a metal gasket (see left part in Fig. 1). The sample volume  
148 has the lateral size of typically 100 - 150  $\mu\text{m}$  and the thickness of a few tens of micrometers.  
149 Decreasing the distance between the anvils results in an increase of pressure in the confined  
150 volume. The pressure can be monitored by a change in fluorescence wavelength of Ruby grains  
151 embedded in the sample. Note that we used two different DACs for our two samples (water ice  
152 and argon). For water ice, the DAC model was Boehler-Almax Plate DAC [24] with diamond  
153 anvils having culets of 300  $\mu\text{m}$  in diameter. For argon, a homemade DAC of the piston-cylinder  
154 type with diamond anvils having culets of 350  $\mu\text{m}$  in diameter was used. The sample volume in  
155 the DAC was filled with condensed argon at room temperature using a gas-loading apparatus  
156 developed by one author of the present paper and built by the company TOP INDUSTRIE.

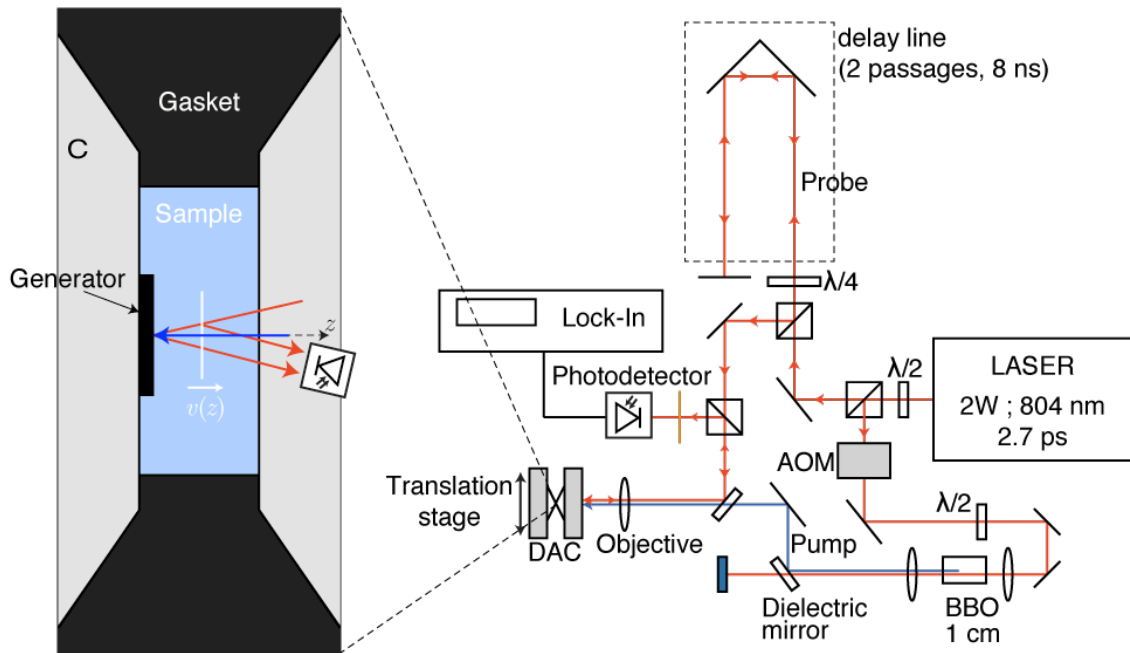
157 Since diamond anvils are transparent to visible light, this experimental device can be coupled  
158 with the picosecond acoustic technique in order to follow pressure-induced changes in the elastic  
159 properties of the light absorbing materials [25] and also of transparent materials if the light  
160 absorbing opto-acoustic transducer is placed in contact with the sample [20].

161

### 162 2.1. Picosecond acoustic interferometry

163 The picosecond laser ultrasonic interferometry or time domain Brillouin scattering (TDBS) is  
164 based on typical pump-probe configuration for transient reflectivity optical measurements, which  
165 is described in Fig. 1. A Ti:Sapphire laser source (Spectra-Physics, 2 W, 808 nm) delivering laser  
166 pulses of 2.7 ps FWHM duration at a repetition rate of 80 MHz was used. The laser beam was  
167 split into two parts with a polarizing cube. The first part was frequency-doubled in a 1 cm-long  
168 BBO non-linear crystal and was used as the pump. The second part of the laser beam was used as  
169 the probe, delayed in time with respect to the pump beam by mean of a mechanical delay line

170 (Fig. 1). The pump was modulated at a frequency of 161.1 kHz by an acousto-optic modulator  
 171 (AOM, Fig. 1) for performing a synchronous detection of the probe light scattered by the sample  
 172 with a lock-in amplifier. Using a 50x objective lens [for water sample: Olympus, numerical  
 173 aperture (NA) 0.5, working distance (WD) 10.5 mm; for argon sample: Mitutoyo, NA 0.42, WD  
 174 20.5 mm], pump and probe were then focused to a circular spot on the surface of an optoacoustic  
 175 generator (*e.g.*, absorbing material such as Fe or Zn foils) compressed together with the  
 176 transparent sample of interest in the DAC. The pump pulses absorbed in the metallic opto-  
 177 acoustic transducer generate, through the thermo-elastic effect, acoustic pulses that propagate  
 178 both inside the generator and in the transparent medium. These coherent acoustic pulses  
 179 composed of coherent acoustic phonons of GHz frequencies can then be detected by the probe  
 180 laser pulses.  
 181



182  
 183  
 184 **Figure 1.** [color online] Experimental laser ultrasonic setup and schematics of the sample  
 185 arrangement in a diamond anvil cell and of the paths of the pump (blue) and probe (red) optical  
 186 rays in the transparent sample.

