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PRESSURE DEPENDENCE OF THE PIEZOELECTRIC POLARIZATION OF $LiNbO_3$ AND $LiTaO_3$[†]

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Linear and nonlinear hydrostatic piezoelectric constants for lithium niobate and lithium tantalate are determined from measurements of the hydrostatic piezoelectric polarization at pressures from 0.05 GPa to 2.6 GPa. The nonlinear constants are found to be large and relatively easy to detect. In $LiTaO_3$ the nonlinear constant is large enough to reduce the piezoelectric coefficient to zero in the vicinity of 2.2 GPa. The nonlinear constants are interpreted in terms of the pressure dependence of the electrostrictive constants. The linear constant measurements indicate that $LiNbO_3$ should prove useful for a wide variety of piezoelectric stress transducers for impulsive loading measurements.

INTRODUCTION

Since the first piezoelectric impulsive loading measurements[1] by D. A. Keys, a student of J. J. Thomson, in 1921, piezoelectric materials have been widely utilized for impulsive loading measurements. The large piezoelectric constants of lithium niobate, in particular the large hydrostatic piezoelectric effect, make this material attractive for these impulsive loading measurements, especially since it is now commercially available in large single crystal boules. Unfortunately, previous measurements of the piezoelectric constants of lithium niobate have shown large variation among the various investigators. Until reproducible piezoelectric properties can be obtained, it is unlikely that $LiNbO_3$ can be widely employed as a stress transducer material.

Although $LiTaO_3$ is less attractive as a transducer material, a study of the piezoelectric properties is of interest because of the structural similarity with $LiNbO_3$.

We have been interested in impulsive loading measurements in the range from a few tens of MPa to several GPa (a few tenths to several tens of kbar). Under these extreme stress conditions, a gauge is often destroyed in use and provision must be made for "one-shot" operation. If they are to be used in this manner, the piezoelectric elements must exhibit excellent material reproducibility since the gauge cannot be calibrated under the conditions of use. Furthermore, the stresses or pressures encountered may be large enough to invoke nonlinear piezoelectric responses. These nonlinear effects are poorly understood and few data are available to describe nonlinear piezoelectric constants.

This paper reports measurements of the hydrostatic piezoelectric polarization of $LiNbO_3$ and $LiTaO_3$ from 0.05 GPa (0.5 kbar) to 2.6 GPa (26 kbar). The data are used to provide the first direct measurements of the linear hydrostatic piezoelectric constants of these crystals and the first nonlinear hydrostatic piezoelectric constants for any material. The measurements on $LiNbO_3$ were conducted on a number of samples in order to evaluate the sample-to-sample reproducibility of the hydrostatic piezoelectric constants.

EXPERIMENTAL

A direct measurement of the hydrostatic piezoelectric polarization was obtained by placing the samples in a fluid, subjecting the fluid to pressure, and detecting the resulting piezoelectric polarization with a high impedance circuit connected to the sample. A 1 μF capacitor connected to the electrodes of the right circular disc samples provides a long RC time constant and reduces the voltage across the crystal. The voltage on the capacitor was measured with a high input impedance (10^{14} Ω) electrometer.[2]

To keep the leakage resistance across the crystal to within an acceptable range, about 10^{11} Ω, a special high pressure lead through was constructed and the periphery of the sample was coated with a thin layer of epoxy. The observed circuit time constant of 3×10^4 to 3×10^5 s allows for a total experimental duration

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of about 3 x 10^3 s with only a small correction for charge leakage.

The high-pressure apparatus was a modified Bridgman piston-cylinder apparatus in which a 50/50 mixture of pentane and isopentane used as the pressure transmitting fluid remains in the liquid state throughout the pressure range utilized in the experiments.[3] Measurements were taken with both soldered and spring-loaded connections to the samples.

The pressure in the pentane was measured with a 150 Ω Manganin coil which was freely suspended in the pentane. The two piezoresistive Manganin pressure gauges used in the various measurements were calibrated by determining the resistance change from atmospheric pressure to a pressure corresponding to the sharp resistance change of a bismuth sample when the bismuth was *loaded* through the BiI to BiII transition at 2.55 GPa. This single point calibration does not provide sufficient data to determine the nonlinearity of the Manganin gauge. The nonlinear calibration procedure is described in Appendix A.

