Electrostriction: Nonlinear Electromechanical Coupling in Solid Dielectrics

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Electrostriction is the basis of electromechanical coupling in all insulators. The quadratic electrostrictive strain $\mathbf{x}_{ij}$ associated with induced polarization components P_k and $\mathbf{P}_l$ is given by $\mathbf{x}_{ij} = \mathbf{Q}_{ijkl}\mathbf{P}_k\mathbf{P}_l$. Two converse electrostrictive effects may also be defined. In this paper, some trends in structure−property relationships that govern electrostriction are identified, along with the problems that limit our understanding of this fundamental electromechanical property. Electrostrictive coefficients range from the $\sim 10^{-3}$ m⁴/C² in relaxor ferroelectrics to $\sim 10^3$ m⁴/C² in some polymers. High-sensitivity techniques, such as interferometry or compressometry, are necessary to accurately measure electrostrictive effects in most insulators. But even in low-K dielectrics, electrostrictive stresses may initiate breakdown in high-field environments such as microelectronic components with small dimensions, high-voltage insulators, or in high-power lasers. In polymeric materials, charge injection mechanisms may produce local electric field concentrations that can cause large electrostrictive strains. The electromechanical properties in polymers have also been observed to vary with the thickness of the specimen. A brief description of the anharmonic nature of electrostriction and its frequency dependence is included.

Introduction

Many of the recent innovations in the field of electroceramics have exploited the nonlinearities of material properties with factors such as electric field, frequency, or temperature. The nonlinear dielectric behavior of ferroelectric ceramics (Figure 1), for example, has opened up new market segments in electronics and communication. In these materials, the polarization increases nonlinarly to a saturation value as the applied electric field is increased.[1] Polarization $\mathbf{P}_i$ varies with applied electric field $\mathbf{E}_j$ as

$$\mathbf{P}_i = \eta_{ij}\mathbf{E}_j + \eta_{ijk}\mathbf{E}_j\mathbf{E}_k + ...$$

where η_{ij} is the dielectric susceptibility and η_{ijk} the higher order dielectric susceptibility. η_{ij} is related to the dielectric constant K_{ij} by the linear relation $\eta_{ij} = (K_{ij} - 1)\epsilon_0$.

Similarly, the nonlinear elastic behavior of materials such as polymers (Figure 2) has also been exploited in composite structures. In the natural vulcanized rubber shown, the strain obtained saturates as stress is increased in the low megapascal range.[2] Linear stress−strain behavior conforming to Hooke's law is observed only in regions of low stress. In the linear region, the strain $\mathbf{x}_{ij}$ is related to the stress $\mathbf{X}_{kl}$ by the relation $\mathbf{x}_{ij} = \mathbf{s}_{ijkl}\mathbf{X}_{kl}$. Nonlinear elastic behavior in general may be described by the equation

$$\mathbf{x}_{ij} = \mathbf{s}_{ijkl}\mathbf{X}_{kl} + \mathbf{s}_{ijklmn}\mathbf{X}_{kl}\mathbf{X}_{mn} + ...$$

where s_{ijkl} is the elastic compliance and s_{ijklmn} the higher order elastic compliance.

Materials which display large electromechanical interactions have been exploited in the areas of stress or displacement sensing and in actuating. While most commercial electromechanical materials and structures are based on linear or piezoelectric mechanisms, nonlinear electromechanical interactions are of interest in engineering material systems and structures with tunable properties.[3] Strains caused by linear and
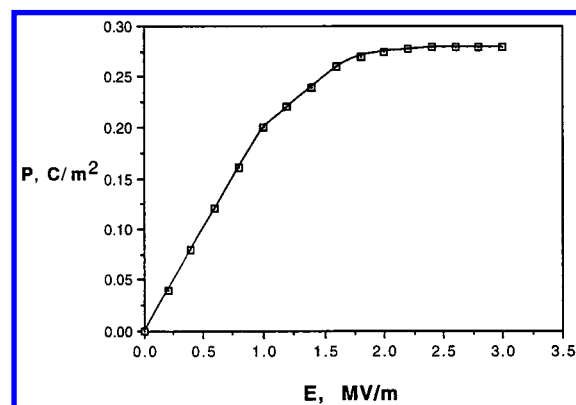