187  
 188 Detection of the acoustic pulses happens in such a way that, at the photodetector, the reflected  
 189 probe laser pulses from various stationary material boundaries interfere with their weak  
 190 reflections from the propagating acoustic pulses (see Fig. 1). The interference is either

191 constructive or destructive, thereby producing quasiperiodic (quasi-sinusoidal) variations in the  
192 reflectivity signal amplitude, i.e., the so-called time-domain Brillouin oscillation (Fig. 2), when  
193 the acoustic pulses are propagating with slowly varying velocity leading to quasi-linearly varying  
194 in time phase shift between the various reflections of the probe. Note that the reflections from  
195 stationary optical inhomogeneities were dominated in the current experiments by those from the  
196 surface of the optoacoustic generator (see the zoomed schema of the sample in a DAC in Fig. 1).

197 The velocity  $v$  of the acoustic wave can then be computed from the frequency of the Brillouin  
198 oscillations by [14, 15, 26]:

$$f_B \cong \frac{2nv \cos \theta}{\lambda_0}, \quad (1)$$

199 where  $f_B$ ,  $\lambda_0$ ,  $n$  and  $\theta$  are the Brillouin oscillation frequency, wavelength of the probe beam,  
200 refractive index of the sample material at this wavelength, and angle between the propagation  
201 directions of probe and the acoustic pulse, respectively. For the experiments with negligible  
202 changes in  $n$  and if  $\theta$  and probe wavelength are known from the optical schema, the sound  
203 velocity can be calculated directly from the measured  $f_B$ . Several measurements conducted at  
204 different angles of probe incidence provide opportunity to determine the local sound velocity and  
205 the optical refractive index simultaneously in cases where they are both importantly spatially  
206 inhomogeneous [19].

207 Both water and argon, the materials of our particular interest here, appear as polycrystalline  
208 solids form when compressed above a few GPa in a DAC. Accordingly, when the photo-  
209 generated coherent acoustic pulse propagates along the DAC axis, orientation changes of the  
210 crystallites in these polycrystalline aggregates lead to changes in acoustic velocity. However,  
211 because both water ice and Argon are of cubic crystallographic symmetry under the pressures of  
212 our current experiments, optical refractive index  $n$  in Eq. (1) is isotropic/scalar and does not  
213 depend on the orientation of the local crystallites in polycrystalline microscopically  
214 inhomogeneous samples. In addition, it has been demonstrated [20] that refraction of a coherent  
215 acoustic pulse at the boundaries between differently oriented crystallites/grains, caused by the  
216 anisotropy of the elastic moduli even in cubic crystallites, leads to variations of the angle between  
217 the acoustic and probe light beams that is negligible in comparison with the elastic anisotropy-  
218 related variations in sound velocity. Thus in our picosecond acoustic interferometry experiments,  
219 if the acoustic pulse propagates through crystallites with different orientations, only the value of  
220 sound velocity at Brillouin frequency will be encoded through Eq. (1) in  $f_B$ . So a measurement of  
221 the time dependency of the Brillouin oscillation frequency would allow probing the in-depth  
222 changes in sound velocity, thus providing information both on poly-crystallinity of the sample



223 and elastic inhomogeneities (texture) inside the sample at a spatial scale exceeding the  
224 dimensions of the individual grains (for example on orientation texturing of groups of  
225 crystallites). We describe one of the signal processing methods that could be applied to perform  
226 such a depth profiling in the following.

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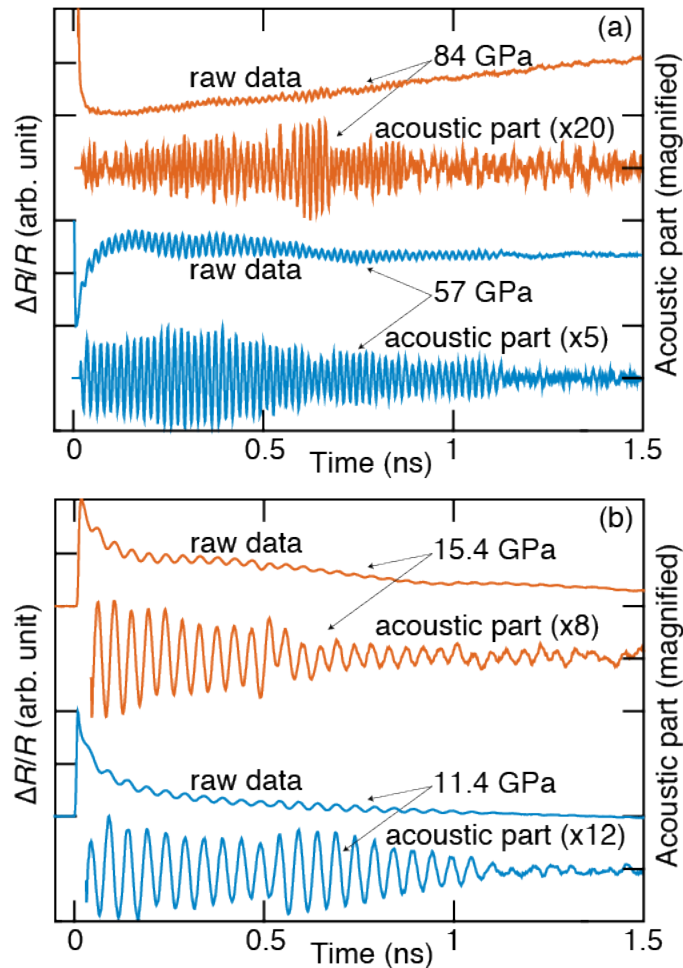
229

## 230 2.2. Imaging technique

231

### 232 *2.2.1. Depth profiling*

233 The frequency components of a temporal signal from a typical TDBS experiment can be brought  
234 out by applying the fast Fourier transform (FFT) to the signal. For this, initially, the experimental  
235 signals were filtered to remove the non-oscillating background caused by a transient heating of  
236 the sample and a transient optical reflectivity (see the acoustic parts of the signals in Fig. 2). Then  
237 the cleaned Brillouin oscillations were converted to their analytical form by applying Hilbert  
238 transformation. The cosines of the phase of the analytical signals are free of the variations in  
239 amplitudes, while the information on the varying frequencies is conserved. The FFTs were then  
240 applied on these “damping”-free signals to bring out the frequencies in it.



