Brillouin Scattering and Elastic Constants of Tetragonal Pentaerythritol

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The Brillouin scattering from tetragonal pentaerythritol crystals was measured by using a helium–neon laser and a pressure-scanned Fabry-Perot interferometer. The Brillouin components from the longitudinal acoustic mode and the transverse acoustic mode polarized parallel to the scattering plane were observed for various crystal directions with the scattering vector in the (001) and (010) planes. From the observed Brillouin shifts, the frequencies and velocities of sound waves with the wavelength of 290 nm were obtained, and the elastic constants were determined, in units of 10^{11} dyn/cm^2, as $C_{11}=3.94\pm0.01$, $C_{13}=0.76\pm0.03$, $C_{16}=0.00\pm0.05$, $C_{33}=1.33\pm0.02$, $C_{44}=0.44\pm0.03$, and $2C_{66}+C_{12}=5.13\pm0.03$. The present hypersonic values of the elastic constants were compared with previous values by the ultrasonic technique.

Brillouin scattering is one of the experimental techniques for determining elastic constants of solid materials. This method has become particularly useful since the development of lasers as monochromatic light sources and of high-resolution interferometers. In Brillouin-scattering measurements, velocities of thermally excited sound waves are observed and accordingly no external acoustic excitation is necessary. Furthermore, only one crystal specimen suffices for determining elastic constants, unlike the ultrasonic technique which generally requires many crystal specimens with particular faces.

In our previous study,[1] the Brillouin scattering from a cubic crystal of potassium bromide was measured and the three elastic constants were determined. The Brillouin measurement was extended, in the present study, to a molecular crystal of tetragonal pentaerythritol $C(CH_2OH)_4$, and the elastic constants were compared with previous results of an ultrasonic study on this crystal.[2]

Experimental

The experimental arrangement for the observation of Brillouin scattering was essentially the same as that was used in our previous study.[1] The light source was a helium–neon gas laser in the fundamental transverse mode, giving radiation at 632.8 nm with an output of about 50 mW. The light scattered from the sample at 90° away from the incident-beam direction was analyzed by a pressure-scanned Fabry-Perot interferometer. In the present measurements, the incident laser beam was focused by a lens inserted just before the sample, so that the beam in the crystal had an appropriately narrow width which allowed the efficient collection of the scattered light. This light-focusing system is particularly important for measuring Brillouin scattering from small crystal specimens. The spacer between the interferometer etalons had a thickness of 6.075 mm, giving the free spectral range of 24.674 GHz.

Crystal specimens of pentaerythritol were generously supplied to us by Dr. H. Yamada.[3] The crystal with dimensions of $5\times3.5\times2.5$ mm^3 was immersed in liquid anethole, which had nearly the same refractive index as that of pentaerythritol. This technique was found to be useful in reducing a large amount of unwanted light scattered from rough crystal surfaces. The sample was supported by a rotatable holder, the same apparatus that was used in the previous study on potassium bromide,[1] which allowed the crystal to be rotated about an axis perpendicular to the scattering plane. Accordingly, any direction in a crystal plane parallel to the scattering plane could be chosen as the direction of the scattering vector. The Brillouin scattering was measured for the scattering vector in two crystal planes, the (001) and (010) planes. The measurements were made at 23 ± 1°C at least five times for each orientation of the crystal. For certain crystal directions, Brillouin shifts were expected to be larger than the half of the free spectral range with the spacer of ~6 mm. Accordingly, auxiliary measurements were also made with a spacer of the 3 mm thickness so that the free spectral range was made as large as ~50 GHz.

The crystal structure of pentaerythritol at room temperature belongs to the tetragonal system with the space group of S^2_4–$I\bar{4}$.[4] The c axis was readily identified, since the crystal was cleaved very easily perpendicular to this axis. This axis was determined by the X-ray diffraction technique.

