REVIEW OF SCIENTIFIC INSTRUMENTS **89**, 086105 (2018)

Note: Elastic wave velocity measurement using ultrasonic system with two-reflectors

L. Li,[a] M. L. Whitaker, and D. J. Weidner
Mineral Physics Institute, Stony Brook University, Stony Brook, New York 11794-2100, USA

(Received 26 May 2018; accepted 24 July 2018; published online 14 August 2018)

We report an experiment protocol for ultrasonic velocity measurements carried out in a synchrotron-based multi-anvil high-pressure apparatus. By adding a second reflector in the cell assembly, ultrasonic signals are significantly stabilized for experiments where samples experience structural changes such as phase transition or partial melting. Features of the elastic wave can be calculated from acoustic impedance allowing us to evaluate the possible interference between the sample reflection and other internal multiple reflections. This new protocol allows various forms of samples including cold-pressed powder samples, for which grain size and porosity can be monitored and controlled *in situ* during the annealing process. *Published by AIP Publishing.* https://doi.org/10.1063/1.5041802

Elastic wave velocities of materials at high pressure and high temperature conditions are important for the understanding of the Earth's interior. An ultrasonic pulse-echo-overlap technique combined with the multi-anvil apparatus is often used for such a velocity measurement,[1–3] in which elastic waves of both P and S waves within the range of 20-70 MHz are generated and received by a dual-mode 10° Y-cut $LiNiO_3$ piezoelectric transducer. This method relies on the flat parallel interfaces to reflect coherent acoustic waves. Even with the maturity of this technique, there are scenarios that ultrasonic signals cannot be observed caused by the changes in the samples incurred by pressure and temperature changes during the experiment.

In this type of high-pressure ultrasonic experiment, a pre-sintered sample is often placed between a buffer rod and a material like NaCl in a cell assembly. The pre-sintered sample has to satisfy a few criteria to warrant a good experimental turnout. First, both the sides of a disc-like sample need well-polished mirror-like surfaces. This is easy to achieve in the laboratory; however, if the sample experiences structural changes during the experiment, the sample may lose a good reflection surface and then the ultrasonic signal disappears. Second, the sample has to have a uniform grain size. The grain size should not be too close to the wavelength of the ultrasonic wave. The grain size should also not be too large to impair a good X-ray powder diffraction spectrum. Certain samples may experience strong grain growth during annealing, causing inferior ultrasonic characteristics. Third, the sample phase and composition should not be altered by the sintering process. For example, for a natural sample like peridotite, annealing at 1500 K and low pressure will cause partial-melting, while annealing at lower temperature will not remove dislocations at grain boundaries. Fourth, the density of the sintered sample has to be near the theoretical density in order for the sample to maintain its shape and polished surfaces during compression.

In this paper, we report a modification of the experimental technique for high-pressure ultrasonic experiments that broadens the range of samples that can be characterized. Instead of using a single buffer rod and a dense, rigid sample, we place a second reflector behind the sample. This modification of the cell assembly design provides the following advantages: (1) the reflection surfaces are stable through all conditions of the experiment; (2) the relative phase shift of the acoustic signals between the buffer rod (sample reflection) and the sample (reflector reflection) is always 180°, removing uncertainty of this quantity; (3) the sample can be a cold-pressed powder, which means the sample could be a non-quenchable sample, or a gel-like sample, or a high pressure phase synthesized sample *in situ*; (4) the sintering process is carried out during the ultrasonic experiment at high pressure and the synchrotron X-ray is used to monitor the porosity, grain size, and deviatoric stress level *in situ*. Using this modified design, we have measured the elastic wave velocities of partially molten minerals[4] and samples going through ferro-elastic phase transitions,[5] which have been an experimental challenge in recent times.