241

242

243 **Figure 2.** [color online] Typical transient reflectivity signals (each normalized to their maximum)  
 244 and their acoustic parts (magnified for better visibility) detected for: (a) the H<sub>2</sub>O ice sample  
 245 compressed to 57 GPa (in blue, bottom) and to 84 GPa (in orange, top); (b) the polycrystalline  
 246 argon sample compressed to 11.4 GPa (in blue, bottom) and to 15.4 GPa (in orange, top)  
 247 pressures

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Yet, treating the entire signal at once gives the information of the various frequencies present in the complete signal, but do not give any information about the moment in time when they show up. Thus this type of signal processing will give information on the sample properties along the complete path of the acoustic pulse propagation in the sample without its in-depth resolution. In order to overcome this limitation, standard time-frequency analysis can be used with a short-time Fourier Transform (STFT), the window size at FWHM of which can be chosen as small as a single Brillouin cycle (if the signal quality permits), so that the frequency corresponding to the

255 temporal window containing the treated Brillouin cycle can be obtained. Once the frequency is  
256 known and thereby the velocity [using Eq. (1)], the time axis can be converted into depth and thus  
257 the depth dependent velocity can be found. The resolution (temporal or in-depth) for the above-  
258 described method of the signal processing is thus governed by the choice of the temporal window  
259 duration. For example, by choosing the window duration equal to the period of the lowest  
260 acoustic frequency importantly contributing to the signal FFT performed over the complete  
261 signal, it is possible to realize the same spatial resolution in imaging along the complete path of  
262 acoustic pulse propagation. The spatial resolution in this case will be limited by the wavelength of  
263 phonon at the considered Brillouin frequency. Note that other methods of signal processing could  
264 lead to a better spatial resolution [17, 19] that is potentially limited not by the acoustic  
265 wavelength at Brillouin frequency, which is in general of the order of the probe optical  
266 wavelength in the medium, but by the spatial scale of the important strain variations in the  
267 coherent acoustic pulse which plays the role of the width of the moving optical mirror.

268 The above-mentioned method of signal processing is well suited for signals containing one  
269 frequency component varying with time. Some issues can arise for signals containing two (or  
270 more) different frequency components simultaneously. If these components are close compared to  
271 the frequency resolution of the STFT, which is inversely proportional to the window size, the  
272 retrieved frequency will be a weighted average of the different individual frequencies. The only  
273 mean to detect close components would be to increase the window size, thus to decrease the  
274 temporal/in-depth resolution. Yet, for signals containing different but well separated frequency  
275 components, an analysis of the individual peaks existing in the spectrogram can allow the  
276 independently retrieving of the different frequency components.

277

### 278 *2.2.2. Imaging and resolution*

279 Combining the above-mentioned depth profiling technique with lateral scans (translation stage of  
280 the DAC in Fig. 1), a 2-dimensional (2D) imaging of the sample under study can be obtained.  
281 This can also be extended to a complete 3-dimensional (3D) image of the specimen by  
282 performing the 2D imaging for the sample position changing in the second lateral direction.

283 The imaging resolution depends mainly on two factors: (i) the duration of the temporal  
284 moving window for the FFT that controls the in-depth resolution as mentioned earlier, and (ii) the  
285 laser beam spot size, which controls the lateral resolution. The laser beam spot size at the focal  
286 plane of the objective, i.e. twice the beam waist  $w_0$ , is linearly proportional to the focal length of  
287 the objective. However, a limitation in decreasing the focal length arises because decreasing  $w_0$   
288 also decreases the Rayleigh range—the range where the laser beam radius remains smaller than

289  $\sqrt{2}w_0$ . If the Rayleigh range is too short, the probed volume in the sample will not be cylindrical  
290 in shape, which may lead to a change in the probed area as a function of the depth. Therefore the  
291 selection of the objective in our experiments depended on two key points: (i) the minimization of  
292 the beam waist, in order to have a good lateral resolution, and (ii) keeping the Rayleigh range  
293 larger than the thickness of the sample, so that the probed cross section remains approximately  
294 the same all along the thickness of the tested material.

295 In our experiments on water ice, where a 50x objective was used, the lateral surface area of the  
296 cylindrical volume (tested by overlapping the probe laser beam and the coherent acoustic beam)  
297 is determined to be approximately  $10 \mu\text{m}^2$  [20]. In the reported below experiments in Ar the  
298 correlation function of the pump and probe beams was measured to be about  $2.7 \mu\text{m}$  in diameter  
299 at FWHM of the highest change in optical reflection, measured when the pump and probe pulses  
300 coincide in time. This provides an estimate of  $5.7 \mu\text{m}^2$  for the cross section of the material  
301 volume tested in each lateral position.

302

303

### 304 **3. Some examples of imaging of highly-pressurized transparent materials**

305

306 Before presenting the experimentally obtained 2D images of water ice and solid argon, a short  
307 highlight on the main goals pursued by conduction of these experiments is proposed.

308

#### 309 3.1. Presentation of water and argon at Megabar pressures

310 Water is an important compound that supports life and stays also as a simplest example of  
311 hydrogen bonding, which explains the numerous investigations that are conducted on this  
312 compound all around the world. Water is known to transform through a variety of phases at  
313 different thermodynamic conditions (pressure and temperature). The pressures we have chosen,  
314 57 GPa and 84 GPa, represent the water ice sample, most probably, in its phase X. We cannot  
315 exclude that at 57 GPa the water ice is still in phase VII because position of the phase boundary  
316 between phases VII and X is not well localized even at room temperature [27]. To give a  
317 milestone, the highest studied pressure (84 GPa) corresponds to the depth of about 2000 km in the  
318 Earth's interior [28].