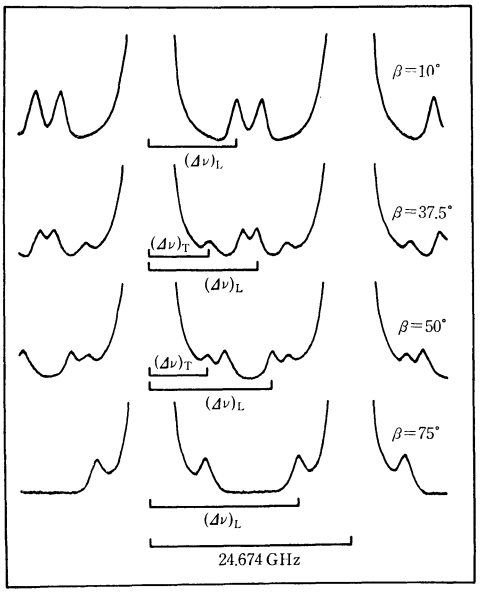

Fig. 1. Brillouin spectra of tetragonal pentaerythritol in Measurement II. $(\Delta\nu)_L$ and $(\Delta\nu)_T$ are the longitudinal and in-plane transverse Brillouin shifts, respectively.

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TABLE 1. FREQUENCIES AND VELOCITIES OF SOUND WAVES AS A FUNCTION OF PROPAGATION DIRECTION IN THE (001) PLANE IN TETRAGONAL PENTAERYTHRITOL (MEASUREMENT I)

Angle α[a] (deg)	Longitudinal mode	
	Frequency[b] (GHz)	Velocity[b] (km/s)
0	17.860(14)	5.289(4)
5	17.939(15)	5.313(4)
10	18.114(12)	5.365(3)
15	18.309(15)	5.423(5)
20	18.512(12)	5.482(3)
25	18.718(12)	5.544(3)
30	18.898(19)	5.597(5)
35	19.051(21)	5.642(6)
40	19.181(22)	5.681(7)
45	19.233(14)	5.696(4)

a) Angle between the scattering vector and the [100] direction in the (001) plane. The experimental error in α was estimated to be $\pm 1°$. b) The experimental error is given in parentheses for the last digits.

TABLE 2. FREQUENCIES AND VELOCITIES OF SOUND WAVES AS A FUNCTION OF PROPAGATION DIRECTION IN THE (010) PLANE IN TETRAGONAL PENTAERYTHRITOL (MEASUREMENT II)

Angle β[a] (deg)	Longitudinal mode		Transverse mode	
	Frequency[b] (GHz)	Velocity[b] (km/s)	Frequency[b] (GHz)	Velocity[b] (km/s)
0	10.738(15)	3.092(4)		
5	10.773(08)	3.103(2)		
10	10.855(10)	3.126(3)		
15	10.954(17)	3.155(5)		
20	11.222(13)	3.232(4)		
22.5	11.437(22)	3.294(6)		
25	11.716(20)	3.374(6)		
27.5			7.550(07)	2.174(2)
30			7.617(06)	2.194(2)
32.5			7.662(11)	2.207(3)
35			7.726(20)	2.225(6)
37.5	13.209(13)	3.804(4)	7.665(08)	2.208(2)
40	13.652(11)	3.932(3)	7.613(09)	2.193(3)
45	14.460(14)	4.165(4)	7.529(24)	2.168(7)
50	15.239(06)	4.389(2)	7.335(25)	2.112(7)
55	15.898(23)	4.579(7)	7.188(15)	2.070(4)
60	16.663(20)	4.799(6)		
65	17.259(11)	4.971(3)		
70	17.682(14)	5.092(4)		
75	17.967(08)	5.174(2)		
80	18.193(12)	5.240(4)		
85	18.309(08)	5.273(2)		
90	18.368(11)	5.290(3)		

a) Angle between the scattering vector and the [001] direction in the (010) plane. The experimental error in β was estimated to be $\pm 1°$. b) The experimental error is given in parentheses for the last digits.

Some typical examples of the observed Brillouin spectra are shown in Fig. 1, and the observed frequency shifts and sound velocities are listed in Tables 1 and 2.

