



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,

$$P_3^h = d_h p + \frac{1}{2} d_{hh} p^2, \quad (1)$$

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 conventional⁶ 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

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 from⁸

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

For LiNbO₃: $\epsilon_i \sim 0.6\%$ for d_h and $\sim 5\%$ for d_{hh} . For LiTaO₃: $\epsilon_i \sim 0.8\%$ for d_h and $\sim 1.5\%$ for d_{hh} . The range of individual measurements for the d_h of LiNbO₃ was $\pm 1.3\%$ and $\pm 14\%$ for d_{hh} . For LiTaO₃ the ranges were $\pm 1\%$ and $\pm 2\%$. Tension is taken as positive.

significant difference between the various samples. The present values differ slightly from our earlier reports⁵ because of the nonlinear calibration of the Manganin gauge described in the appendix.

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 LiNbO₃ from various sources, is shown in Table II. The recent work by Smith and Welsh⁹ probably represents the most complete work on modern LiNbO₃ and LiTaO₃.

TABLE II
Linear Hydrostatic Piezoelectric Constants of LiNbO₃ and LiTaO₃.

	$(d_{33} + 2d_{31}), 10^{-12}$ CN ⁻¹	
	LiNbO ₃	LiTaO ₃
Warner <i>et al.</i> ¹⁰	4.0	4.0
Yamada <i>et al.</i> ^{11,15}	14.5	3.2
Chkalova <i>et al.</i> ¹²	21.5	—
Korolyuk <i>et al.</i> ¹³	8.8	—
Smith and Welsh ⁹	4.3	-0.3
Iwasaki <i>et al.</i> ¹⁶	—	3.2
Present work (Table I)	$d_h = (6.31 \pm 0.014)$	(2.00 ± 0.012)

The present d_h value for LiNbO₃ 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 measurement¹⁴ of e_{33} .

The reproducibility of the piezoelectric constants of LiTaO₃ has not been investigated in the present work as carefully as for LiNbO₃. However, data from LiTaO₃ 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,

$$S_m = s_{mn}^P T_n + Q_{klm} P_k P_l + R_{ijklm} P_i P_j P_k P_l, \quad (2)$$

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 that¹⁵ the piezoelectric constants of interest here are given by

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

and

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

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

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

and the pressure derivative is

$$\begin{aligned} \frac{dd_h}{dp} = & \frac{dL_h}{dp} 2\epsilon_0 P_s \left(\frac{\epsilon_{33}^T}{\epsilon_0} - 1 \right) + \frac{dP_s}{dp} L_h 2\epsilon_0 \left(\frac{\epsilon_{33}^T}{\epsilon_0} - 1 \right) \\ & + \frac{d\epsilon_{33}^T}{dp} 2L_h P_s \end{aligned} \quad (6)$$

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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