Determination of elastic, piezoelectric, and dielectric constants of an R : $BaTiO_3$ single crystal by Brillouin scattering*

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From the sound velocity measured using the Brillouin scattering technique, the elastic, piezoelectric, and dielectric constants of a high-quality monodomain tetragonal Rh:$BaTiO_3$ single crystal are determined at room temperature. The elastic constants are in fairly good agreement with those of the $BaTiO_3$ single crystal, measured previously by Brillouin scattering and the low-frequency equivalent circuit methods. However, their electromechanical properties are significantly different. Based on the sound propagation equations and these results, the directional dependence of the compressional modulus and the shear modulus of Rh:$BaTiO_3$ in the (010) plane is investigated. Some properties of sound propagation and electromechanical coupling in the crystal are discussed.

Keywords: Brillouin scattering, elastic and piezoelectric constants, Rh:$BaTiO_3$ single crystal

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1. Introduction

Barium titanate ($BaTiO_3$, or BTO) is one of the most interesting materials due to its large ferroelectric response, high electro–optical coefficient and high nonlinear optical properties.[1,2] In addition, it exhibits a high two-beam coupling gain and self-pumped phase-conjugate reflectivity without the need of applying fields or moving gratings. These results indicate that $BaTiO_3$ is promising for applications in pyroelectric detectors, solid capacitors, nonvolatile memory, displays, surface-acoustic wave devices and nonlinear optical devices.[3,4] For these reasons, much theoretical and experimental research work has been recently performed in order to fully characterize the properties of $BaTiO_3$ as well as its structure. Recently, it was found that the optical and electrical properties of $BaTiO_3$ could be greatly improved when some transition metals with low-level doping are substituted into it.[5−7] For example, excellent nonlinear optical effects and photorefractive properties in Ce-, Er-, and Rh-doped $BaTiO_3$ reach the high values reported, compared with those of $BaTiO_3$ crystals.[6−8] Hence, the substituted $BaTiO_3$ crystals can open up possibilities for its application in different fields, thereby making the substituted $BaTiO_3$ a subject of many experimental and theoretical investigations.[5−10]

The physical properties of most crystals make their parameters dependent on each other. This complete data set of material properties, such as dielectric constants, elastic constants, piezoelectric stress tensor, and so on, will provide not only the necessary input for device design using the domain engineered crystal systems, but also the basis for further theoretical studies on the principle of the domain engineering process.[11] A complete set of elastic, piezoelectric, and dielectric constants could be determined by a hybrid method through combining ultrasonic and resonant techniques.[12] However, this method needs some different oriented samples and thus arises the problem of property variation from sample to sample, in addition, some parameters are sensitive to the measurement frequencies. These variations should be avoided during the experimental measurement. Therefore, it is desirable to undergo a full investigation on the elastic and electromechanical properties of the domain engineered crystals by the high frequency (∼100 GHz) laser Brillouin scattering. Brillouin scattering should

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allow a more complete characterization of crystal elasticity and a novel probe of a crystal with a small size or thin overlayers and superlattices with a typical thickness of a few nanometers.[9,13] Meanwhile, Rh-doped $BaTiO_3$ crystals have also been studied widely because of their excellent photorefractive properties in the near infrared.[6−8] However, to our knowledge, the dielectric, elastic, and piezoelectric properties of Rh:$BaTiO_3$ have not yet been reported. In the present paper, we report on the determination of the complete set of elastic, piezoelectric, and dielectric constants of the Rh:$BaTiO_3$ single crystal by using high-resolution Brillouin scattering in which all experimental data are collected from only one [001]-poled single crystal. In addition, the directional dependence of the compressional modulus and the shear modulus of the crystal in (010) plane is also investigated.