Figure 1. Nonlinear polarization vs electric field behavior for the relaxor ferroelectric 0.9 PMN−0.1 PT in its paraelecric regime (ref 1).
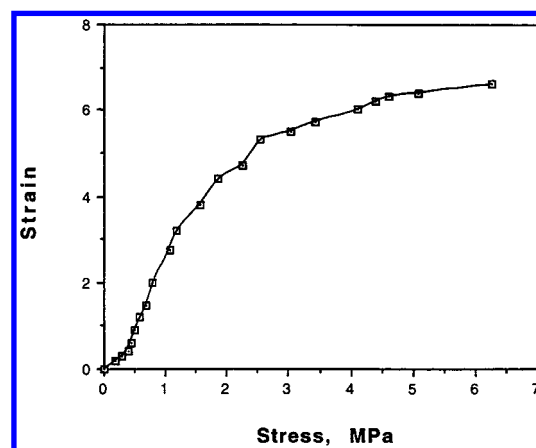

Figure 2. Nonlinear strain vs stress behavior of a typical natural vulcanized rubber (ref 2).

nonlinear electromechanical interactions may be expressed as

$$x_{ij} = g_{ijm}\mathbf{P}_m + \mathbf{Q}_{ijmn}\mathbf{P}_m\mathbf{P}_n + ...$$

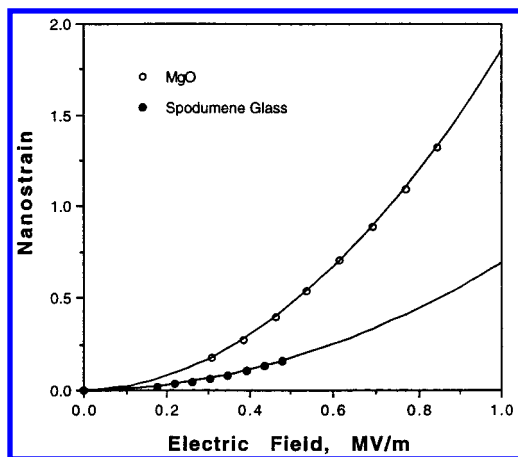where the linear effect is associated with the piezoelectric

Figure 3. Electrostrictive strain can be observed in all insulating materials. Quadratic strain vs electric field relationships for single-crystal-<100>-oriented MgO and spodumene glass measured by interferometry are illustrated here.
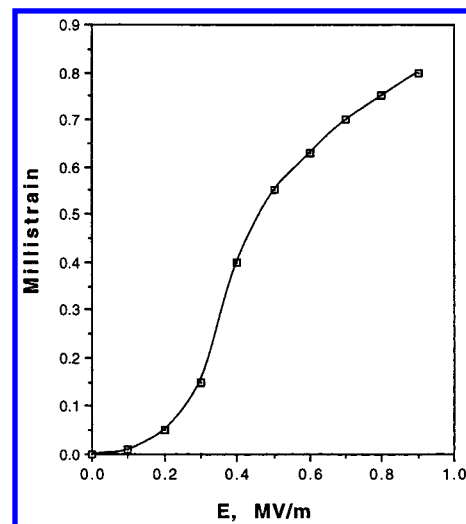

Figure 4. Electrostrictive strain is not always quadratic with electric field, especially for high K materials such as PMN (ref 1).

constants g_{ijm} and quadratic nonlinear effect with the electrostriction coefficients $\mathbf{Q}_{ijmn}$. These strains may also be expressed in terms of electric-field-related coefficients $\mathbf{d}_{ijm}$ and $\mathbf{M}_{ijmn}$ as

$$x_{ij} = \mathbf{d}_{ijm}\mathbf{E}_m + \mathbf{M}_{ijmn}\mathbf{E}_m\mathbf{E}_n + ...$$

Piezoelectricity is absent in centric crystals, but electrostriction, being a tensor property of even rank, can be observed in all insulating materials. Quadratic electrostrictive strain in MgO and spodumene glass ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$) is illsurated in Figure 3.[4] It is also the primary electromechanical coupling mechanism in centrosymmetric materials. In this review, we look at nonlinear electromechanical interactions in the different ways in which it may be observed in materials, along with trends in structure property relationships that affect these interactions.

