

PRESSURE-INDUCED REVERSAL OF THE SIGN OF THE HYDROSTATIC PIEZOELECTRIC CONSTANT OF LITHIUM TANTALATE*

R.A. Graham

Sandia Laboratories, Albuquerque, New Mexico 87115, U.S.A.

(Received 19 September 1973 by A.A. Maradudin)

Measurements of the piezoelectric polarization of lithium tantalate for hydrostatic pressures up to 26 kbar show that the hydrostatic piezoelectric constant decreases smoothly to zero at a pressure of 22 kbar. Above this pressure the piezoelectric constant smoothly changes sign. This is believed to be the first observation of such an effect.

THE piezoelectric polarization of single-crystal lithium tantalate has been measured for hydrostatic pressures from 1/2 to 26 kbar. The measurements indicate that the hydrostatic piezoelectric constant decreases strongly with increasing pressure, becomes zero in the vicinity of 22 kbar, and smoothly changes sign for higher pressures. The object of this communication is to describe the experimental observation of this unusual effect.

Single-crystal, single-domain disks of Z-cut lithium tantalate were obtained from a commercial source.¹ The disks, 12.5 mm in diameter and 2.54 mm in thickness, were cut with an axial alignment within one degree of the specified axis and had major faces vapor-plated with a chromium-gold film.

Hydrostatic pressure was applied to the sample disks with a movable piston 30 kbar Bridgman high pressure apparatus² which utilizes a 50–50 pentane–isopentane mixture as the pressure transmitting medium. Pressure in the pentane surrounding the sample was measured with a piezoresistive manganin gauge for which an assumed linear calibration was obtained based on the Bi I–II transition at 25.4 kbar.³ Previous studies^{4–6} of manganin in this pressure range indicate that the resistance change

is linear to about 1%.

The piezoelectric polarization at a given pressure was determined from an open circuit voltage measurement on a large, 10^{-6} F, capacitor connected across the sample. The voltage was indicated with a digital electrometer with an input impedance of $10^{14} \Omega$. Leakage resistance of about $10^{11} \Omega$ in the high pressure lead-throughs resulted in a circuit time-constant of about 10^5 sec. The typical experimental durations of about 3×10^3 sec required that a small correction for charge leakage be applied to the data. This correction was based on a time-constant measurement taken under pressure at the end of each experimental 'run'.

Each of the two samples were subjected to two experimental runs, one from 1/2 to 5 kbar and another from 5 kbar to either 20 or 26 kbar. In order to avoid pyroelectric effects accompanying the rapid increase in pressure from point to point, the sample was allowed to come to equilibrium temperature by waiting five minutes before recording the voltage reading.

The data of piezoelectric polarization, P_h , versus hydrostatic pressure, p , are shown in Fig. 1. Data from the two samples indicate excellent sample-to-sample reproducibility. The data show a smoothly decreasing slope with increasing pressure with a maximum in

* This work was supported by the U.S. Atomic Energy Commission.