2. Experimental details

The high-quality Rh:$BaTiO_3$ single crystals with a doping concentration of 20 ppm used in the study were grown by the top seed solution method.[14] A crystal sample in the form of a parallelepiped oriented as [100]/[010]/[001] with a size of 4 mm×2 mm×2 mm was selected for the Brillouin scattering measurement. The sample was polished and poled in a dc electric field to obtain a single domain. Brillouin scattering was used to measure the sound velocity and the anisotropic velocity of sound in the crystal. Back scattering, 90° scattering, and platelet geometric configurations were used at room temperature in order to obtain the complete set of elastic, piezoelectric, and dielectric constants from only one crystal sample. A total of 168 sets of phonon velocity, V_q (or Brillouin shift) measurements were made for the longitudinal acoustic (LA) and transverse acoustic (TA) modes in the 85 directions. The excited source for Brillouin scattering was an argon laser of $\lambda = 514.5$ nm at a power of 50 mW. The scattering light was analysed by a six-pass tandem Fabry–Perott interferometer, detected by a photon counting photomultiplier, and output to a multichannel scaler. The free spectrum range (FSR) is 80 GHz. The finesse of the instrument, defined as the ratio of FSR and instrumental width, was approximately 120 at 514.5 nm. In order to observe both the LA and TA phonons, the polarization of scattered light was not analysed in the experiment.

3. Results and discussion

As is well known, when a plane wave propagates in a piezoelectric material, the equation of motion can be expressed as[15,16]

$$\rho V_q^2 u_i = \Gamma_{ijkl} q_j q_l u_k, \tag{1}$$

where V_q is the velocity of the acoustic phonon propagating with wave vector q, which can be determined from the Brillouin scattering frequency shift, u_i is the polarization of the wave, Γ_{ijkl} is piezoelectrically stiffened elastic modulus given by

$$\Gamma_{ijkl} = C_{ijkl}^{\mathrm{E}} + \left[(e_{rij}q_r)\,(e_{skl}q_s) \,/\, (\varepsilon_{mn}^{\mathrm{s}} l_m l_n)\right] C_{ijkl}, \tag{2}$$

and $\rho = 6.07$ g/cm^3 is the density of Rh:$BaTiO_3$. In Eq. (2), C_{ijkl}^{E} is the elastic stiffness modulus in a constant electric field, e_{rij} is the piezoelectric stress constant, and $\varepsilon_{mn}^{\mathrm{s}}$ is the permittivity at constant strain, whereas l_m and l_n are the directional cosines of the wave propagation direction, i.e., the cosines of the angles between the wave propagation direction and the three coordinate axes. For tetragonal Rh:$BaTiO_3$ ($P4mm$), there are a total of 11 independent electroelastic constants: six elastic (C_{ijkl}), three piezoelectric (e_{rij}), and two dielectric constants ($\varepsilon_{mn}^{\mathrm{s}}$) to be determined. They are C_{11}^{E}, C_{33}^{E}, C_{12}^{E}, C_{13}^{E}, C_{44}^{E}, C_{66}^{E}, e_{15}, e_{31}, e_{33}, $\varepsilon_{11}^{\mathrm{s}}$, and $\varepsilon_{33}^{\mathrm{s}}$ in Voigt notation, respectively. In Table 1, we present the wave vectors and mode designations of the phonons used for determining the elastic, piezoelectric, and dielectric constants. The phonon velocity, V_q, is related to the Brillouin shift, $\Delta\upsilon_{\mathrm{B}}$, by the equation

$$V_q = \Delta\upsilon_{\mathrm{B}}/k_q = c\Delta\upsilon_{\mathrm{B}}/2\upsilon_0 n \sin(\theta/2), \tag{3}$$

where υ_0 is the frequency of the incident light, n is the refractive index of the scattering material, k_q is the phonon wave vector involved in the scattering process, and θ is the scattering angle between the incident wave vector and the scattering wave vector.

From Table 1, four elastic constants, i.e., C_{11}^{E}, C_{12}^{E}, C_{44}^{E}, and C_{66}^{E} and a ratio of the square of piezoelectric constant to permittivity, $e_{15}^2/\varepsilon_{11}^{\mathrm{s}}$ can be determined directly by measuring an LA and two TA phonon velocities along [100], [001], and [101] using backscattering and 90° scattering, respectively. In order to obtain the remaining independent constants, Brillouin scattering in the platelet geometry

Table 1. Relationships between acoustic phonon velocities and elastic, piezoelectric, and dielectric constants for the [001] poled Rh:$BaTiO_3$, the direction along which the velocities V_q, are measured under Brillouin scattering geometries ($\rho = 6.07$ g/cm^3).