319 For conducting high-pressure experiments, pressure-transmitting medium (PTM) are  
320 mandatory to obtain hydrostatic compression of the compound under study. Among others, argon  
321 is widely used as PTM because of its soft nature and chemical inertness. However it was reported  
322 that argon starts to become non-hydrostatic at pressures above 30 GPa [29]. More interesting are

323 reports on a significant elastic anisotropy of solid argon starting from the pressure of its  
324 solidification of 1.35 GPa even though its crystal structure is cubic [29, 30]. Such elastic  
325 anisotropy, combined with non-hydrostaticity, could strongly affect the sound velocity values  
326 derived from the classical Brillouin spectroscopic measurements performed for a sample  
327 compressed in a DAC. The main reason is the absence in such experiments of any information on  
328 preferred orientations of argon crystallites, texture and/or distribution of elastic inhomogeneities  
329 in the sample volume. Pressure distribution measurements can also not provide information on  
330 the orientation of the crystallites and the texturing/ordering of the groups of the crystallites. The  
331 proposed imaging based on picosecond ultrasonic interferometry can overcome these limitations  
332 and shed light on in-depth and in-plane distribution of inhomogeneities in solid argon compressed  
333 in a DAC with sub-micrometric to, potentially, nanometric resolution. The chosen pressures to  
334 analyze the hydrostaticity of solid argon are 11.4 and 15.4 GPa.

335 It will be now described how we have used the experimental setup and the explained signal  
336 processing to image inhomogeneities in two compressed transparent materials: water ice and solid  
337 argon, both of which are in polycrystalline form at pressures above 10 GPa. In the following, the  
338 obtained images for the water ice and solid argon are presented and discussed.

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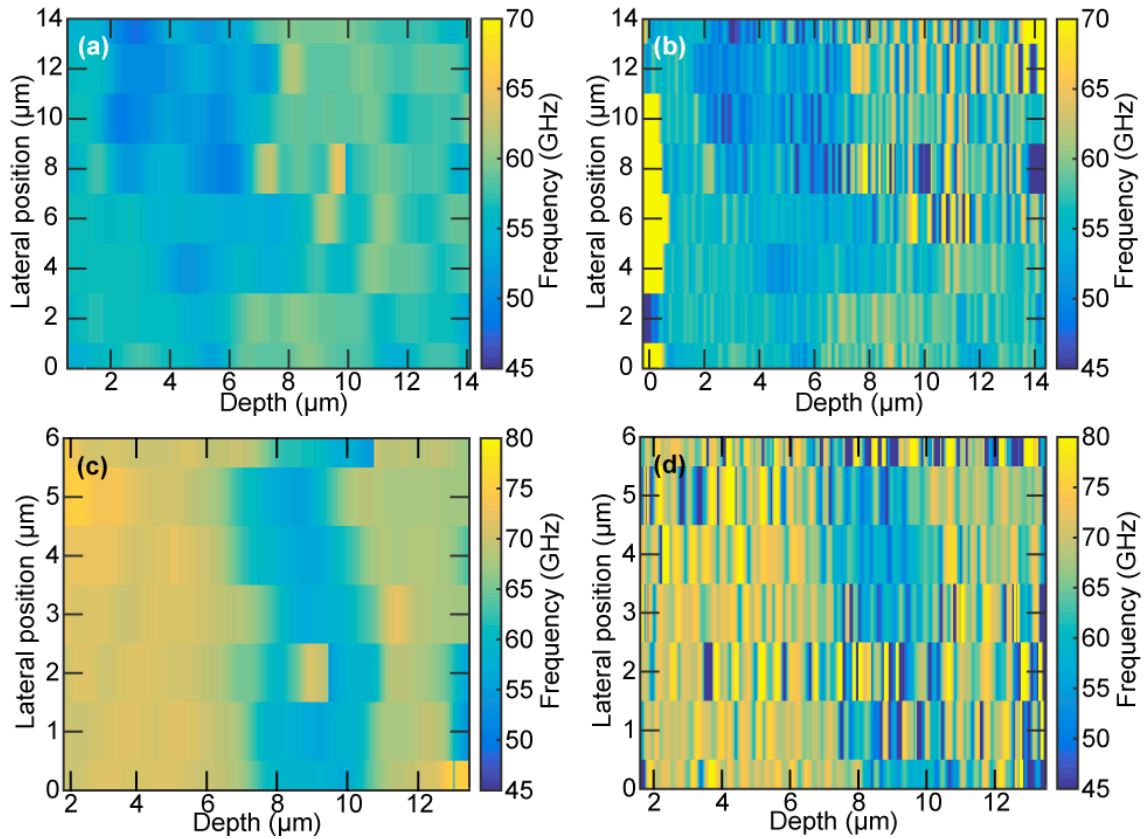
### 340 3.2. Imaging experiments

341

#### 342 3.2.1. *Water compressed to 57 GPa and 84 GPa*

343 Change of the sound frequencies as a function of depth at several lateral positions are displayed in  
344 Fig. 3 for the water ice sample at two pressures: 57 GPa [(a)-(b)] and 84 GPa [(c)-(d)]. The lateral  
345 scans are accumulated with a step of 2  $\mu\text{m}$  (1  $\mu\text{m}$ ) for 57 GPa (84 GPa) along the surface of the  
346 optoacoustic transducer. Thicknesses of the ice samples at 57 GPa and 84 GPa were measured to  
347 be 14.4  $\mu\text{m}$  and 13.5  $\mu\text{m}$ , respectively, using the interference patterns generated by illumination  
348 with the broadband light. The thicknesses were also determined from the time of propagation of  
349 the acoustic pulse between the generator and the opposite diamond anvil culet. A higher precision  
350 in the depth calculations was obtained where the time when the acoustic pulse reaches the  
351 diamond culet was chosen as the starting depth value. Then the depth coordinate has been  
352 reversely calculated back to the generator position. This helps to eliminate the uncertainties in the  
353 depth caused by generator thickness irregularities and lower precision of our signal processing  
354 technique at short distances from the opto-acoustic transducer. At such distances there is a  
355 significant contribution to transient reflectivity related to a direct dependence of the reflectivity  
356 on the temperature in the generator and the sample [20]. We used a color scale to image the 2D

357 sound frequency distribution in the ice samples at 57 GPa and 84 GPa, collected with two  
358 different in-depth resolutions (Fig. 3).