The modified experimental technique is based on the DIASCoPE acoustic system, which has been installed at Beamline 6-BM-B of the Advanced Photon Source at Argonne National Laboratory.[3] In this system, a multi-anvil apparatus (D-DIA[6]) is used as the pressure and temperature provider and has been fully integrated with the acoustic system using the EPICS control system. Synchrotron X-rays travel through the sample that is encapsulated in a cell assembly (Fig. 1). The energy dispersive X-ray diffraction spectrum is captured and provides information on the sample structure. The transmitted X-rays are converted to visible light by a single-crystal YAG scintillator. The X-ray radiograph is recorded by using a Prosilica CCD camera as a direct measurement of the sample length.[2] Both ends of the sample are marked by 1 μm thick gold foils, which are shown as boundary markers in X-ray images. The ultrasonic interferometer collects both P and S wave data (Fig. 2) while the sample is under high pressure and temperature conditions. We collect the P and S data individually by using a narrow band signal either at 60 MHz (for P waves) or at

[a]Author to whom correspondence should be addressed: li.li.2@stonybrook.edu.

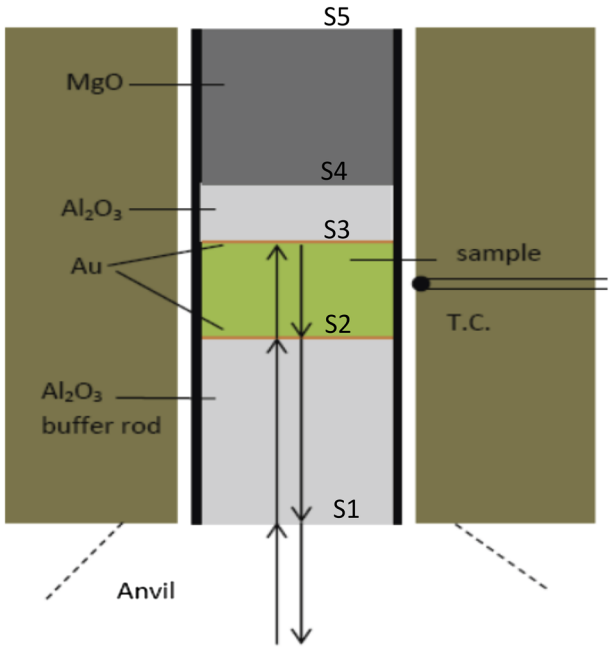

FIG. 1. High-pressure ultrasonic cell assembly. The sample occupies a cylindrical hole in the amorphous-boron epoxy 6 mm cube. The cylindrical hole is lined with a corundum sleeve with a graphite sleeve inside, that is, the heater. From the bottom is a corundum buffer rod of 2.35 mm length and 2.5 mm diameter, polished on both ends with a 1 μm thick gold foil on the polished surface. The sample of length 1.3 mm is above the buffer rod, and a corundum reflector of length 0.74 mm is above the sample. The sample side of the reflector is polished, and the interface is also lined with a gold foil disk. An MgO plug fills in the rest of the cylinder. The potentially reflecting surfaces are labeled as S1–S5. The lines with arrowhead indicate the path of the S3 reflection.

35 MHz (for S waves). This is in contrast to the study[1] which uses a wide band input signal that produces both P and S waves simultaneously and then separates them with a narrow band filter as a post-experiment process on the recorded data. The travel time is analyzed using the pulse-echo-overlap method[7] on the recorded data that are illustrated in Fig. 2. The velocity is calculated from dividing the sample length by single-trip travel time.

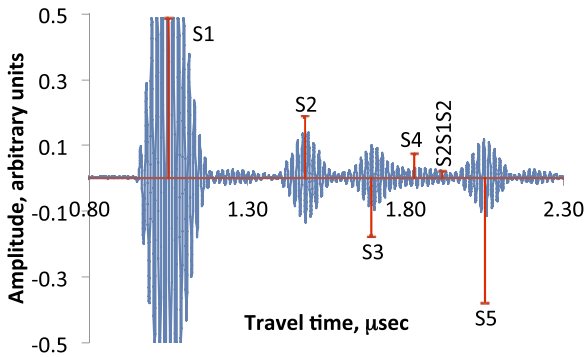

FIG. 2. Observed acoustic signal recorded in file KLB-1_74_31.udat for a sample of KLB-1.[4] Acoustic reflections from a 60 MHz tone burst that generated P waves are recorded as a function of time in this figure. The arrival time and amplitude of reflections from various interfaces in the sample are calculated and displayed as S1–S5 corresponding to the interfaces in Fig. 1. The time difference between S2 and S3 defines the round trip travel time in the sample.