Analysis of Brillouin Spectra

The frequency shift in Brillouin scattering, $\Delta\nu$, is related to the velocity of elastic waves in the medium, v, by[5]

$$\Delta\nu/\nu_i = \pm(v/c)(n_i^2+n_s^2-2n_in_s\cos\theta)^{1/2}, \quad (1)$$

where ν_i is the frequency of the incident light wave, c is the velocity of light in vacuum, n_i and n_s are the refractive indices of the medium for the incident and scattered directions, and θ is the angle of scattering. In a crystal, there are three modes of elastic waves, one longitudinal and two transverse modes, propagating with different velocities.[6] Accordingly, observation of three pairs of Brillouin components with different frequency shifts is expected for any crystal, unless double refraction is taken into account. However, the Brillouin scattering from one of the transverse modes polarized perpendicular to the scattering plane (out-of-plane transverse mode) is usually not observable, since this mode gives in general much weaker Brillouin intensities than the longitudinal mode or the other transverse mode polarized parallel to the scattering plane (in-plane transverse mode). The longitudinal and in-plane transverse modes are mixed with each other for general crystal directions.

The tetragonal pentaerythritol crystal is uniaxial, and accordingly has the optical property of double refraction. In uniaxial crystals, two refractive indices of n' and n'' for ordinary and extraordinary rays, respectively, are related, by the following equations, to the principal refractive indices of $n_a=n_b$ and n_c, where the suffixes represent the principal crystal axes,

$$n' = n_a \quad (2)$$

and

$$n'' = n_an_c/(n_a^2\sin^2\phi+n_c^2\cos^2\phi)^{1/2}, \quad (3)$$

where ϕ is the angle between the c axis and the direction of the wave vector of light. In the present measurements, the Brillouin scattering was observed for the scattering vector in the (001) plane (Measurement I) and the (010) plane (Measurement II). Since the crystal was rotated about an axis perpendicular to the scattering plane, the incident and scattered lights were also in the (001) plane or the (010) plane. For Measurement I, $\phi=90°$ for both incident and scattered lights, and accordingly the refractive indices of the ordinary and extraordinary rays are given by

$$n_i' = n_s' = n_a \quad (4)$$

and

$$n_i'' = n_s'' = n_c. \quad (5)$$

For Measurement II,

$$n_i' = n_s' = n_a, \quad (6)$$

$$n_i'' = n_an_c/(n_a^2\sin^2\phi_i+n_c^2\cos^2\phi_i)^{1/2}, \quad (7)$$

and

$$n_s'' = n_an_c/(n_a^2\sin^2\phi_s+n_c^2\cos^2\phi_s)^{1/2}. \quad (8)$$

The ordinary and extraordinary rays are polarized lights whose electric vectors are perpendicular and parallel, respectively, to the plane determined by the wave vector of light and the optical axis of the crystal

(c axis in tetragonal crystals). Hence, it may be more convenient to give the refractive indices according to the polarization of the incident and scattered lights. The refractive indices for the incident light with the vertical (V) and horizontal (H) electric vectors and for the scattered light with the vertical (v) and horizontal (h) electric vectors (the scattering plane being horizontal) are given by; for Measurement I

$$n_V = n_v = n_c \text{ (extraordinary ray)} \tag{9}$$

and

$$n_H = n_h = n_a; \text{ (ordinary ray)} \tag{10}$$

and for Measurement II

$$n_V = n_v = n_a, \text{ (ordinary ray)} \tag{11}$$

$$n_H = n_a n_c/(n_a^2 \sin^2\phi_i + n_c^2 \cos^2\phi_i)^{1/2}, \text{ (extraordinary ray)} \tag{12}$$

and

$$n_h = n_a n_c/(n_a^2 \sin^2\phi_s + n_c^2 \cos^2\phi_s)^{1/2}. \text{ (extraordinary ray)} \tag{13}$$

The Brillouin measurements were attempted in the present study with the incident laser beam with vertical (V) and horizontal (H) electric vectors. The vertically polarized light gave a pair of Brillouin components in Measurements I and II, with an additional pair for certain crystal directions in Measurement II, but the horizontally polarized light gave no detectable Brillouin components. The Brillouin spectra reported here are, accordingly, those observed by the incident light with a vertical polarization (V). The polarization of the observed scattered light was found to be vertical (v). Hence, the refractive indices for Measurement I are $n_V=n_v=n_c$, and for Measurement II, $n_V=n_v=n_a$. Equation (1) is now reduced, under the present experimental condition, to the following equations; for Measurement I