Directions	Mode	Parameters	Scattering geometries
[100]	LA	$\rho V_q^2 = C_{11}^{\rm E}$	backscattering
	TA1	$\rho V_q^2 = C_{66}^{\rm E}$	backscattering
	TA2	$\rho V_q^2 = C_{44}^{\rm E} + e_{15}^2/\varepsilon_{11}^{\rm s}$	platelet geometry
[001]	LA	$\rho V_q^2 = C_{33}^{\rm E} + e_{33}^2/\varepsilon_{33}^{\rm s}$	backscattering
	TA1	$\rho V_q^2 = C_{44}^{\rm E}$	backscattering
	TA2	$\rho V^2 = C_{44}^{\rm E}$	backscattering
	LA	$\rho V_q^2 = (C_{11}^{\rm E} + C_{12}^{\rm E} + 2C_{66}^{\rm E})/2$	90° scattering
[101]	TA1	$\rho V_q^2 = C_{44}^{\rm E} + e_{15}^2/\varepsilon_{11}^{\rm s}$	90° scattering

was employed to determine velocities within the (010) plane. Based on the equations listed in Ref. [17], the elastic constants, $C_{33}^{\rm E}$ and $C_{13}^{\rm E}$, the ratios of the square of piezoelectric constant to permittivity, $e_{31}^2/\varepsilon_{11}^{\rm s}$ and $e_{33}^2/\varepsilon_{11}^{\rm s}$, and the ratio of permittivities, $\varepsilon_{33}^{\rm s}/\varepsilon_{11}^{\rm s}$ were calculated by combining algebraic computations with a computer-based nonlinear least-squares fitting method. However, the Brillouin frequency shifts measured in (100), (010), and (001) planes of a Rh:$BaTiO_3$ single crystal are used to obtain the data of the phonon velocity and the velocity anisotropy. The complete set of elastic, piezoelectric, and dielectric constants of Rh:$BaTiO_3$ are calculated by nonlinear least-squares fitting based on Eqs. (1) and (2). From the previous results, mechanical resonances of the dielectric constants occur in a frequency range from 100 kHz to a few MHz, and they become constant at a higher frequency. Thus the dielectric constants of Rh:$BaTiO_3$, $\varepsilon_{11}^{\rm s}$ and $\varepsilon_{33}^{\rm s}$, in our high frequency Brillouin scattering are considered to be 1.98×10^{-8} F/m and 5.2×10^{-10} F/m respectively. The elastic constants of the $BaTiO_3$ single crystal are determined by Brillouin scattering in this work in order to compare with that of Rh:$BaTiO_3$. Our data of $BaTiO_3$ are in fairly good agreement with those of the $BaTiO_3$ single crystal measured previously by the low-frequency equivalent circuit methods and Brillouin scattering.[10] All results are listed in Table 2. The errors of determined values of the constants are within about ±5% except for the elastic stiffness moduli, which are indicated in Table 2. Corresponding data of both $BaTiO_3$ and Ce:$BaTiO_3$ are shown in Table 2 for comparison.

It can be seen from Table 2 that the differences in the elastic coefficient between $BaTiO_3$ and Rh:$BaTiO_3$ and between $BaTiO_3$ and Ce:$BaTiO_3$ are negligible. It suggests that the substitution of the Rh ions that occupy the Ti ion sites of $BaTiO_3$ almost has no effect on the $BaTiO_3$ crystal structure. This result accords with that of Raman scattering.[20] However,

Table 2. Elastic coefficients (GPa) and piezoelectric coefficients (cm^{-2}).