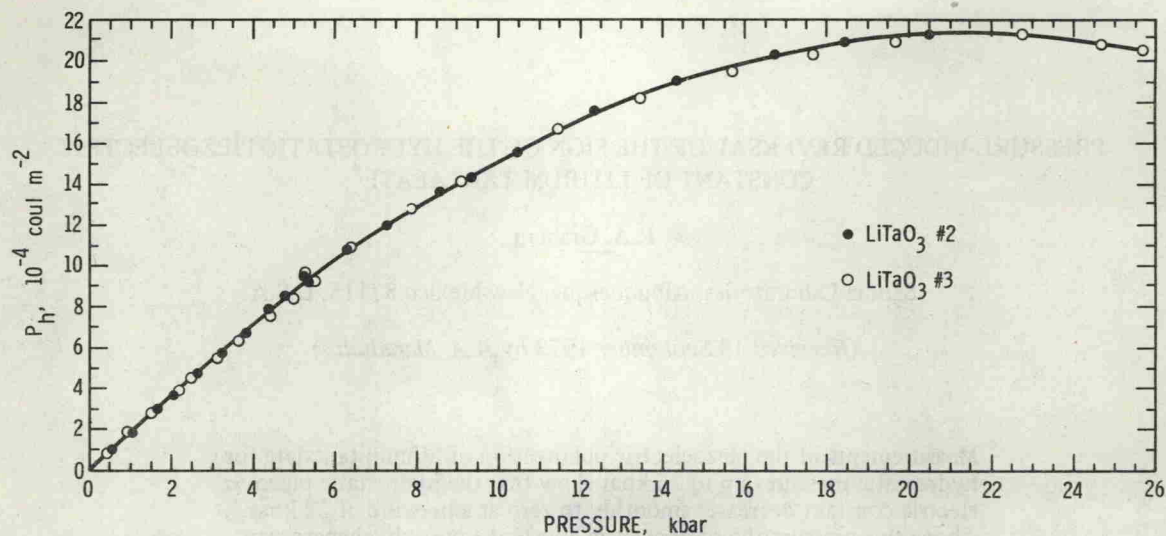


FIG. 1. The piezoelectric polarization, P_h , is shown as a function of hydrostatic pressure. The hydrostatic piezoelectric constant is the local slope of the observed curve. The slope is observed to reach a maximum corresponding to a zero value for the piezoelectric constant at a pressure of 21.6 kbar. At higher pressures the piezoelectric constant is observed to change sign.

polarization and a corresponding zero value for the hydrostatic piezoelectric constant, d_h , in the vicinity of 22 kbar. Above this pressure, d_h smoothly changes sign. The data are fit by the relation $P_h = (1.97 \pm 0.012)p - (0.0456 \pm 0.00049)p^2$ with a standard deviation, $\sigma = 0.148$. The \pm indicates the standard error and the units of P_h are 10^{-4} C m^{-2} and the units of p are kbar. The corresponding linear and non-linear hydrostatic piezoelectric constants are $d_h = (1.97 \pm 0.012) \times 10^{-12} \text{ C N}^{-1}$ and $(1/d_h) d(d_h)/dp = -(0.0463 \pm 0.00047) \text{ kbar}^{-1}$. Based on the measured pressure derivative, the hydrostatic piezoelectric constant becomes zero at $p = 21.6$ kbar.

Because lithium tantalate derives its piezoelectric properties from the ferroelectric character of the unit cell, it is instructive to consider the consequences of the observed zero value of d_h . It is known that lithium tantalate can be accurately represented as a one-dimensional ferroelectric for which the metal ions are displaced along the polar axis.⁷ Furthermore, it has been demonstrated that the polarization of one-dimensional ferroelectrics is strongly dependent upon metal ion displacement.^{8,9} In the one-dimensional model the hydrostatic piezoelectric constant is a consequence of metal ion displacements along the polar axis resulting from pressure along and normal to the polar axis.

In the present experiments, the strain is related to the pressure through the axial and transverse linear compressibilities. Both the linear compressibilities and the corresponding piezoelectric strain constants, d_{33} and $2d_{31}$, may have different dependencies on pressure. Since the pressure derivatives of these coefficients are not known, an unknown combination of pressure-dependent elastic and piezoelectric constants can lead to the zero hydrostatic piezoelectric constant at 22 kbar. Nevertheless, symmetry arguments can be used to demonstrate¹⁰ that a solid must have a polar axis to exhibit a nonzero d_h . It appears that the condition for zero d_h can arise from either a nonpolar structure or a fortuitous condition whereby polarization is not changed by application of pressure.

Although there is insufficient data to connect the macroscopic properties with structural characteristics of the ferroelectric unit cell, it appears that measurements of other related properties of lithium tantalate in the vicinity of 22 kbar could lead to interesting structural conclusions.

Acknowledgements – The author is pleased to acknowledge the excellent technical assistance of R.D. Jacobson.