The recording of each datum point requires about 300 seconds to ensure that thermal equilibrium is established. (The incremental loading time is about 15 to 30 s.) Hence, to fully describe the piezoelectric polarization within the total allowable experiment duration of 3.0 to 3.6 x 10^5 s, two experimental runs were made to characterize each sample. The first run characterized the piezoelectric polarization for pressures between 0.05 GPa and 0.5 GPa in pressure increments of 0.05 GPa. The charge decay was then measured over a 900 s interval to establish the circuit time constant. The pressure was then released, the seals on the piston were replaced, the apparatus was cleaned and the sample was reloaded to 0.5 GPa. The pressure was then increased in 0.1 GPa increments to 1.0 GPa. Above 1.0 GPa, the pressure was increased in 0.2 GPa increments until the maximum pressure was reached. In order to make an accurate correction for charge leakage, the time of each reading and the RC time constant was carefully recorded as above.

Data were obtained at 21 °C from five transducer grade $LiNbO_3$ samples cut from two different boules, one optical grade $LiNbO_3$ sample and two $LiTaO_3$ samples from a single boule, all obtained from Crystal Technology Inc. The samples, 12.5 mm in diameter and 2.5 mm thick, were X-ray oriented to within ±1° of the *z*-axis.

The error introduced by the charge leakage correction depends on the particular experiment, but is estimated to be typically $\pm\frac{1}{2}\%$. The nonlinearity of the Manganin gauge introduces an error of $\pm\frac{1}{2}\%$ and the irreproducibility of the Manganin gauge is estimated to be $\pm\frac{1}{2}\%$. Thus, the total error of measurement is estimated to be less than $\pm 1\frac{1}{2}\%$. The total precision is estimated to be $\pm\frac{1}{2}\%$.

RESULTS

Piezoelectric polarization *versus* pressure data for two transducer grade transducer grade samples from different boules are plotted in Figure 1. The dashed line represents an extrapolation of the linear behavior observed at low pressure while the solid line is a fit to the data. The slope of the polarization-pressure curve is the hydrostatic piezoelectric coefficient. It is observed that the piezoelectric coefficient shows a substantial decrease with increasing pressure. The excellent reproducibility of the data shown in Figure 1 is typical of the various experiments on the five $LiNbO_3$ samples. On one sample, data obtained on unloading showed no hysteretic effects.

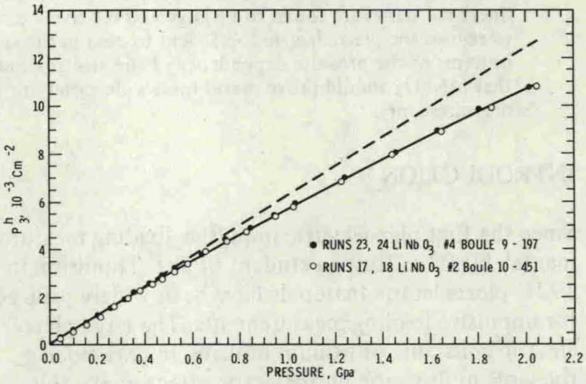

FIGURE 1 The hydrostatic piezoelectric polarization, P^h_3, for lithium niobate determined at various pressures for two samples from two different boules. The dashed line indicates an extrapolation of linear behavior observed at low pressure.

Similar data on two $LiTaO_3$ samples are shown in Figure 2. In this case the linear constant is observed to be only about one-third as large as that for $LiNbO_3$. The nonlinear constant is sufficiently large to reduce the piezoelectric coefficient to zero in the vicinity of 2.2 GPa. Above that pressure the piezoelectric coefficient smoothly changes sign. This is the first material for which a pressure induced sign reversal has been observed.[5]

Extrapolation of the $LiNbO_3$ data to higher pressure indicates that a similar reversal in piezoelectric coefficient would occur in the vicinity of 7.0 GPa.