359  
360

361 **Figure 3.** [color online] 2D-images of sound frequency inhomogeneities in water ice compressed  
362 in a DAC to 57 GPa [(a)-(b)] and 84 GPa [(c)-(d)]. Absolute values of the frequencies can be  
363 derived from the color bars on the right hand side of each plot. The in-depth spatial resolution is  
364 about  $1.05 \mu\text{m}$  in (a) and (c) and  $0.26 \mu\text{m}$  in (b) and (d).

365 The frequency values in the images were obtained by applying the previously presented STFT  
366 processing. The chosen FWHM of the Hann window was 70 ps (3 to 4 oscillations of the longest  
367 Brillouin cycle) in Figs. 3(a) and 3(c), and 17.5 ps (nearly equal to the length of the longest  
368 Brillouin cycle) in Figs. 3(b) and 3(d). For the 84 GPa sample, these time windows correspond to  
369 in-depth resolutions of about 0.9 - 1.2  $\mu\text{m}$  for 70 ps window [Fig. 3(c)] and 0.22 - 0.28  $\mu\text{m}$  for  
370 17.5 ps window [Fig. 3(d)]. The characteristic dimension of individual crystallites in both  
371 polycrystalline ice samples was estimated to be around  $0.45 \mu\text{m}$  using XRD techniques [20].  
372 Considering the best in-depth resolution controlled by the chosen signal processing and the lateral  
373 dimensions of the pump-probe overlap at FWHM of  $10 \mu\text{m}^2$ , the minimal opto-acoustically tested  
374 volume was about  $2.6 \mu\text{m}^3$ . This means that the frequencies are averaged at least over

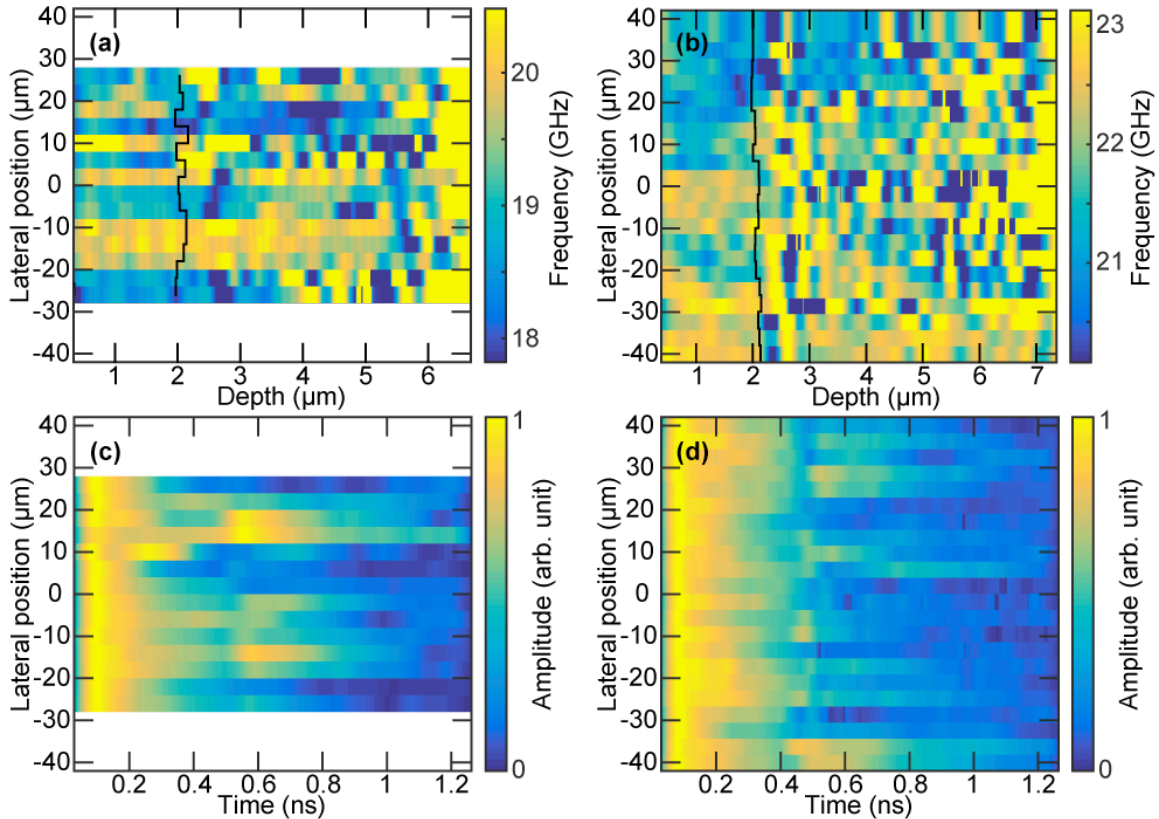
375 approximately 30 individual crystallites. The images at 84 GPa show clearly a low frequency  
376 layer in the depth region of 7-11  $\mu\text{m}$  [Fig. 3(c)-(d)], while for the 57 GPa sample the in-depth  
377 texturing/structuring of the water ice is less pronounced. The maximum changes of the Brillouin  
378 frequency relative to the average level revealed in the experiments with water ice are  
379 approximately  $\pm 26\%$  [20]. The local axial changes in frequency cannot be related to the axial  
380 pressure gradients inside the sample because this would also require large pressure gradients in  
381 the lateral direction, much higher than the observed maximal difference of about 10 GPa. The in-  
382 depth variation in frequencies thus reveals that the phase X of water ice is strongly anisotropic  
383 and the variation of frequencies is dominated by the variation in the orientation of individual  
384 crystallites or groups of crystallites [20]. The velocity variations between the adjacent maxima to  
385 minima were found to approach about  $\pm 13\%$ , which is rather close to the theoretically predicted  
386 value, of  $\pm 16\%$ , reported in Ref. [31]. The observed lowest frequency in our sample can be  
387 attributed to the orientation of crystallites (texturing) in the direction  $\langle 100 \rangle$  at which the sound  
388 velocity is the lowest compared to other orientations:  $\langle 110 \rangle$  and  $\langle 111 \rangle$ . Similarly, the highest  
389 frequency can be attributed to the fastest  $\langle 111 \rangle$  direction. Taking this fact into account we can  
390 conclude that the sample is stronger textured at 84 GPa than at 57 GPa. From the analysis of Figs.  
391 3(b) and 3(d) where the in-depth resolution is the highest, it can be deduced that the samples  
392 contain elastically homogeneous mesoscopic crystallite groups up to 1  $\mu\text{m}$  lateral size and about  
393 0.3 to 0.6  $\mu\text{m}$  thickness [20].

