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Giant enhancement in effective piezoelectric sensitivity by pyroelectric coupling

RODERIC LAKES
Department of Engineering Physics, Engineering Mechanics Program,
Department of Materials Science
University of Wisconsin
541 Engineering Research Building (ERB),
1500 Engineering Drive, Madison, WI 53706-1687
Phone (608) 265-8697, Fax (608) 263-7451,
email lakes@engr.wisc.edu

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Abstract
We report stable two layer composites that exhibit large enhancement of effective piezoelectric sensitivity to more than 20,000 pC/N in the presence of a thermal gradient. They are based on coupled fields in the non-equilibrium presence of energy flux that is modulated by force. Thermal flux is modulated by a granular contact layer so that electric polarization of pyroelectric origin contributes to stress generated electric polarization. Effective piezoelectric sensitivity is enhanced by at least two orders of magnitude and is higher than that of known commercial and research materials. The result illustrates the potential of relaxing the usual assumption of equilibrium in the presence of coupled field to attain extremely high effective properties.

Piezoelectric materials convert electrical signals to mechanical deformation or the reverse. They are used in many applications such as sensors and actuators, microphones, acoustic emitters, and ultrasonic transducers. Piezoelectric ceramics such as lead titanate zirconate are commonly used for such applications. The search for better materials such as relaxor ferroelectrics [1], [2] is driven in part by the expansion of applications of such materials. Piezoelectricity is a kind of coupled field phenomenon. *All* materials exhibit at least one coupled field effect [3] but only materials lacking a center of inversion symmetry can be piezoelectric. Other examples include coupling between mechanical and thermal variables: thermal expansion relates strain to temperature and the piezocaloric effect relates stress to temperature change. Such coupled fields have many ramifications. For example, the difference between adiabatic and isothermal compressibility forms the basis of heat engines and refrigerators. Materials exhibiting coupled field phenomena (fig. 1a) also include piezomagnetic and magnetostrictive [4] solids which couple stress and strain to magnetic field, and thermoelectric [5] solids that couple temperature changes to electric field; also, in fluid-filled porous materials such as rock, deformation is coupled to fluid pressure and flow. The coupling exhibited by such materials forms the basis of sensors, actuators and related devices. Enhancement of such coupling as in magneto-resistive materials [3] and in electro-caloric materials [6] as well as piezoelectric and pyroelectric materials, is consequently pertinent.

In ferroelectric materials that exhibit piezoelectricity and pyroelectricity, stress σ and strain ε are linked to electric field E and electric displacement D as follows [3], with J as material compliance for zero electric field and with k as permittivity, p as pyroelectric sensitivity, α as thermal expansion, T as temperature, and d as piezoelectric sensitivity (a third rank tensor) :

$$\varepsilon = J\,\sigma + d_c\,E + \alpha\,\Delta T \quad (1)$$

$$D = d_d\,\sigma + k\,E + p\,\Delta T \quad (2)$$

The usual equality between for the coefficient d_c for the converse effect and d_d for the direct effect arises from the assumption of equilibrium and the existence of an energy function [3]. The present experiments are done in a non-equilibrium condition in which there is heat flow by design. The effective direct response, which is measured here, is enhanced by modulated coupling as described below but the converse effect is not, so the coefficients are no longer equal.

Composite structure can be used to design materials with enhancement of piezoelectric response as well as other physical properties. For example, layered structures can be analyzed by Voigt type (rule-of-mixtures) and Reuss type equations to determine the effective piezoelectric coefficient of composites [7 8]. While the d_{33} charge coefficient (charge density due to polarization in 3 direction divided by stress in 3 direction) is given by a rule of mixtures, the voltage coefficient g_{33} (open circuit electric field divided by stress) in a laminar composite of piezoelectric and compliant dielectric layers can be substantially greater than that of the piezoelectric constituent alone [9]. Piezoelectric composites [10] with a matrix of negative Poisson's ratio [11] can exhibit enhanced response to hydrostatic pressure. In all these composites, other fields, such as temperature, that are coupled to the electrical and mechanical variables, are assumed to be uniform and constant.