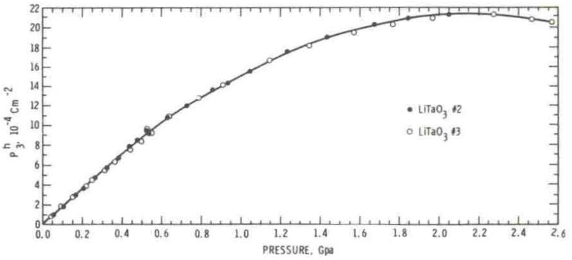

FIGURE 2 The hydrostatic piezoelectric polarization, P_3^h, for lithium tantalate determined at various pressures for two samples. The piezoelectric coefficient, which is the slope of the curve, is observed to decrease to zero in the vicinity of 2.2 GPa. Above that pressure, the coefficient smoothly changes sign.

A fit to the data is obtained from the relation,

$$P_3{}^h = d_h p + \tfrac{1}{2} d_{hh} p^2, \tag{1}$$

where $d_h = \partial P_3{}^h/\partial p$ and $d_{hh} = \partial^2 P_3{}^h/\partial p^2$. The linear constant is the conventional hydrostatic piezoelectric constant. For crystals of symmetry $3m$, $d_h = d_{33} + 2d_{31}$, where d_{33} and d_{31} are conventional[6] linear piezoelectric constants. In Eq. (1), d_{hh} is the nonlinear hydrostatic piezoelectric constant. Like d_h, d_{hh} is a vector property directed along the unique polarization axis of the crystal.

DISCUSSION

A summary of the analytical fits to the data is shown in Table I. We are unable to detect any statistically significant difference between the various samples. The present values differ slightly from our earlier reports[5] because of the nonlinear calibration of the Manganin gauge described in the appendix.

TABLE I

Hydrostatic Piezoelectric Constants

	d_h 10^{-12} CN^{-1}	d_{hh} 10^{-2} CM^{-2} GPA^{-2}	d_{hh}/d_h GPa^{-1}
$LiNbO_3$	6.31 ± 0.014	0.088 ± 0.0005	0.14
$LiTaO_3$	2.00 ± 0.012	0.092 ± 0.0006	0.46

The statistical errors ϵ are computed from the individual standard errors ϵ_i of each measurement from[8]

$$\epsilon = \left[\sum_{i=1}^{N} \frac{1}{\epsilon_i^2}\right]^{-\frac{1}{2}}$$

For $LiNbO_3$: $\epsilon_i \sim 0.6\%$ for d_h and $\sim 5\%$ for d_{hh}. For $LiTaO_3$: $\epsilon_i \sim 0.8\%$ for d_h and $\sim 1.5\%$ for d_{hh}. The range of individual measurements for the d_h of $LiNbO_3$ was ±1.3% and ±14% for d_{hh}. For $LiTaO_3$ the ranges were ±1% and ±2%. Tension is taken as positive.

The observed differences in constants and the magnitude of the errors among all the samples are well accounted for by the errors associated with the measuring instruments. We conclude that the sample-to-sample variation in the linear piezoelectric constants is small compared to the $1\frac{1}{2}\%$ experimental error.

The data for the linear constant of $LiNbO_3$ from various sources, is shown in Table II. The recent work by Smith and Welsh[9] probably represents the most complete work on modern $LiNbO_3$ and $LiTaO_3$.

TABLE II

Linear Hydrostatic Piezoelectric Constants of $LiNbO_3$ and $LiTaO_3$.

	$(d_{33} + 2d_{31})$, 10^{-12} CN^{-1}	
	$LiNbO_3$	$LiTaO_3$
Warner *et al.*[10]	4.0	4.0
Yamada *et al.*[11,15]	14.5	3.2
Chkalova *et al.*[12]	21.5	–
Korolyuk *et al.*[13]	8.8	–
Smith and Welsh[9]	4.3	−0.3
Iwasaki *et al.*[16]	–	3.2
Present work (Table I)	d_h = (6.31 ± 0.014)	(2.00 ± 0.012)

The present d_h value for $LiNbO_3$ differs by about 30% from their value of $d_{33} + 2d_{31}$. This difference is about the same as was observed between the e_{33} constant of these authors and our recent measurement[14] of e_{33}.

