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Elastic Properties of Glassy Baltic Amber under High-Pressure: Ultrasonic Measurement using Paris–Edinburgh Press

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1. Introduction

Amber is a unique example of a fragile glass that has been extensively aged below its glass transition temperature, thus reaching a state that is not accessible under normal experimental conditions. Recently, the medium range order (MRO) of Baltic amber was studied by x-ray diffraction (XRD) at high pressures. [1)] The pressure dependences of the low-angle XRD intensity between 0 and 5 Å^{-1} were measured to study the MRO from 0 to 7.3 GPa by the energy dispersive XRD. The first diffraction peak at 1.1 Å^{-1} and ambient pressure has a doublet structure consisting of the first sharp diffraction peak (FSDP) at 1.05 Å^{-1} and the second feature at 1.40 Å^{-1}. The peak position and the width of the FSDP increase as the pressure increases, while the intensity of the FSDP decreases. Below P_0=2.4 GPa, the rapid increase of the FSDP peak position was observed, while above P_0 the gradual increase was observed. Below P_0 voids and holes in a relatively low-density state are suppressed, whereas above P_0 the suppression becomes mild. Such a change suggests the crossover from the low-density to high-density states at P_0. There will be a close correlation between the pressure dependence between the XRD and elastic properties. In the present paper, the ultrasonic measurement of Baltic amber under high-pressure is reported from the ambient pressure to 7.3 GPa at room temperature.

2. Experimental method

Baltic Amber is a fossil pine resin of the Eocene Period and is about 40 million years old. The Baltic amber imported from Lithuania was purchased from Planey Co., Ltd., Japan, and used without any thermal treatment.

The Paris–Edinburgh press has been installed at station 16-BM-B (HPCAT) of the Advanced Photon Source, Argonne National Laboratory. Both synchrotron x-ray diffraction (XRD) and ultrasonic measurements were carried out up to 7.3 GPa using cupped anvils with a 3 mm diameter flattened bottom.[2)] We attached the ultrasonic transducer to opposite ends of the top WC anvil and the co-axial cable was connected through a hole at the top of the PE press.

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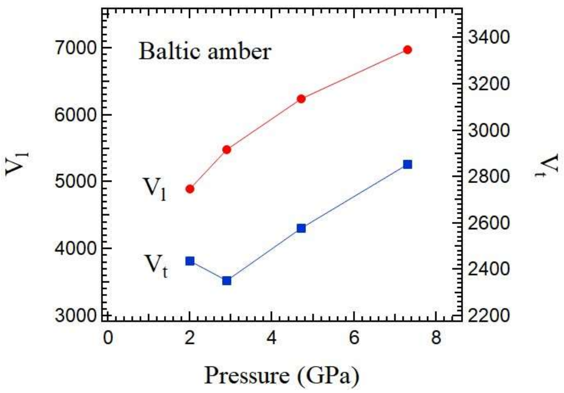

Fig. 1 The pressure dependence of transverse sound velocity V_t and longitudinal sound velocity V_l.

The pulse-echo method is the most accurate measurement in the ultrasonic methods to determine sound velocities.[3)] A 10° Y-cut $LiNbO_3$ piezoelectric transducer was used to generate and detect transverse and longitudinal acoustic waves. Electrical sine waves of 20 MHz for transverse waves and 30 MHz for longitudinal waves were generated by a pulse generator. Acoustic waves generated by the $LiNbO_3$ transducer passed through the WC anvil and propagated into the Al_2O_3 buffer rod and the sample. A series of reflected acoustic wave pulses came from the interfaces of anvil/buffer rod, buffer rod/sample, and sample/backing reflector. The travel distance of the acoustic waves, corresponding to the sample length, was determined by x-ray radiography. It is important to accurately determine the group velocities of TA and LA modes based on the measured travel time in the sample.