$$\Delta\nu/\nu_i = \pm 2(v/c)n_c \sin(\theta/2), \tag{14}$$

and for Measurement II

$$\Delta\nu/\nu_i = \pm 2(v/c)n_a \sin(\theta/2). \tag{15}$$

The refractive-index values of $n_a=1.5537$ and $n_c=1.5109$ (for 659 nm)[7] were used in the present analysis of Brillouin spectra of tetragonal pentaerythritol. From the polarization of the incident and scattered lights and the intensities, the observed Brillouin components were assigned to the acoustic mode almost entirely longitudinal with admixture of the transverse mode. The additional weaker components observed in Measurement II were assigned to the mode primarily in-plane transverse mixed with the longitudinal mode. The polarization of the acoustic waves were confirmed by examining eigenvectors of the Christoffel-equation matrix as will be mentioned later.

Since the Brillouin-scattering measurements were made for the scattering angle $\theta=90°$, the wavelength of the scattering sound wave, λ_s, is given by; for Measurement I

$$\lambda_s = \lambda_i/(\sqrt{2}\,n_c), \tag{16}$$

and for Measurement II

$$\lambda_s = \lambda_i/(\sqrt{2}\,n_a), \tag{17}$$

where λ_i is the wavelength of the incident light in a vacuum. By substituting $\lambda_i=632.8$ nm for a helium–neon laser, the wavelength of the sound wave is obtained as $\lambda_s=296.2$ nm for Measurement I and $\lambda_s=288.0$ nm for Measurement II.

The crystallographic a axis was determined by the X-ray diffraction technique with experimental error less than $\pm1°$. The observed sound velocities were obtained by Eqs. (14) and (15), and are listed in Tables 1 and 2. The direction of the scattering vector, which is equivalent to the propagation direction of the sound wave responsible for Brillouin scattering, is described in Table 1 by the angles α and β for Measurements I and II, respectively. α is the angle between the scattering vector and the [100] direction in the (001) plane, and β is the angle between the scattering vector and the [001] direction in the (010) plane.

Calculation of Elastic Constants

The crystal structure of pentaerythritol at room temperature belongs to the tetragonal system with the space group of S_4^2–$I\bar{4}$.[4] Accordingly, the number of independent elastic constants is reduced to seven; namely $C_{11}=C_{22}$, C_{33}, $C_{44}=C_{55}$, C_{66}, C_{12}, $C_{13}=C_{23}$, and $C_{16}=-C_{26}$ (other elastic constants vanish by symmetry). Hence, the Christoffel equation,[8] which relates the elastic constants and elastic-wave velocities, v, is given for this crystal by

$$\begin{vmatrix} \lambda_{11}-\rho v^2 & \lambda_{12} & \lambda_{13} \\ \lambda_{12} & \lambda_{22}-\rho v^2 & \lambda_{23} \\ \lambda_{13} & \lambda_{23} & \lambda_{33}-\rho v^2 \end{vmatrix} = 0, \tag{18}$$

where $\lambda_{11}=l^2C_{11}+m^2C_{66}+n^2C_{44}+2lmC_{16}$, $\lambda_{22}=l^2C_{66}+m^2C_{11}+n^2C_{44}-2lmC_{16}$, $\lambda_{33}=(l^2+m^2)C_{44}+n^2C_{33}$, $\lambda_{12}=(l^2-m^2)C_{16}+lm(C_{66}+C_{12})$, $\lambda_{13}=nl(C_{44}+C_{13})$, $\lambda_{23}=mn(C_{44}+C_{13})$, l, m, and n are the direction cosines of the propagation direction of the sound waves, and ρ is the mass density. It is more convenient to express λ's in terms of the angle α or β. For Measurement I ($l=\cos\alpha$, $m=\sin\alpha$, and $n=0$), $\lambda_{11}=C_{11}\cos^2\alpha+C_{66}\sin^2\alpha+2C_{16}\cos\alpha\sin\alpha$, $\lambda_{22}=C_{11}\sin^2\alpha+C_{66}\cos^2\alpha-2C_{16}\cos\alpha\sin\alpha$, $\lambda_{33}=C_{44}$, $\lambda_{12}=(C_{12}+C_{66})\cos\alpha\sin\alpha+C_{16}(\cos^2\alpha-\sin^2\alpha)$, and $\lambda_{13}=\lambda_{23}=0$, and for Measurement II ($l=\sin\beta$, $m=0$ and $n=\cos\beta$), $\lambda_{11}=C_{11}\sin^2\beta+C_{44}\cos^2\beta$, $\lambda_{22}=C_{66}\sin^2\beta+C_{44}\cos^2\beta$, $\lambda_{33}=C_{33}\cos^2\beta+C_{44}\sin^2\beta$, $\lambda_{12}=C_{16}\sin^2\beta$, $\lambda_{13}=(C_{44}+C_{13})\cos\beta\sin\beta$, and $\lambda_{23}=0$.