In the present study the restriction of constant uniform temperature is relaxed. Specifically, to achieve extremely high effective values of piezoelectric sensitivity, a thermal gradient is intentionally provided to enable temperature to increase with stress in a two layer composite. One layer is piezoelectric and pyroelectric; the other layer has a stress-dependent thermal conductivity. The applied stress therefore modulates the corresponding flow of heat, fig. 1b. In the experiments described below, this is done with a contact condition [12] in which increased force results in increased contact area; this is best known in the classic Hertz solution for sphere contact but also occurs for all convex shapes. Hence greater heat flux occurs in response to applied force, which causes a temperature change that causes a charge due to pyroelectricity. It could also be done by material piezoresistance [13 14]. The total gradient in temperature is partitioned into a region of thermal conductance that depends on force and a region of constant conductance so that the temperature of a ferroelectric disc hence its pyroelectric charge, is modulated by force. Neither rigid interfaces nor perfect bonds are assumed in the analysis or attempted in the experiments. Large effects are anticipated because ferroelectric ceramics exhibit large pyroelectric charge density response from moderate temperature variations. Specifically, such ceramics have representative piezoelectricity d_{33} =100 pC/N and pyroelectric coefficient p = 1 nC/cm^2 K. So a modulation that gives rise to a 1°C oscillation gives rise to 1000 pC, a charge substantial compared with piezoelectric charge over a 1 cm^2 area.

Experimental demonstration of enhanced stress generated polarization was done as follows. Piezoelectric, ferroelectric discs were subjected to oscillatory force by action of a coil upon a permanent magnet 12 mm in diameter, 3.2 mm thick (fig. 2); calibration was done with an analytical balance. The electric current to the coil was prescribed as a sinusoid from a Stanford Research SRS DS345 function generator; frequencies were well below any natural frequency of the system. Charge upon the piezoelectric disk was measured using a Kistler charge amplifier with time constant appropriate for the frequency used. The force was applied to an electric resistance heating element via a tubular ceramic stalk. Waveforms for force and charge were captured with a Tektronix TDS 420A digital oscilloscope. Modulation of heat flow, hence a pyroelectric contribution to charge that depends on force, was achieved as follows. Tin powder, 100 mesh (0.15 mm diameter), about 0.15 grams, was placed between the heating element and the piezoelectric disk. Tin was used because it has a relatively high thermal conductivity. As force increases, contact thermal resistance decreases, resulting in increased heat flow that gives rise to a force controlled temperature increase, hence a signal of pyroelectric origin that contributes to effective piezoelectric response. Piezoelectric, ferroelectric ceramics used were lead metaniobate, 12 mm diameter, 2.5 mm thick, and a commercial Panametrics ultrasonic transducer (for nondestructive testing) of 10 MHz natural frequency, also 12 mm in diameter. These materials exhibit a pyroelectric effect as well as a piezoelectric effect.

Experimental results shown in fig. 3 disclose the piezoelectric sensitivity of lead metaniobate under isothermal conditions (24°C) to be representative of published values. For the experiments with temperature gradient, the same heater power was used for both. The lead metaniobate top surface was at 70°C, bottom surface upon an aluminum cylinder used as a heat sink was at 35°C. The NDT transducer top was at 90°C; the bottom cannot be compared directly because its piezoelectric disc is part of a structure; nevertheless comparison of its frequency dependence shows a shift to the right corresponding to faster thermal transport in a thinner disc. Effective piezoelectric sensitivity of the two layer composite in the presence of thermal gradient is more than two orders of magnitude. The following analysis of enhancement of stress generated electric polarization and its dependence on time or frequency indeed discloses a strong response at the lower frequencies.