The sample cell is shown in Fig. 1. The sample is placed in a cylindrical hole in a boron-epoxy cube. A graphite sleeve is nested in an alumina sleeve and used as a furnace. A thermocouple is placed next to the sample. Inside these sleeves is the sample column. On the bottom is a fully dense corundum buffer rod. Both sides of the buffer rod, which is 2.35 mm long and 2.5 mm in diameter, are mirror-polished. The cold-pressed sample pellet that is ~1.3 mm long and between 2 and 2.5 mm in diameter is above the buffer rod (the diameter of the sample is controlled by whether or not a chemical environmental chamber is necessary to maintain state variables such as the oxygen fugacity). On the top of the sample is a 0.74 mm long and 2.5 mm diameter corundum rod that serves as an acoustic reflector. This is different from the conventional assembly that has a mixture of NaCl and boron nitride in this position.[1,3] One side of this corundum rod is mirror-polished; the other side is flat but not mirror polished. The mirror side is in contact with the sample. A porous MgO rod is placed above the short corundum rod. The acoustic wave travels through the anvil first, then the buffer rod, and finally the sample. There are five reflection surfaces, S1 through S5 (Fig. 2, where we label the reflection by the reflecting surface). There are possible multiple reflections such as S2S1S2 that have made multiple round trips inside the buffer rod. The travel time within the sample is the time difference between S3 and S2.

For aligned, flat surfaces, it is possible to predict the relative amplitudes of the recorded signals. For these conditions, the reflection coefficient, for a plane wave in medium 1 at the interface with medium 2, R_{12}, is given by[8]

$$R_{12} = (I_1 - I_2)/(I_1 + I_2), \quad (1)$$

while the transmission coefficient T_{12} is given by

$$T_{12} = 2I_1/(I_1 + I_2), \quad (2)$$

where I is the acoustic impedance given by the product of the density and the velocity of the respective medium. For a wave with an incident amplitude of 1, the amplitude of the reflected or transmitted wave is simply the reflection coefficient or the transmission coefficient.

Figure 2 is a typical ultrasonic data set (as part of the study on peridotite[4]). As the tone burst electronic signal into the transducer was set at 60 MHz, the resonant frequency of the longitudinal vibration, a P wave was generated and displacement signal amplitudes are recorded as a function of time. When the tone burst is set at the resonant frequency of the shear vibration, 35 MHz, then a similar S wave signal is generated and observed. Multiple acquisitions, typically a thousand, are collected and summed up for stronger signals.[3] Also illustrated in Fig. 2 are the calculated relative amplitudes and arrival times of several reflections. S1, the anvil–buffer rod reflection, is taken as the reference amplitude and arrival time from which the other reflections are evaluated using Eqs. (1) and (2). Lines that are below zero reflect a sign change in the signal relative to S1. The amplitude of S1 is assigned the value 0.5, which is clearly less than the actual signal that has been cropped by the recording. Nonetheless, all observed signals are less than the model value indicating loss of acoustic energy,

probably dominated by the geometric spreading of the wave. Here we see a significant signal for each of the 5 interfaces that include both tungsten carbide anvils, with the unpolished S4 interface being the smallest. We also recognize a signal corresponding to the multiple reflection S2S1S2, which is the only reflection that might possibly interfere with either of the sample reflections. The calculations indicate that it is about an order of magnitude smaller than the sample reflections S2 or S3, and the observation is consistent with this.

A few details need attention to warrant good ultrasonic signals. One is that the length of all elements that generate reflections should be carefully chosen so that the sample reflections are well resolved. Two is that the surfaces S1, S2, and S3 should be parallel and flat. For a cold-compressed powder sample, a uniform density is required. Three is that the sample can be annealed during the high pressure run at appropriate conditions based on the properties of the sample. A good annealing process is often concluded with a sound X-ray powder diffraction pattern and a much-strengthened ultrasonic signal.