The reproducibility of the piezoelectric constants of $LiTaO_3$ has not been investigated in the present work as carefully as for $LiNbO_3$. However, data from $LiTaO_3$ samples are in good agreement with each other. These results may be compared with previous studies in Table II. There is a wide variation among the values reported by the various investigators. (Note that Yamada, *et al.*[15] and Iwasaki, *et al.*[16] report results from the same investigation.)

The large variation in the value of $d_{33} + 2d_{31}$ from previous investigators is principally a result of different values for the d_{33} constant. When the full set of constants determined by the various investigators is examined, there is good agreement on the values for the d_{15} and d_{22} constants. Apparently, the determination of the d_{33} constants is more sensitive to subtle changes in material properties. It is well known that the conventional, but relatively indirect, techniques for determining piezoelectric constants from ultrasonic velocity measurements often involve taking differences in measured quantities of comparable magnitude. The problem of sample inhomogeneity is also somewhat compounded in $LiNbO_3$ and $LiTaO_3$ since the determination of a full set of four piezoelectric constants requires measurements along more crystallographic orientations than for crystals with fewer piezoelectric constants.

In spite of the large variations in certain of the piezoelectric constants of $LiNbO_3$ reported by previous investigators, the present measurements demonstrate that sample-to-sample variations in the hydrostatic piezoelectric constants obtained from one supplier are small. The direct nature of the present measurements, the study of various samples and the good accuracy and precision obtained in the present measurements give confidence that the present values are an accurate determination of the hydrostatic piezoelectric constants.

Most previous work on the effects of pressure on ferroelectric materials has been performed on crystals whose spontaneous polarization, P_s, and Curie temperature are strongly dependent on pressure. In those cases, a reduction of P_s with pressure would lead to a null value for the piezoelectric coefficient when the pressure reduces P_s to zero. This interpretation cannot explain the reversal in sign of the piezoelectric coefficient and is not supported by the magnitude of the observed piezoelectric polarization which is only a few percent of P_s. Furthermore, there is no evidence for a pressure-induced Curie point transition in either of these crystals.

To verify that there are no transitions associated with the 2.2 GPa piezoelectric null, the permittivity of one of the Z-cut $LiTaO_3$ samples was measured with increasing and decreasing pressure to 2.6 GPa. The permittivity showed a small, 2.8% GPa^{-1}, continuous linear decrease with pressure with no change in behavior in the vicinity of 2.2 GPa. Apparently, the observed nonlinear piezoelectric behavior is best accounted for by a consideration of the electrostrictive properties of the crystals at constant P_s.

The electrostrictive interpretation of the data follows the development of Yamada, *et al.*,[15] who determined electrostrictive coefficients for lithium tantalate. The constitutive relation in the paraelectric state is taken to be,

$$S_m = s^P_{mn}T_n + Q_{klm}P_kP_l + R_{ijklm}P_iP_jP_kP_l, \tag{2}$$

where S is the strain, T the stress, P the polarization, Q the lowest order electrostrictive constant and R is a higher order electrostrictive constant. If this relation holds in the ferroelectric state and P_s is large compared to other polarizations, it can be shown that[15] the piezoelectric constants of interest here are given by

$$d_{33} = [Q_{333} + 2R_{33333}P_s^2]\,2\epsilon_0\left(\frac{\epsilon_{33}^T}{\epsilon_0} - 1\right)P_s \tag{3}$$

and

$$d_{31} = [Q_{331} + 2R_{33331}P_s^2]\,2\epsilon_0\left(\frac{\epsilon_{33}^T}{\epsilon_0} - 1\right)P_s. \tag{4}$$

where ϵ_{33}^T is the unclamped permittivity and ϵ_0 is the permittivity of free space. For convenience of notation, let $L_{33} = Q_{333} + 2R_{33333}P_s^2$, $L_{31} = Q_{331} + 2R_{33331}P_s^2$ and $L_h = L_{33} + 2L_{31}$. The hydrostatic piezoelectric constant is then