394

### 395 *3.2.2. Argon compressed to 11.4 GPa and 15.4 GPa*

396 For the argon sample, the in-depth dependency of the Brillouin oscillation frequency with respect  
397 to lateral positions is shown in Fig. 4 at pressure values of 11.4 GPa (a) and 15.4 GPa (b). The  
398 lateral distance between adjacent depth profiles is 4  $\mu\text{m}$ . Here again the frequencies are  
399 represented by colors and their values are given in the corresponding color bars. The signals at  
400 both pressures are treated using the previously described STFT processing, though with a Hann  
401 window having temporal size of 60 ps at FWHM (nearly equal to the length of the longest  
402 Brillouin cycle). This window duration corresponds to an in-depth resolution of about 0.32  $\mu\text{m}$  at  
403 11.4 GPa [Fig. 4(a)] and 0.36  $\mu\text{m}$  at 15.4 GPa [Fig. 4(b)]. Considering the best in-depth resolution  
404 controlled by the chosen signal processing and the lateral dimensions of the pump-probe overlap  
405 at FWHM of 5.7  $\mu\text{m}^2$ , the minimal optoacoustically tested volume was about 1.8  $\mu\text{m}^3$ .

406



407

408

409 **Figure 4.** [color online] 2D-images of Brillouin frequencies of solid argon compressed in a DAC  
 410 to 11.4 GPa (a) and 15.4 GPa (b). The in-depth spatial resolution is about  $0.32 \mu\text{m}$  in (a) and  $0.36$   
 411  $\mu\text{m}$  in (b). Absolute values of the frequencies can be derived from the color bars on the right hand  
 412 side of each plot. The related Brillouin amplitude images, though vs. time rather than depth, of  
 413 solid argon compressed to 11.4 GPa and 15.4 GPa are shown in (c) and (d), respectively. In (a)  
 414 and (b), the black lines stand for delimiting the depth after which the influence of the second  
 415 acoustic pulse on the images could be important.

416

417 In the experiments with argon, contrary to the case of water ice, the time moment when the  
 418 generated acoustic pulse reaches the argon/diamond interface is not visible in the frequency  
 419 versus depth plots. Both from the decay of particular Brillouin oscillations in Fig. 2 and from the  
 420 amplitude images presented in Fig. 4 (c) and (d), it follows that the signal at the Brillouin  
 421 frequency completely vanishes after propagating in solid argon during 1 ns, corresponding to the  
 422 penetration depths of less than  $6 \mu\text{m}$ . For comparison, the optically measured thickness of the  
 423 sample at 11.4 GPa is about  $28 \mu\text{m}$ . This vanishing of the acoustic signal is due to a strong  
 424 attenuation of the coherent acoustic pulses in argon, which was earlier noticed, although at



425 different Brillouin frequency, in the experiments in Ref. [25] where argon was used as a pressure-  
426 transmitting medium. On the other hand, as reported in Ref. [20] and discussed above, the signal  
427 cannot be processed accurately at the time close to the launching of the sound pulse by the opto-  
428 acoustical generator because of imperfect filtering of the thermo-reflectance contribution at GHz  
429 frequencies. Thus, to determine the depth coordinate, the choice has been made to consider that  
430 the acoustic pulse propagates at the mean velocity from time  $t=0$  of its generation up to the time  
431 where the determination of the Brillouin frequency becomes sufficiently exact. This explains the  
432 starting non-zero depth value in the 2D images shown in Fig. 4 (a) and (b).

433 An important observation that emerged from the analysis of the experimental data obtained for  
434 solid argon is that, under particular circumstances, the choice of the thickness of the optoacoustic  
435 generator/transducer could play an important role in the depth-profiling experiments. The pump  
436 laser pulse initially generates two acoustic pulses one of which starts to penetrate in the solid  
437 argon while another propagates inside the generator towards its interface with the diamond culet.  
438 The acoustic pulse propagating across a thin generator can thus be reflected at the  
439 generator/diamond interface and propagate back to the generator/argon interface where a second  
440 acoustic pulse is then launched in the solid argon. The second coherent acoustic pulse penetrating  
441 in the argon produces additional scattering of the probe light and, in general, causes degradation  
442 of the transient reflectivity signal and loss of in-depth spatial resolution of this imaging technique.  
443 This is because in the signal of transient optical reflectivity the information on the material  
444 properties from two spatially separated points will be mixed. However, under particular  
445 circumstances the second coherent acoustic pulse launched in the sample could be useful. For  
446 example, this could be the case, if the first acoustic pulse launched in the sample and the transient  
447 temperature related background in the optical reflectivity signal are both importantly attenuated at  
448 the delayed time moment of the second acoustic pulse launching. Then the picosecond acoustic  
449 interferometry signal from the second coherent acoustic pulse launched in the sample will provide  
450 a background-free Brillouin oscillation in the immediate vicinity of the optoacoustic transducer  
451 and thus an opportunity for a precise depth-profiling of material properties in this region, which  
452 in the case of the first acoustic pulse is strongly suffering from the temporal overlap of the  
453 Brillouin oscillation with transient heating-induced reflectivity variations. Potentially, the  
454 thickness and the material of the optoacoustic transducer could be selected/selected for the  
455 sample imaging with the second echo pulse. Further discussion of possible consequences of the  
456 acoustic pulses reverberation inside the optoacoustic transducer (ringing of the optoacoustic  
457 transducer) is beyond the scope of the present work. We just note that the above-presented

