GRAH-RA 76-0423

Ferroelectrics
1976, Vol. 10, pp. 65–69

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

R. A. GRAHAM

Sandia Laboratories, Albuquerque, NM 87115, USA

(Received June 9, 1975; in final form September 25, 1975)

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

---

† This work was supported by the U.S. Energy Research and Development Administration, ERDA.

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 $\pm1\frac{1}{2}\%$. 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.

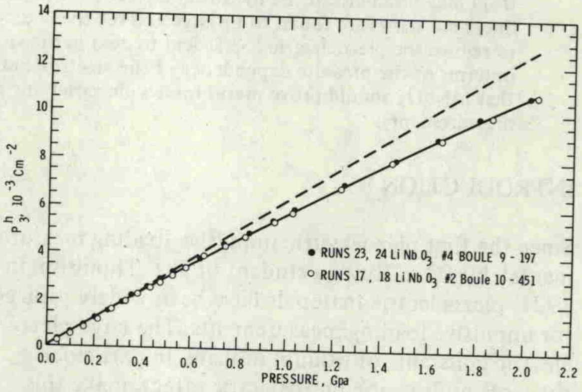

FIGURE 1 The hydrostatic piezoelectric polarization, P^h_3, for lithium niobate determined at various pressures for two samples from two different boules. The dashed line indicates an extrapolation of linear behavior observed at low pressure.

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.