$$d_h = L_h\epsilon_0\left(\frac{\epsilon_{33}^T}{\epsilon_0} - 1\right)P_s \tag{5}$$

and the pressure derivative is

$$\frac{dd_h}{dp} = \frac{dL_h}{dp}2\epsilon_0P_s\left(\frac{\epsilon_{33}^T}{\epsilon_0} - 1\right) + \frac{dP_s}{dp}L_h2\epsilon_0\left(\frac{\epsilon_{33}^T}{\epsilon_0} - 1\right) + \frac{d\epsilon_{33}^T}{dp}2L_hP_s \tag{6}$$

The measurements of $d\epsilon_{33}/dp$ for $LiTaO_3$ show that this term is small. Furthermore, the measurements of the total piezoelectric polarization to the pressure for the null piezoelectric coefficient place an upper limit on dP_s/dp which is small. Thus the nonlinear constant is determined principally by the pressure dependence of the electrostrictive coefficient, L_h. Since L_h is the sum of two coefficients of opposite sign they may easily act to enhance or cancel one another depending upon the magnitudes and signs of the pressure derivatives.

The present nonlinear piezoelectric constant measurements and those of previous investigations[14,17-20] indicate that nonlinear piezoelectric constants are relatively large and not difficult to detect. Clearly, piezoelectricity should not be viewed as an inherently linear phenomenon.

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Appendix

NONLINEAR PIEZORESISTIVE MANGANIN GAUGE CALIBRATION

Although the piezoresistive behavior of Manganin under hydrostatic pressure is almost linear the nonlinearity in response may be sufficient to cause significant errors for precise experiments. Although the nonlinear behavior would not be expected to be the same for all gauges, in the absence of specific calibration data at multiple fixed pressures it appears reasonable to utilize typical values of nonlinearity obtained by various investigators. The observed range of nonlinear parameters can serve as a measure of the expected uncertainty due to the nonlinear response.

Consider that the pressure is a quadratic function of the relative change in resistance

$$p = a(\Delta R/R_0) + b(\Delta R/R_0)^2, \qquad \text{(A1)}$$

where p is the pressure, ΔR is the change in resistance, R_0 is the original resistance, and "a" and "b" are material constants of the Manganin gauge. For a calibration at a fixed pressure, p_c, the coefficients can be expressed as

$$a = \frac{p_c}{\left(\frac{\Delta R}{R}\right) + \frac{b}{a}\left(\frac{\Delta R}{R}\right)^2} . \qquad \text{(A2)}$$

For fixed b/a, a nonlinear calibration can be established.

Measurements of the nonlinearity in Manganin gauge response have been summarized by R. C. Lincoln.[4] The data are shown in Table A-1.

TABLE A-1

Nonlinearity parameters for Manganin gauges

Source	b/a
Newhall (a)	0.279
Johnson (b)	0.331
Lincoln (c)	0.352
Boren *et al.* (d)	0.600
Zeto *et al.* (e)	0.615
Midpoint between above extremes	0.447

(a) Private communication from D. H. Newhall, Harwood Engineering, to R. C. Lincoln. (b) Private communication from D. P. Johnson, National Bureau of Standards, to R. C. Lincoln. (c) Ref. 4. (d) M. D. Boren, S. E. Babb and G. J. Scott, *Rev. Sci. Instr.* **36**, 1456 (1965). (e) R. J. Zeto and H. B. Van Fleet, *J. Appl. Phys.* **40**, 2227 (1969).

Even though b/a shows a wide range among the various investigators, the actual effect on the predicted pressure is small due to the relatively small values of $\Delta R/R_0$.

We have chosen to use the midpoint, $b/a = 0.447$, between the observed extreme values of 0.279 and 0.615 as a representative value for b/a. For our gauges we found this range of b/a introduced an uncertainty of ±1% in the first pressure derivative of our data. Failure to include a nonlinear effect would have led to bias in the first pressure derivative from 1.3% to 3.8% depending on the gauge. To eliminate this bias it appears best to utilize Eq. (A1) to establish the pressure from the $\Delta R/R_0$ readings.