458 general principles are preliminary confirmed by the experiments in argon, the results of which are  
459 presented in Figs. 2 and 4.

460 In fact we observed a significant and abrupt increase of Brillouin frequency in experiments  
461 conducted at 15.4 GPa at depths around  $2.3 - 2.5 \mu\text{m}$  [Fig. 4 (b)]. This is not the signature of the  
462 in-depth layering of the sample, as it could have been tentative to suggest in the spirit of our  
463 observations in water ice [see Fig. 3 (a) for example], but the manifestation of launching at the  
464 generator-argon interface of the second coherent acoustic pulse. This hypothesis is confirmed by  
465 the corresponding Brillouin amplitude image in Fig. 4 (d) demonstrating that the amplitude of the  
466 coherent acoustic phonon is strongly attenuated before the time moment of around  $0.4 - 0.5 \text{ ns}$ ,  
467 which corresponds to the distances of abrupt increase of frequency in the Brillouin frequency  
468 images in Fig. 4 (b). Using the values of sound velocities in iron from Ref. [32] we estimated that  
469 the time delay of  $0.4 - 0.5 \text{ ns}$  corresponds to approximately  $2.7 - 3.4 \mu\text{m}$  propagation distance of  
470 coherent acoustic pulses. Thus  $0.4 - 0.5 \text{ ns}$  time delay could correspond to the delay of the second  
471 acoustic pulse launched in argon relative to the first one in the generator of  $1.3 - 1.7 \mu\text{m}$   
472 thickness. This estimate of the generator thickness is in accordance both with its measurements at  
473 ambient conditions before loading the generator in the DAC and also with the results of optical  
474 measurements of the thickness of the sample at high pressure in two neighbor lateral positions,  
475 one on the generator and another outside the generator. The data accumulated at 11.4 GPa are in  
476 favor of our hypothesis on various possible manifestations of the second acoustic pulse in argon  
477 imaging as well. Although in Fig. 4 (a) the zone of the Brillouin frequency increase is less  
478 pronounced than in Fig. 4 (b), it is still distinguishable at depths around  $2.0 - 2.2 \mu\text{m}$ . At the same  
479 time the Brillouin amplitude images in Fig. 4 (c) (see also the Brillouin oscillation in lower part  
480 of Fig. 2) are providing even more convincing picture of the acoustic echo arrival in argon around  
481  $0.5 \text{ ns}$ . We note that the above estimates are very roughly obtained through visible inspection of  
482 the images with an attempt to get an idea of the phenomena manifested in average over the lateral  
483 scan. For finding the precise correspondence between the echo-type features in the Brillouin  
484 amplitude images and the abrupt increase of the frequency in the Brillouin frequency images, the  
485 estimates should be done in each lateral point separately.

486 We conclude that our estimates and experiments indicate that the features in frequency images  
487 of argon at depth exceeding about  $2.0 - 2.3 \mu\text{m}$  are related to the launching of the second coherent  
488 acoustic pulse in argon. Note that in the experiments with water ice the thickness of the  
489 optoacoustic transducer was about 1.5 times larger than in the experiments with argon and we  
490 have not found in the images any features at the estimated delay time for launching the second  
491 acoustic pulse in  $\text{H}_2\text{O}$ , that could indicate the influence of the second pulse on the images. This

492 could be because of either a stronger attenuation of the sound pulse in Fe at larger distances in  
493 comparison with those in the argon experiments or due to a significantly weaker attenuation of  
494 coherent sound in water ice at pressures around between 57 and 84 GPa than in argon at pressures  
495 between 11.4 and 15.4 GPa, or to both.

496 In the current study we have not used “effect” of the second launched pulse to improve  
497 precision in evaluation of the material parameters, because the goal was to present qualitatively  
498 the richness of the information obtained using the presented laser ultrasonic imaging even without  
499 profiting from this effect. In Fig. 4 (a) and (b) the black lines stand for delimiting the depth after  
500 which the influence of the second acoustic pulse on the images could be important. To the right of  
501 the black lines not just the determined Brillouin frequencies but also the estimated depths are  
502 supposed to be biased/poisoned by the presence of the second coherent acoustic pulse in argon.  
503 The zone of our analysis in Fig. 4 (a) and (b) is to the left of the black lines, where the measured  
504 values are not affected by the second launched pulse. The frequencies at both pressures show  
505 strong changes in lateral direction sometimes even between two adjacent in-depth profiles, and  
506 smooth and similar at each separately taken lateral position when the in-depth coordinate  
507 changes. Generally speaking, in the images of solid argon reported here in Fig. 4 (a) and (b), the  
508 lateral texturing dominates over the in-depth one, while in the images of water ice in Fig. 3 the  
509 situation is opposite. At 15.4 GPa, the image shows clearly two regions, before and after the  
510 center of the generator in the lateral direction, with different mean frequencies. On the other hand,  
511 at 11.4 GPa, the strong frequency changes do not have similar distribution that could be clearly  
512 split into two parts. In order to check whether these differences in frequencies could come from  
513 non-hydrostatic loading of the DAC, we have estimated the changes in pressure that correspond  
514 to the equivalently strong changes in frequencies using the dependencies of the velocity and  
515 refractive index on pressure reported in Ref. [33]. Note that the refractive index of solid argon is  
516 weakly dependent on pressure in the considered pressure interval [33]. The estimates demonstrate  
517 that the pressure gradients needed to cause the corresponding frequency (or velocity) changes  
518 (1.56 GPa per 4  $\mu\text{m}$ ) are an order of magnitude higher than what we have measured over the  
519 entire cell by means of the ruby fluorescence-scale (1.5 GPa difference between ruby particles  
520 separated by about 45  $\mu\text{m}$ ). On the contrary, the longitudinal velocity anisotropy (estimated as the  
521 difference between the minimum and maximum velocity values) has been reported in Ref. [34] to  
522 be around 16% for pressures close to 11.4 GPa and 15.4 GPa. Considering the velocity anisotropy  
523 in our measurements, the highest relative change in the mean velocity between adjacent lateral  
524 positions is only 8% at 11.4 GPa and 4% at 15.4 GPa. If we consider the velocity variations for a  
525 single lateral position, the largest difference is measured to be 12% at 11.4 GPa and 10% at 15.4