Table 3. Elastic constants of tetragonal pentaerythritol at room temperature, in units of 10^{11} dyn/cm^2

	Ultrasonic[a]	Present study (Brillouin scattering)
C_{11}	4.05±0.04	3.94±0.01
C_{12}	2.66±0.21	...
C_{13}	1.05±0.03	0.76±0.03
C_{16}	0.31±0.24	0.00±0.05
C_{33}	1.39±0.01	1.33±0.02
C_{44}	0.274±0.003	0.44±0.03
C_{66}	0.252±0.003	...
$2C_{66}+C_{12}$	3.16±0.22	5.13±0.03

a) Ref. 2.

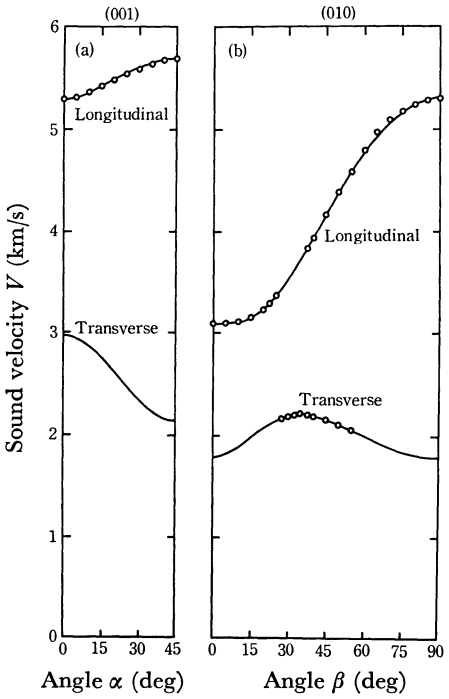

Fig. 2. Sound velocity of the longitudinal and in-plane transverse modes in tetragonal pentaerythritol, in Measurement I (a) and Measurement II (b). The sound velocity of the in-plane transverse mode in Measurement I was calculated by assuming $C_{12}=2.66\times10^{11}$ and $C_{66}=1.24\times10^{11}$ dyn/cm^2. ○: observed value; ——: calculated value.

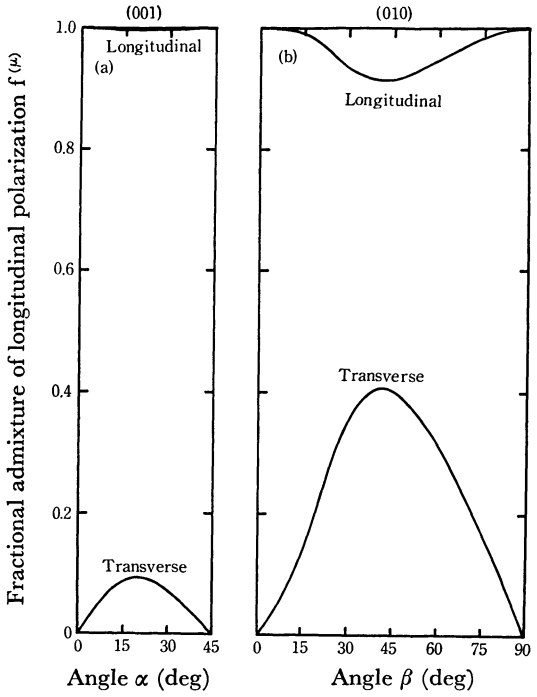

Fig. 3. Fractional admixture of longitudinal polarization for the longitudinal and in-plane transverse modes in tetragonal pentaerythritol, in Measurement I (a) and Measurement II (b).

