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Determination of elastic, piezoelectric, and dielectric constants of $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.33PbTiO_3$ single crystal by Brillouin scattering

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We report the determination of the complete set of elastic, piezoelectric, and dielectric constants of a $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.33PbTiO_3$ (0.67PMN-0.33PT) single crystal by using Brillouin scattering in which all experimental data were collected from one $[001]_{cub}$-poled crystal sample. The values of determined constants are similar to those previously determined from four crystal samples by using a hybrid method combining both ultrasonic and resonant techniques. The directional dependence of the compressional and shear modulus of the crystal in the (001) plane was investigated. A new weak broad peak appears at the low frequency side (~18 GHz) between 45° and 65° scattering angles and the possible origins of the peak are discussed. © *2007 American Institute of Physics*.
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Relaxor based ferroelectric $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.33PbTiO_3$ (0.67PMN-0.33PT) single crystal exhibits extraordinary large electromechanical coupling and piezoelectric coefficients after being poled along $[001]_{cub}$.[1–4] This domain engineered crystal system has become a promising material in many electromechanical applications.[5,6] It is important to have a complete set of elastic, piezoelectric, and dielectric constants both for practical applications and theoretical investigations. This complete set of material property data not only will provide the necessary input for device design using this crystal system, but also will provide the bases for further theoretical studies on the principles of the domain engineering process. Such a complete set of the constants for the 0.67PMN-0.33PT were recently determined by Zhang *et al.* using a hybrid method combining ultrasonic and resonant techniques,[7] in which though the least number of different oriented samples (one for ultrasonic and three for resonant) are needed to obtain a full set of the constants, it suffers from the problem of property variation from sample to sample and the unreliable geometries in the resonance method. Furthermore, the physical properties of most crystals make their parameters (or constants) dependent on each other and the values of some parameters are sensitive to measuring frequency. Therefore, it is desirable to investigate the elastic and electromechanical properties of the 0.67PMN-0.33PT by using high-frequency (~100 GHz) laser Brillouin scattering, which allows a complete characterization of the elastic and electromechanical properties of a crystal with a small size.[8,9] In this paper, we report the determination of the complete set of elastic, piezoelectric and dielectric constants of the 0.67PMN-0.33PT crystal by using high-resolution Brillouin scattering in which all experimental data were collected from only one $[001]_{cub}$-poled crystal sample. In addition, the directional dependence of the compressional and shear modulus of the crystal in (010) and (001) planes was also investigated.

The 0.67PMN-0.33PT single crystal was grown using a modified Bridgman method. A crystal sample in the form of a parallelepiped oriented as [100]/[010]/[001] with a size of $5\times2\times2$ mm^3 was selected to complete Brillouin scattering measurements. The sample was polished and poled along $[001]_{cub}$ in silicon oil for 5 min under an applied field of 10 kV/cm at 150 °C and then cooled down to room temperature with the applied field. After poling the global macroscopic symmetry of the original rhombohedral crystal sample can be treated as a pseudotetragonal 4mm.[7,10] For the tetragonal symmetry, there are a total of 11 independent electro-elastic constants: six elastic, three piezoelectric, and two dielectric constants to be determined. Brillouin scattering was used to measure the sound velocity and the anisotropic velocity of sound. The light source for Brillouin scattering was an argon laser of $\lambda=514.5$ nm at a power of ~100 mW. Backscattering, 90° scattering, and platelet geometries configurations were used in order to obtain the complete set of elastic, piezoelectric, and dielectric constants from only one crystal sample. The sound velocity V is related to Brillouin scattering frequency shift $\Delta\nu$ through $V=\Delta\nu/q$, where q is the phonon wave vector, $4\pi n/\lambda$, n, and λ are the refractive index of the crystal and the wavelength of laser, respectively. The refractive index of 0.67PMN-0.33PT used in this work, $N=2.54$ ($\lambda=514.5$ nm), was measured by angle of the minimum deviation method.[11] A total of 160 sets of velocity, V, (or Brillouin shift) measurements were made for the longitudinal acoustic (LA) and transverse acoustic (TA) modes in 80 directions. The scattering light was analyzed by a six-pass tandem Fabry-Pérot interferometer (JRS TFP-1) detected by a photon counting photomultiplier, and output to a multi-