Analysis of enhancement of stress generated electric polarization and its dependence on time or frequency is as follows. To determine the stress generated electric displacement due to modulated heat flow, consider two segments in contact; define $\Phi_1 = kA/L$ with thermal conductivity k, length L, area A. The second segment has a stress dependent thermal conductivity, e.g. by a contact condition; $\Phi_2 = \Phi_2(\sigma)$. The total difference in temperature $(T_2 - T_1)$ is assumed to be constant in time. The heat flow due to a difference in temperature is, with T_b as the temperature at the interface,

$$dQ/dt = \Phi_2(T_2 - T_b) = \Phi_1(T_b - T_1) \tag{3}$$

The transient response to a step input in time is found by relating the flow rate to the heat capacity, $dQ/dT = C_p$, so since $(dQ/dT)(dT/dt) = C_p\, dT/dt$, $C_p dT_b/dt = \Phi_2 T_2 - \Phi_2 T_b - \Phi_1 T_b - \Phi_1 T_1$.

Consider an exponential time dependence with $T_c = T_{b\,final}$

$$T_b(t) = T_c + T_d \exp\{-t/\tau\}. \tag{4}$$

Temperatures and the time constant are

$$T_c = (\Phi_2 T_2 + \Phi_1 T_1) / (\Phi_2 + \Phi_1);\ T_d = T_1 - T_c\,;\ \tau = C_p / (\Phi_2 + \Phi_1).$$

The effective time dependent direct piezoelectric coefficient is $d_d^{eff}(t) = D(t)/\sigma$ so from eq. (2),

$$d_d^{eff}(t) = d + (p/\sigma)\,[T_b(t) - T_1] \tag{5}$$

The temperature $T_b(t)$ depends on stress via the contact condition. The contact condition gives a stress dependent thermal conductivity that for small stress excursions can be linearised, $\Phi_2(\sigma) = f\sigma$. The zero of this time scale is the time at which the load is applied. In the frequency domain, the counterpart to the exponential in time is $\omega^2\tau^2/(1 + \omega^2\tau^2)$, a characteristic that favours a strong response at the lower frequencies as is observed in the experiments. Multiple contacts will give rise to a distribution of exponentials in time or Debye transitions in frequency; that will broaden the frequency response.

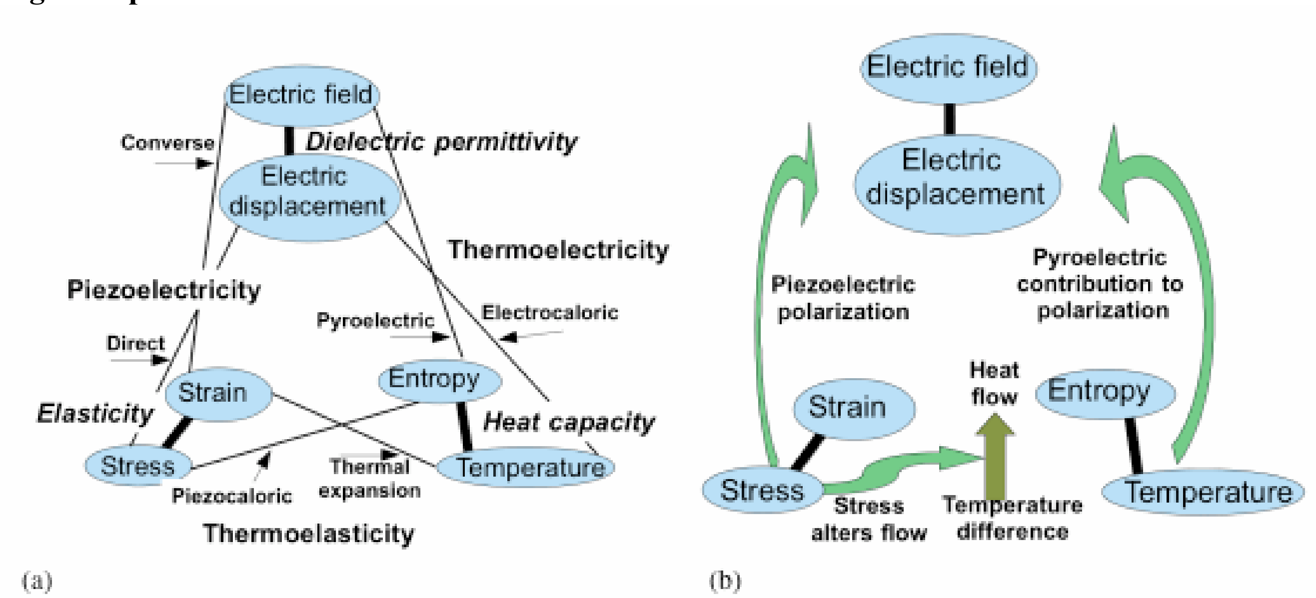
Enhanced stress generated polarization is observed in the presence of a thermal gradient and a stress-sensitive thermal conductivity. The enhancement is at least several orders of magnitude to more than 20,000 pC/N. For comparison [15], the piezoelectric d coefficients of several commonly used materials are d_{11} = 2.3 pC/N for quartz, d_{33} = 190 pC/N for barium titanate ceramic, 85 pC/N for lead metaniobate ceramic, 152 pC/N and 593 pC/N for lead titanate zirconate (PZT) compositions PZT-2 and PZT-5H respectively. The observed sensitivity also substantially exceeds the 2,500 pC/N reported in single crystal relaxor ferroelectrics [2]. Because the presently observed effect depends on thermal diffusion, its rate is limited by thermal time constants. In view of the macroscopic 2.5 mm thickness of the lead metaniobate ferroelectric disc, the frequency scale for strong response is in the sub audio region. A strong response at higher frequencies can be had by scaling down the size scale because the time scale for thermal diffusion is proportional to the *square* of the thickness. Therefore realistic thickness values suffice to attain sonic and ultrasonic frequency response.