	Present Rh:$BaTiO_3$	Ding[9] Ce:$BaTiO_3$	Li[10] $BaTiO_3$	Ishidate[18] $BaTiO_3$	Freir[19] $BaTiO_3$
Elastic stiffiness moduli/GPa					
$C_{11}^{\rm E}$	230 ± 3	227 ± 4	211 ± 6	222.9	275.1
$C_{33}^{\rm E}$	175 ± 5	189 ± 8	160 ± 11	/	164.8
$C_{12}^{\rm E}$	110 ± 2	104 ± 2	107 ± 5	/	178.9
$C_{13}^{\rm E}$	177.5 ± 2	174 ± 3	114 ± 8	147	151.5
$C_{44}^{\rm E}$	58.2 ± 2	54 ± 2	56.2 ±1.7	61.7	54.3
$C_{66}^{\rm E}$	127 ± 5	125 ± 3	127 ± 4	133.7	113.1
Piezoelectric stress constant/(C/m^2)					
e_{15}	33.4± 3	28.3	32.6 ± 2.3	21.3	
e_{31}	−13.45 ± 1	−12.5	−3.88 ± 0.58	−2.69	
e_{33}	6.31 ± 0.67	3.0	5.48±0.82	3.65	
Dielectric constants					
ε_{11}	$1992\varepsilon_0$± 8		$1980\varepsilon_0$ ± 12		
ε_{33}	$52\varepsilon_0$± 4		$48\varepsilon_0$± 9		

the apparent difference in e_{31} between $BaTiO_3$ and Rh:$BaTiO_3$ indicates that Rh-atom doping affects the electronic structure of $BaTiO_3$. The reason why Rh:$BaTiO_3$ has better photorefractive properties than $BaTiO_3$ may be because Rh atoms play an important role as an electron source.

The directional dependences of both the compressional modulus and shear modulus of Rh:$BaTiO_3$ in the (010) plane are calculated and presented in Fig. 1, in which solid lines represent the angular dependences of ρV^2 for different modes calculated from Eq. (1) and Table 2, and circles denote experimentally measured data in the first quadrant. It turns out that the velocities of the compressional mode (LA) change obviously for different propagation directions. On the other hand, the velocities of the first shear mode (TA1) and the second shear mode (TA2) show a strong orientation dependence for all the different propagation directions. The TA1 and TA2 modes represent the shear waves propagating in the (010) plane with particle displacements perpendicular to the plane. The TA1 and TA2 modes each have a maximal velocity in [100] and a minimal velocity in [101], which indicates the presence of a "soft shear acoustic mode" in [101] of the Rh:$BaTiO_3$ single. The anisotropies of the measured elastic, piezoelectric, and dielectric properties are similar to those of both $BaTiO_3$ and Ce:$BaTiO_3$ crystals reported in the literature.[9,10] This soft shear acoustic mode along the [110] direction was also observed in the relaxor-based ferroelectric $Pb(Zn_{1/3}Nb_{2/3})O_3$-4.5%$PbTiO_3$ crystal reported by Yin *et al.*[21]

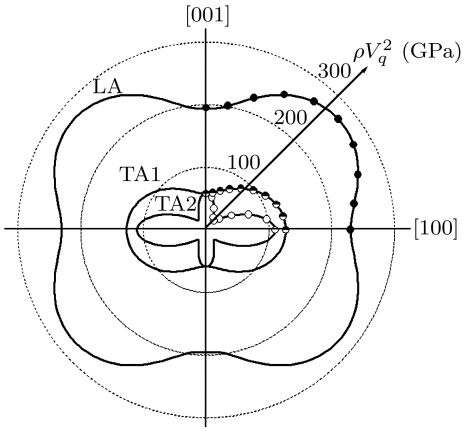


Fig. 1. Compressional modulus $\rho V_{\rm L}^2$ (GPa) including the piezoelectric effect, and shear moduli corresponding to the two transverse modes, $\rho V_{\rm T1}^2$ uncoupled to piezoelectricity and $\rho V_{\rm T2}^2$ (GPa) including the piezoelectric effect in the (010) plane.

To demonstrate the effect of frequency relaxation on the electromechanical property of tetragonal Rh:$BaTiO_3$, values of ρv^2 for two special directions, obtained from different measurement methods, are listed in Table 3. It can be seen that about 22% of compression energy are converted into electrical energy due to electromechanical coupling in the [00l] direction. On the other hand, about 55% of the shear energy is converted into electrical energy for the TA_2 mode in the [100] direction.