The annealing process is to eliminate pores, to homogenize the stress field to hydrostatic, and to generate a flat contact surface between the sample and the two corundum rods. The first two goals can be analyzed with the diffraction pattern, and the last goal is confirmed by the quality of the ultrasonic signal. If there are any pores in the sample, then the adjacent grains are at zero stress. As a result, their diffraction peaks will reflect lattice spacings that have not changed from room pressure. Thus, the large *d-spacing* part of the peak will not change from room pressure. We have observed such phenomena with very strong powdered samples such as quartz[9] and diamond.[10] The heterogeneity of the stress field is reflected in the peak width.[11] Temperature reduces the strength of the sample and thus reduces the stress heterogeneity. Successful annealing yields peaks that have the same sharpness as the room pressure peaks. It has also been our experience that a powder sample will demonstrate a greater amount of broadening with increasing pressure but will anneal more completely with increased temperature than a hot pressed sample.

Here we demonstrate experimental data that have been collected using this modified technique. We have collected data on the velocities of partial molten peridotite[4] and the velocities of neighborite perovskite going through orthorhombic to cubic phase transitions.[5] In the latter study, we not only measured the velocities near the phase boundary but also detected attenuation of the ultrasonic signal.[5] Both experiments were at a pressure of 2 ~ 3 GPa and up to 1500 K which is easy to achieve in the multi-anvil apparatus. However, there are few experimental acoustic velocities that have been reported in the literature for these types of samples despite the relative importance of such data. We suggest that one possible reason is the loss of the reflecting surface S3, which is defined by the polished surface of the sample that is adjacent to the soft salt/boron nitride mixture. Perhaps the phase transformation disrupts the reflectivity of the sample. In the cell reported here, the reflective surface is maintained by the polished corundum reflector and not by the sample.

In summary, we report a modified high-pressure ultrasonic measurement method. It is through placing a second reflector next to the sample. This modification removes the need for a pre-sintered sample with polished acoustic reflective surfaces that remain throughout the experiments. Our reported data demonstrate that we can measure properties of materials that have been particularly difficult to measure using the conventional method such as materials going through phase transitions or partial-melting.

This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357 on beamline 6BMB with the support of Haiyan Chen. The research was supported by NSF Grant Nos. EAR 1361463 and EAR 1547556 (L.L. and D.J.W.). This research was partially supported by COMPRES, the Consortium for Materials Properties Research in Earth Sciences, under NSF Cooperative Agreement No. EAR 1606856.

[1]B. Li, J. Acoust. Soc. Am. **125**(4), 2653 (2009).
[2]B. Li, J. Kung, and R. C. Liebermann, Phys. Earth Planet. Inter. **143**, 559–574 (2004).
[3]M. L. Whitaker, K. J. Baldwin, and W. R. Huebsch, Rev. Sci. Instrum. **88**(3), 034901 (2017).
[4]D. J. Weidner, L. Li, M. L. Whitaker, and R. Triplett, J. Geophys. Res.: Solid Earth **123**(2), 1252–1261, https://doi.org/10.1002/2017jb014753 (2018).
[5]L. Li, D. J. Weidner, M. L. Whitaker, and R. Triplett, "Ultrasonic acoustic wave velocities of Neighborite (NaMgF3) across orthorhombic to cubic phase boundary at high P-T," Phys. Earth Planet. Inter. (submitted).
[6]W. B. Durham, D. J. Weidner, S.-i. Karato, and Y. Wang, in *Plastic Deformation of Minerals and Rocks*, edited by S.-i. Karato and H.-R. Wenk (Mineralogical Society of America, San Francisco, 2002), pp. 21–49.
[7]E. P. Papadakis, in *Physical Acoustics: Principles and Methods*, edited by Warren P. Mason and R. N. Thurston (Academic Press, Orlando, FLA, 1976), Vol. XII, pp. 277–374.
[8]T. Lay and T. Wallace, *Modern Global Seismology* (Academic Press, San Diego, CA, 1995).
[9]C. S. N. Cheung, D. J. Weidner, L. Li, P. G. Meredith, H. Chen, M. L. Whitaker, and X. Chen, J. Geophys. Res.: Solid Earth **122**(4), 2724–2735, https://doi.org/10.1002/2016jb013653 (2017).
[10]D. J. Weidner, Y. Wang, and M. T. Vaughan, Science **266**, 419–422 (1994).
[11]D. J. Weidner, Y. B. Wang, G. L. Chen, J. Ando, and M. T. Vaughan, in *Properties of Earth and Planetary Materials at High Pressure and Temperature*, edited by M. H. Manghnani and T. Yagi (American Geophysical Union, 1998), Vol. 101, pp. 473–482.