526 GPa. However, when considering the entire scanned volume, the global difference between the  
527 highest and the lowest observed frequencies was found to be 18% and 14% at pressures 11.4 GPa  
528 and 15.4 GPa, respectively. These values are in the range of the expected 16% longitudinal  
529 velocity anisotropy [34]. So the differences in the local frequencies revealed by our laser  
530 ultrasonic imaging of solid argon can be attributed to the difference in the orientation of the  
531 crystallite groups inside the polycrystalline sample.

532

### 533 3.3. Quantitative estimates of the acoustic velocities in compressed argon and compressed 534 water

535 The technique of time-domain Brillouin scattering that was applied by us here for imaging can be  
536 used similar to classic Brillouin scattering for the quantitative evaluation of the acoustic  
537 properties of materials at high pressures when this is required. As an example, a summary of the  
538 quantitative estimates of velocity for each presented case is now proposed. The average values are  
539 included in Tab. I and compared with velocities measured using classical Brillouin scattering and  
540 reported in the literature. The window sizes at FWHM used to process the experimental data for  
541 quantitative estimates were: 66.5 ps for solid argon and 45 ps for water ice. The average  
542 velocities for each of the samples at a particular pressure were obtained as follows. Primarily, the  
543 complete set of signals, for instance, 14 signals for argon 11.4 GPa experiment, measured in a  
544 sample were processed using STFT approach with the mentioned window size. Secondly, the  
545 frequency values coming from the noisy signal parts together with parts corresponding to a  
546 second acoustic pulse, if any, were removed. These steps gave some tens of depth dependent  
547 Brillouin frequency values for each signal, which produce a few hundreds of Brillouin frequency  
548 values for the tested sample volume. Finally, these Brillouin frequency values from the whole  
549 tested volume were averaged and the velocity was calculated using Eq. (1) for a given sample at a  
550 particular pressure. The refractive index data were taken from the literature. It was considered  
551 that the angle between the propagation directions of probe and the acoustic pulse is equal to zero  
552 [20]. The wavelength of the probe beam is 804 nm. The uncertainties in the indicated velocities  
553 stated in Tab. I are only due to the uncertainties in the reported values of the refractive index. The  
554 values of the average velocity obtained in this paper (Tab. I) are in a very good agreement with  
555 values reported in the literature both for argon sample and water ice sample, at each pressure.  
556 Careful processing of the measured minimum and maximum frequencies could provide the values  
557 for the complete set of single crystal elastic constants, though this is beyond the scope of the  
558 present paper.

559

560 **Table I.** Summary of the quantitative estimates of velocity for each presented experiment and  
 561 comparison with the reported in the literature velocities measured using classical Brillouin  
 562 scattering.

Pressure (GPa)	Average velocity (km/s)	Window size at FWHM (ps)	Density (kg/m <sup>3</sup> )	Refractive index at 800nm	Velocity from the literature (km/s)
<i>Argon</i>					
11.4	4.8±0.3*	66.5	3000 <sup>⋄</sup>	1.6±0.1 <sup>⋆</sup>	4.6-5.5 <sup>⋄</sup> 4.2-5.4 <sup>⋄</sup>
15.4	5.5±0.3*	66.5	3300 <sup>⋄</sup>	1.6±0.1 <sup>⋆</sup>	5.1-6.0 <sup>⋄</sup> 4.5-5.9 <sup>⋆</sup>
<i>Water ice</i>					
57	12.5±0.1*	45	2770 <sup>⋄</sup>	1.79±0.02 <sup>⋄</sup>	13±0.3 <sup>⋄</sup>
84	14.5±0.1*	45	3120 <sup>⋄</sup>	1.81±0.02 <sup>⋄</sup>	15.5±0.3 <sup>⋄</sup>

563 \* Indicated uncertainty of the average velocity is calculated from the uncertainty of the refractive  
 564 index data only.

565 <sup>⋄</sup> ref. [34]; <sup>⋆</sup> ref. [33]; <sup>⋄</sup> ref. [35]; <sup>⋄</sup> ref. [36]

566

567

#### 568 **4. Conclusion**

569

570 We have presented an experimental method of 2D imaging of polycrystalline water ice and solid  
 571 argon aggregates compressed to high pressures in a DAC obtained by applying the technique of  
 572 picosecond laser ultrasonic interferometry (time-domain Brillouin scattering). Our experimental  
 573 results demonstrate that this technique is an effective tool for imaging the texturing/structuring of  
 574 polycrystalline transparent aggregates providing a significantly better in-depth resolution when  
 575 compared with the classical frequency-domain Brillouin scattering. Our experiments reveal  
 576 differences in texturing of water ice and solid argon that definitely require more elaborated  
 577 additional investigations in larger intervals of pressures.

578

579

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581

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584

585

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