The enhanced effective properties depend on a thermal gradient that gives rise to energy flux. Ordinarily one seeks to minimize thermal gradients in experiments because such gradients give rise to measured properties that are an average of temperature dependent properties over the sample. Unintentional gradients do not ordinarily give rise to any extreme or unusual results. In the present experiments, the temperature gradient is provided by design so that modulation of heat flux gives rise to temperature fluctuations that generate giant enhancement of effective properties.

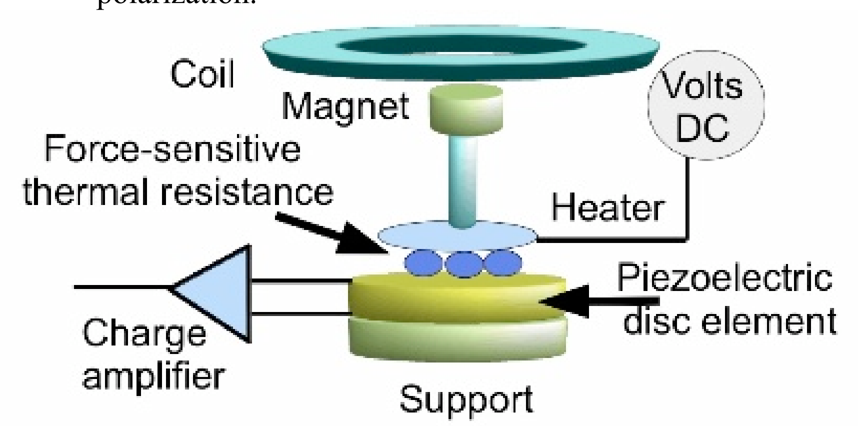
Extreme values of physical properties can be obtained in several ways. For example it is possible to exceed bounds [16 17] on composite elastic moduli or viscoelastic properties by relaxing the assumption [18] of positive definite energy density [19]. This is a mathematical way of expressing the assumption of materials or systems with no stored energy. Stored energy is present in materials in the vicinity of phase transitions, also in structural elements that have been buckled. Composites that contain partially constrained inclusions that can undergo phase transformation can attain extremely high stiffness [20] or viscoelastic damping [21] via balance [22] between positive and negative stiffness. The negative stiffness is understood in the context of the Landau energy theory for phase transitions. Negative stiffness entails instability unless the material is constrained, as it is by the matrix in a composite. Attainment of extreme values of physical properties via negative stiffness from stored energy requires tuning of the system near the stability limit. Large anelastic effects have been observed in designed all-ceramic systems via this concept [23]. The present approach, by contrast, makes use of a non-equilibrium flux of energy rather than stored energy. This method has recently been used to attain stable singular stiffness or stable negative stiffness [24]. The energy flux approach does not require tuning near a limit of stability.