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TABLE I. Relationships between acoustic phonon velocities and elastic, piezoelectric and dielectric constants for the $[001]_{cub}$ poled 0.67PMN-0.33PT, the directions along which the velocities, V, were measured and Brillouin scattering geometries ($\rho = 8.093 \times 10^3$ kg/m^3).

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

channel scalar. Based on the sound propagation equations and measured velocity data, the full set of elastic, piezoelectric, and dielectric constants can be determined. A computer-based nonlinear least-squares fitting method was developed in order to accurately obtain the numerical values of elastic, piezoelectric, and dielectric constants and to ascertain their signs.

For the pseudotetragonal 0.67PMN-0.33PT, 11 independent electro-elastic constants 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}, ε_{11}^s, and ε_{33}^s. Table I shows the relationships between the measured parameters, ρV^2 (ρ is the density of 0.67PMN-0.33PT) and the corresponding electro-elastic constants, and the directions along which the velocities were measured and corresponding Brillouin scattering geometries. From Table I, four elastic constants, C_{11}^E, C_{44}^E, C_{66}^E, and C_{12}^E, and one ratio of the square of piezoelectric constant to permittivity, $e_{15}^2/\varepsilon_{11}^s$, can be determined directly by measuring one LA and two TA phonon velocities along [100], [001], and [110] using backscattering and 90° scattering, respectively. In order to obtain the remaining independent constants, Brillouin scattering in the platelet geometry was employed to determine velocities within the (010) plane. Based on the equations listed in Appendix, the elastic constants, C_{33}^E and C_{13}^E, the ratios of the square of piezoelectric constant to permittivity, $e_{31}^2/\varepsilon_{11}^s$ and $e_{33}^2/\varepsilon_{11}^s$, and the ratio of permittivity, $\varepsilon_{33}^s/\varepsilon_{11}^s$, were calculated by combining algebraic computations with a computer-based nonlinear least-squares fitting method. The complete set of elastic, piezoelectric, and dielectric constants measured and derived are shown in Table II. The values of the constants determined in this work are similar to those (in parentheses) previously determined from four samples by a hybrid method combining both ultrasonic and resonant techniques.[7] However, only one crystal sample was needed in this work for the determination of a complete set of the electro-elastic constants by Brillouin scattering. Since the measurements were carried out at high frequencies (~100 GHz), the sensitivity of parameters to measuring frequency is significantly reduced. The error of determined values of the constants is about ±5% except for the elastic stiffness moduli, which are indicated in the Table II.

Figure 1 shows the orientation dependence of the compressional and shear modulus of the 0.67PMN-0.33PT crystal in (001) plane, in which solid lines represent the angular dependence of ρV^2 for different modes calculated from Eq. (A3) in the Appendix and open circles represent experimentally measured data in the first quadrant. It turns out that the velocity of the compressional (or LA) mode changes only slightly for different propagation directions and that the velocity of the first shear (TA1) mode does not change at all for different propagation directions. On the other hand, the velocity of the second shear (TA2) mode shows strong orientation dependence. The TA1 and TA2 modes represent the shear waves propagating in the (001) plane with its particle displacements perpendicular to the plane for the TA1 mode and with its particle displacements in the same plane for the TA2 mode, respectively. The TA2 mode has a maximum velocity in [100] and a minimum velocity in [110], which indicates the presence of a "soft shear acoustic mode" in $[001]_{cub}$ poled 0.67PMN-0.33PT, as previously reported by Zhang *et al.*[7] The anisotropy of the measured elastic, piezoelectric, and dielectric properties are similar to that reported in the literature. This soft shear acoustic mode along [110] was also observed in $Pb(Zn_{1/2}Nb_{2/3})O_3$-4.5%$PbTiO_3$ crystal by Yin *et al.*[12]

During the measurements it was found that the intensity of the acoustic phonon shifts including LA, TA1, and TA2 modes changes as the scattering angle θ changes, as illus-

TABLE II. The elastic, piezoelectric and dielectric constants of the $[001]_{cub}$ poled 0.67PMN-0.33PT single crystal determined by Brillouin scattering.