The elastic constants of tetragonal pentaerythritol were determined, by solving Eq. (18), from 38 observed values for the sound velocity by the least-squares method. The mass density[2] of $\rho=1.398$ g/cm^3 was used in the calculations. In the least-squares adjustment of the elastic constants, the values of C_{12} and C_{66} were hardly settled, but a combination of $2C_{66}+C_{12}$ was determined fairly accurately. The determined values of the elastic constants are listed in Table 3, in comparison with values obtained previously by the ultrasonic technique.[2] The observed and calculated sound velocities are shown in Fig. 2. Figure 3 shows the fractional admixture of longitudinal polarization $f^{(\mu)}$ for the longitudinal and in-plane transverse modes, defined by

$$f^{(\mu)} = \boldsymbol{e}_{\mathrm{pol}}^{(\mu)}\cdot\boldsymbol{e}_{\mathrm{prop}}, \tag{19}$$

where μ is an index for the acoustic modes, $\boldsymbol{e}_{\mathrm{pol}}^{(\mu)}$ is a unit vector in the polarization direction of the mode μ of the sound wave [corresponding to the eigenvector of Eq. (18) for the mode μ], and $\boldsymbol{e}_{\mathrm{prop}}$ is a unit vector in the propagation direction of the sound wave [corresponding to the direction cosines l, m, and n appearing in Eq. (18)].

Discussion

The elastic constants of tetragonal pentaerythritol determined in the present study may be compared with values obtained by the ultrasonic pulse technique with a frequency of 5 MHz.[2] The Brillouin values of C_{11} and C_{33} are in excellent agreement with the ultrasonic values. Also, the agreement for C_{13} and C_{44} is almost satisfactory, considering experimental errors involved. The discrepancy in values of elastic constants may also be attributable in part to the dispersion of the sound velocities for the hypersonic and ultrasonic regions. However, the Brillouin value of $2C_{66}+C_{12}$ is much larger than the ultrasonic value. Indeterminacy of separate values for C_{12} and C_{66} in the present study does not allow further discussion on this discrepancy. The C_{11} value of pentaerythritol (3.9×10^{11} dyn/cm^2) is very close to the values of the corresponding constant for alkali halides [$(3—4)\times10^{11}$ dyn/cm^2].[1,9] The intermolecular hydrogen bonds formed in planes parallel to the (001) plane are, at least in part, responsible for the C_{11} value comparable to those of ionic crystals.

In the present study, the longitudinal Brillouin components were observed in both Measurements I and II, but the in-plane transverse components were observed only for $\beta=27.5—55°$ in Measurement II. It is evident from Fig. 3 that the appreciable mixing with the longitudinal mode allowed the observation of the transverse Brillouin components for these crystal directions. On the contrary, in Measurement I, the mixing is too small to enhance the transverse Brillouin intensities.

In Brillouin-scattering measurements, only one crystal specimen suffices for determining elastic constants, unlike the ultrasonic technique which generally requires many crystal specimens with particular faces. Accordingly, the Brillouin scattering technique is free from experimental errors arising in the process of cutting and polishing crystal specimens. This is one of the

advantages of the Brillouin-scattering method over the ultrasonic method. Also, in the Brillouin scattering, measurements of sound velocities are possible for any desired crystal direction, once the crystallographic axes are determined. However, the Brillouin scattering from the three acoustic modes, one longitudinal and two transverse modes, are generally not all observed in the spectra. This disadvantage is compensated in part by measuring sound velocities of the observable modes for many crystal directions. However, this experimental limitation sometimes makes it difficult to determine all of independent elastic constants. In the present study, separate values for C_{12} and C_{66} could not be determined uniquely because of the lack of experimental sound velocities for the in-plane transverse mode in Measurement I. The present study has nevertheless indicated that the Brillouin-scattering technique, using a laser and a high-resolution interferometer, is useful in determining elastic constants of crystals. So far only a few molecular crystals have been reported,[10-12] whose elastic constants were determined by this method, but it is expected that an increasing number of crystals will be studied by the Brillouin-scattering technique.

Numerical calculations in the present study were carried out with a NEAC 2200-700 computer at the Computer Center of Osaka University. The authors wish to thank Dr. Haruka Yamada of Kwansei Gakuin University for supplying them with crystal specimens of pentaerythritol, and Professor Masao Kakudo and Dr. Nobuo Tanaka of Osaka University for measuring X-ray diffraction of the sample.

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