To conclude, effective piezoelectric sensitivity is enhanced by at least two orders of magnitude due to stress-modulated pyroelectric coupling in a two layer composite under a thermal gradient. The approach can be generalised to composites with many layers and to other sensitivity coefficients associated with coupled fields.

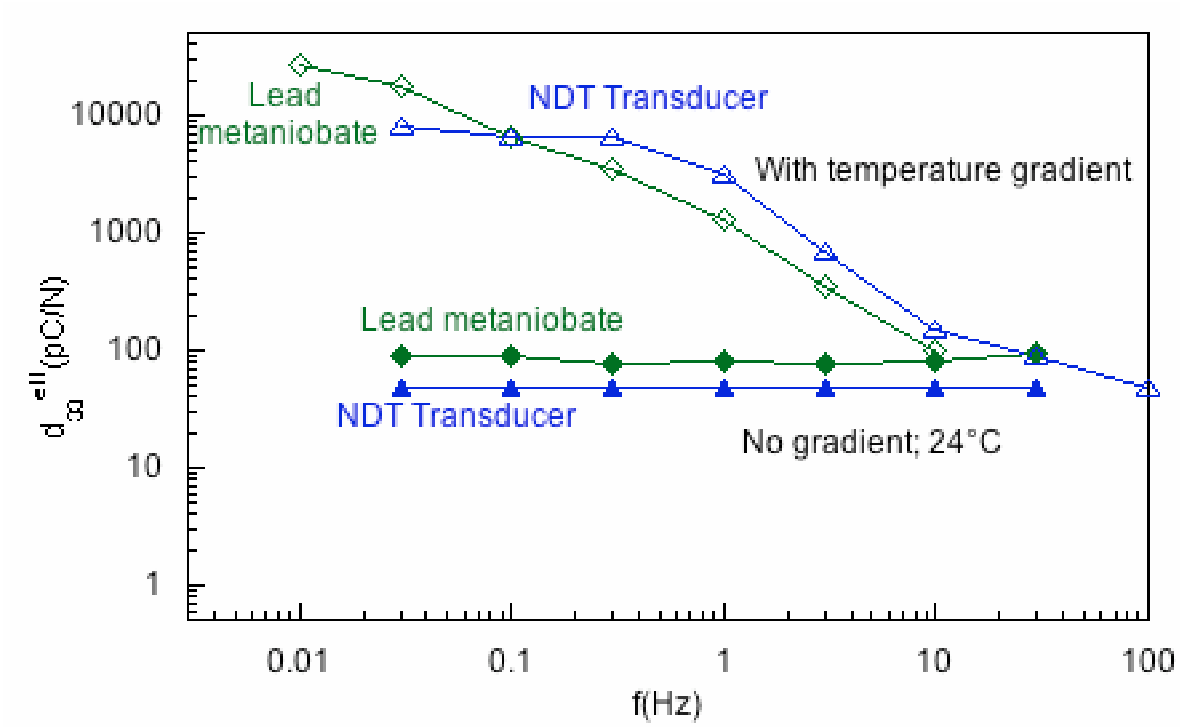
Figure captions



1. (a) Coupling paradigm adapted from Nye [*3*] . Thick lines represent primary cause-effect relations; thin lines represent coupling which depends on the material. (b) Stress-induced modulation (curved arrows) of flux to achieve extreme enhancement of stress generated electric polarization.



2. Experimental configuration.



3. Measured effective piezoelectric coefficients vs. frequency for two layer composites containing a lead metaniobate disc (diamonds) and containing an ultrasonic NDT transducer (triangles) vs. frequency under isothermal conditions (solid symbols) and with a temperature gradient (open symbols).

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