Elastic stiffness moduli (GPa)

C_{11}^E	C_{33}^E	C_{12}^E	C_{13}^E	C_{44}^E	C_{66}^E
156.7±3%	117.2±5%	146.1±4%	76.4±5%	52.5±3%	29.56±3%
(115±1.5)[a]	(103±3)	(103±1.6)	(103±1.6)	(69±0.5)	(66±0.5)

Piezoelectric stress constant: e (C/m)^2

e_{15}	e_{31}	e_{33}
31.75	–5.31	30.2
(10.1)	(–3.9)	(20.3)

Dielectric constants: ε

ε_{11}^S	ε_{33}^S
4945	1382
(1434)	(680)

[a]The values in parentheses were obtained by Zhang *et al.* using a hybrid method of combining ultrasonic and resonant techniques (Ref. 7).

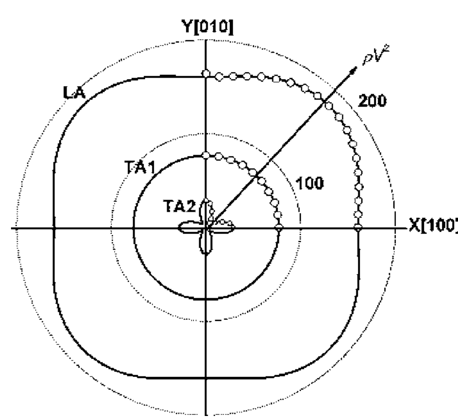

FIG. 1. Measured values of ρV^2 for the compressional (LA) and two shear modes (TA1 and TA2) in the (001) plane of $[001]_{cub}$-poled 0.67PMN-0.33PT.

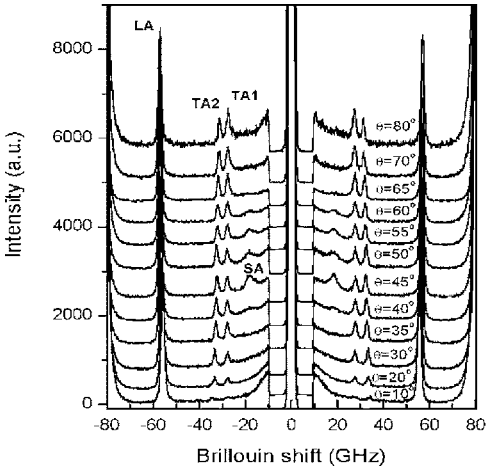

FIG. 2. Brillouin frequency shifts and the intensity of the LA, TA1, and TA2 modes as a function of the scattering angle θ between the phonon wave vector and the c axis for the $[001]_{\mathrm{cub}}$-poled 0.67PMN-0.33PT.

trated in Fig. 2. Among the observed spectra, the TA1 and TA2 modes show a drastic change in intensity with respect to θ. On the other hand, the intensity of the LA mode varies slightly with changing θ. The intensity of the TA1 mode increases with increasing θ whereas the intensity of the TA2 mode has a maximum value at $\theta=50°$ and then decreases quasisymmetrically with respect to θ. The anomalous variation of the intensities in the TA1 and TA2 modes with respect to θ may be associated with the strong anisotropic piezoelectric interaction present in the $[001]_{\mathrm{cub}}$ poled 0.67PMN-0.33PT. In addition, it is noted that a weak broad peak, denoted SA, appears at about 18 GHz in the spectra as the angle θ is near 40°, and the peak has a minimum value in frequency shift and a maximum value in intensity at $\theta=45°$. The new peak may be related to the microheterogeneity of the crystal, to a soft shear wave mode associated with the domain wall motion or to other excitations present in the crystal. Both experimental and theoretical works are needed to elucidate the physical origin of this new peak.