Table 3. Comparisons of ρV^2, elastic, and electromechanical constants (GPa).

	$\rho V_{\rm L}^2[100] = C_{33}^{\rm E} + (e_{33}^2/\varepsilon_{33}^{\rm s})$			$\rho V_{\rm T2}^2[100] = C_{44}^{\rm E} + (e_{15}^2/\varepsilon_{11}^{\rm s})$		
	$\rho V_{\rm L}^2$	$C_{33}^{\rm E}$	$e_{33}^2/\varepsilon_{33}^{\rm s}$	$\rho V_{\rm T2}^2$	$C_{44}^{\rm E}$	$e_{15}^2/\varepsilon_{11}^{\rm s}$
Prsent Rh:$BaTiO_3$	196	175	21	114	58	56
Ding *et al.*[9] for Ce:$BaTiO_3$	245	189	56	125	54	71
Li *et al.*[10] for $BaTiO_3$	230	160	70.2	117	56.2	60.8
Shaefer *et al.*[22] for $BaTiO_3$	153.0	147.9	5.1	125.5	54.9	70.6

During the measurement, it was found that the intensities of the acoustic phonon shifts including LA, TA1, and TA2 modes change as the direction of the crystal changes as illustrated in Fig. 2. In the observed spectra, the intensity of the LA mode varies slightly with a change in direction of the crystal, while the TA1 and TA2 modes each show a drastic change in intensity with respect to the direction of the crystal. The intensity of the TA1 mode decreases with the direction of the crystal changing from [001] to [100] whereas the intensity of the TA2 mode increases with the direction of the crystal varying from [001] to [100] and has a maximal value in the [101] direction, then decreases quasi-symmetrically as the direction of the crystal changes from [101] to [100]. The anomalous variations of the intensities in the TA1 and TA2 modes with the direction of the crystal may be associated with the strong anisotropic piezoelectric interaction present in the [001] poled Rh:$BaTiO_3$. The kind of directional dependences determined in this work of the

elastic constant and of the conversion of mechanical energy into electrical energy, as well as the variation of the intensity of the acoustic phonon shifts including LA, TA1, and TA2 modes with the direction of the crystal change have a bearing on the potential application of this material in sensors and other devices.

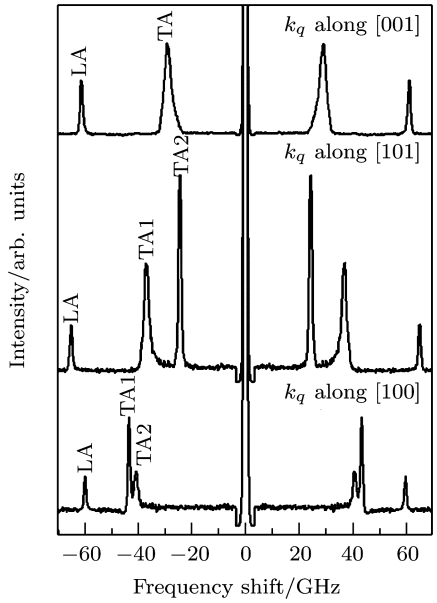


Fig. 2. Brillouin spectra from a Rh:$BaTiO_3$ single crystal in backscattering geometry at $\lambda_0 = 514.5$ nm. The phonon wave vector k_q is along the different directions of the crystal.

4. Conclusion

In the present paper, the complete set of elastic, piezoelectric, and dielectric constants of the [001] poled Rh:$BaTiO_3$ single crystal is determined by Brillouin scattering from only one sample in this work. Based on the sound propagation equations, the directional dependences of both the compressional modulus and the shear modulus of Rh:$BaTiO_3$ in the (010) plane are presented. Some characteristics of sound propagation and electromechanical coupling are also discussed. The directional dependences of the elastic modulus and the conversions of mechanical energy into electrical energy, determined in this work, have a bearing on the potential applications of this material in sensors and other devices.

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