3. Results and discussions

The observed transverse sound velocity V_t and the longitudinal sound velocity V_l of Baltic amber are plotted as a function of pressure up to 7.3 GPa as shown in Fig. 1. The magnitude of the elastic moduli is governed by both the atomic bond energy and the atomic packing density, while the Poisson's ratio is related to the degree of symmetry of the structural units existing at the molecular scale.[3] The Poisson's ratio σ is also calculated by the following equation using observed values of transverse and longitudinal velocities.

$$\sigma = \frac{V_l^2 - 2V_t^2}{2(V_l^2 - V_t^2)} \quad (1)$$

The pressure dependence of Poisson's ratio is shown in Fig. 2. The previous result of Brillouin scattering is also plotted for the comparison. These results are in good agreement with those determined

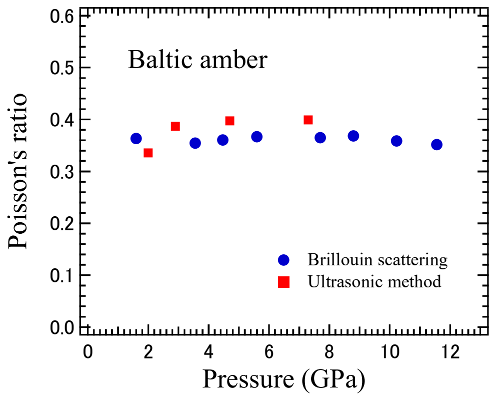

Fig. 2 The pressure dependence of Poisson's ratio determined by Brillouin scattering (solid circle)[6,7] and the ultrasonic method (solid square). with different histological characteristics.

by Brillouin scattering spectroscopy in the GHz range within the experimental uncertainty[4-7]. It is found that its pressure dependence is small as shown in Fig. 2. The pressure dependences of Poisson's ratio of several kinds of polymers are also very small and the values are close to that of Baltic amber.[7] Such a small pressure dependence of the Poisson's ratio was also observed in glass-forming glycerol.[8]

In the energy-dispersive XRD study under high-pressure, it was recently reported that the ratio of the diffraction intensities of the first and second peaks of Baltic amber shows the change at 2.4 GPa as shown in Fig. 3.[1] This crossover is related to the transition from the low-density to the high-density states, which was observed in silica glass, amorphous GaSb, and amorphous ice. To confirm such anomaly the detailed pressure dependence of sound velocity is necessary.

4. Conclusions

Amber is a unique example of a fragile glass that has been extensively aged below its glass transition temperature, thus reaching a state that is not accessible under normal experimental conditions.

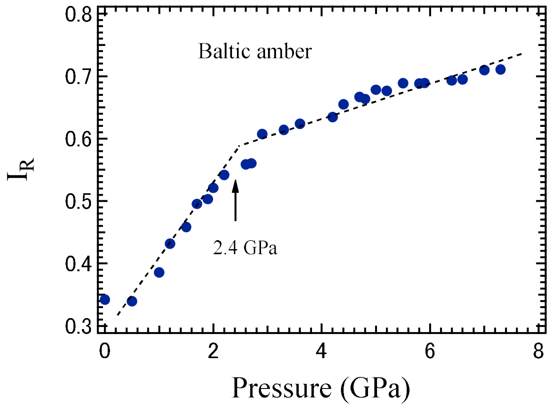

Fig. 3 The pressure dependence of the ratio $I_R = I_2/I_1$, where I_1 and I_2 are the peak intensity of first and second diffraction peaks. The change of slope of I_R occurs at about 2.4 GPa[1].

Recently, the low-density to high- density transition of Baltic amber was observed by XRD at high pressures.[1] To confirm this transition, the pressure dependence of transverse and longitudinal velocities of Baltic amber were measured by the ultrasonic pulse-echo method using the Paris-Edinburgh press at room temperature. The transverse sound velocity V_t and the longitudinal sound velocity V_l of Baltic amber were accurately determined as a function of pressure up to 7.3 GPa. The pressure dependence of Poisson's ratio is also determined. It is found that its pressure dependence is small. Such a nature may be common in polymer glasses.

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