The complete set of elastic, piezoelectric and dielectric constants of $[001]_{\mathrm{cub}}$ poled $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.33PbTiO_3$ single crystal was determined by Brillouin scattering from only one sample in this work. The data obtained are similar to those previously determined from four samples by a hybrid method combining ultrasonic and resonant techniques. The orientation dependence of the compressional and shear modulus of the crystal in (001) plane was investigated. The shear (TA2) mode shows strong orientation dependence of its velocity and has a minimum velocity in [110]. The intensity of TA1 and TA2 modes shows a strong dependence on the scattering angle. A new weak broad peak appears at the low frequency (~18 GHz) side between 40° and 65° scattering angles, and the physical origin of the peak is under investigation.

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APPENDIX

The elastic constants, C_{33}^E and C_{13}^E, the ratios of the square of piezoelectric constant to permittivity, $e_{31}^2/\varepsilon_{11}^s$ and $e_{33}^2/\varepsilon_{11}^s$, and the ratio of permittivity, $\varepsilon_{33}^s/\varepsilon_{11}^s$, can be obtained by measuring the velocities of propagation in the (010) plane along $[h,0,1]$ directions and by calculation using combined algebraic computations with a computer-based nonlinear least-squares fitting method.

In general, for a given direction, there are three velocities, corresponding to three eigenvalues of the secular equation

$$|\Gamma_{i1} - \rho V^2 \delta_{i1}| = 0, \tag{A1}$$

where Γ_{i1} is the piezoelectric-stiffened elastic modulus. In the case of wave propagation in (010) plane $(q//[h,0,1])$

$$q_1 = \cos\theta,\quad q_3 = \sin\theta,\quad q_2 = 0.$$

Here θ is the angle between the wave propagation direction and [100] axis. The secular Eq. (A1) can be written as

$$\begin{pmatrix} \Gamma_{11} - \rho V^2 & 0 & \Gamma_{13} \\ 0 & \Gamma_{22} - \rho V^2 & 0 \\ \Gamma_{13} & 0 & \Gamma_{33} - \rho V^2 \end{pmatrix} = 0, \tag{A2}$$

where

$$\Gamma_{11} = C_{11}^E \cos^2\theta + C_{44}^E \sin^2\theta + (e_{15} + e_{31})^2 \sin^2\theta \cos^2\theta/\varepsilon',$$

$$\Gamma_{22} = C_{66}^E \cos^2\theta + C_{44}^E \sin^2\theta,$$

$$\Gamma_{33} = C_{44}^E \cos^2\theta + C_{33}^E \sin^2\theta + (e_{15}\cos^2\theta + e_{33}\sin^2\theta)^2/\varepsilon',$$

$$\Gamma_{13} = (C_{13}^E + C_{44}^E)\cos\theta\sin\theta + (e_{15} + e_{31}) \times \sin\theta\cos\theta(e_{15}\cos^2\theta + e_{33}\sin^2\theta)/\varepsilon',$$

and

$$\varepsilon' = \varepsilon_{11}^s \cos^2\theta + \varepsilon_{33}^s \sin^2\theta.$$

Equation (A2) gives the following results:

$$\rho V_{T1}^2 = \Gamma_{22} = C_{66}^E \cos^2\theta + C_{44}^E \sin^2\theta,$$

$$\rho V_L^2 + \rho V_{T2}^2 = \Gamma_{11} + \Gamma_{33},$$

$$\rho V_L^2 \rho V_{T2}^2 = \Gamma_{11}\Gamma_{33} - \Gamma_{13}^2. \tag{A3}$$

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