Phenomenology of Electrostriction

Nonlinearity in electrical, elastic, and electromechanical properties may be defined using the Devonshire formalism.[5,6] The elastic Gibbs function G for the free energy of a material may be expressed in differential form as

$$d\mathbf{G} = -S\,dT - x_{ij}\,d\mathbf{X}_{ij} + \mathbf{E}_j\,d\mathbf{P}_i$$

where S is the entropy, T the temperature, x_{ij} are elements of the elastic strain tensor $\mathbf{x}$, $\mathbf{X}_{ij}$ are elements of the stress tensor X, and $\mathbf{E}_{ij}$ and $\mathbf{P}_i$ are elements the electric field and polarization vectors $\mathbf{E}$ and $\mathbf{P}$. Properties relating derived variables such as S, x_{ij}, or $\mathbf{E}_i$ to fixed variables of state such as T, $\mathbf{X}_{ij}$, or $\mathbf{P}_i$ are obtained by taking the second derivative of this free energy function. For example, the first-order terms for inverse dielectric susceptibility χ_{mn} and elastic compliance s_{ijkl} may be expressed as

$$\chi_{mn} = (d\mathbf{E}_m/d\mathbf{P}_n)_{\mathbf{X},T} = (d^2\mathbf{G}/d\mathbf{P}_m\,d\mathbf{P}_n)_{\mathbf{X},T}$$

and

$$s_{ijkl} = (dx_{ij}/d\mathbf{X}_{kl})_{\mathbf{P},T} = (d^2\mathbf{G}/d\mathbf{X}_{ij}\,d\mathbf{X}_{kl})_{\mathbf{P},T}$$

Cross-coupled properties can be derived by changing the differentiation variable for the second differential. The properties that introduce strain in a material are derived by differentiating the elastic Gibbs function with respect to stress. The tensor properties associated with these effects are elastic constants, linear and nonlinear thermal expansion, linear piezoelectric constants (g_{ijm}), and quadratic ($\mathbf{Q}_{ijmn}$) electrostriction constants.

These electromechanical interactions can be expressed in a power series to the second order (fixed $\mathbf{X}$, T) as

$$x_{ij} = g_{ijm}\mathbf{P}_m + \mathbf{Q}_{ijmn}\mathbf{P}_m\mathbf{P}_n + ...$$

Electrostriction may be thus defined as the quadratic coupling between strain and electric field, or between strain and polarization. It is a fourth-rank tensor defined by the following relationship:

$$x_{ij} = \mathbf{M}_{ijmn}\mathbf{E}_m\,\mathbf{E}_n$$

or

$$x_{ij} = \mathbf{Q}_{ijmn}\,\mathbf{P}_m\,\mathbf{P}_n$$

where $\mathbf{M}_{ijmn}$ are elements of the fourth-rank-field-related electrostriction tensor and $\mathbf{Q}_{ijmn}$ are elements of hte the fourth rank polarization related electrostriction tensor. The $\mathbf{M}$ and $\mathbf{Q}$ coefficients are equivalent in linear dielectrics. Conversions between the two coefficients are carried out using the field-polarization relationships $\mathbf{P}_m = \eta_{mn}\mathbf{E}_n$ and $\mathbf{E}_n = \chi_{mn}\mathbf{P}_m$ where η_{mn} is the dielectric susceptibility tensor, and χ_{mn} is the inverse dielectric susceptibility tensor. The need for defining a polarization related electrostriction tensor arises from the fact that ferroelectrics and other materials often show nonlinearity of dielectric properties with changing electric fields. Electrostrictive strain is not always quadratic with electric field, especially in high permittivity materials with nonlinear $\mathbf{P}_i - \mathbf{E}_j$ relationships (Figure 4). Thus, it is useful to define a polarization related electrostriction coefficient $\mathbf{Q}_{ijmn}$ better express the quadratic nature of electrostriction in all materials.

The M coefficients are defined in units of m^2/V.[2] Their values range from about 10^{-24} m^2/V^2 in low-permittivity materials to 10^{-16} m^2/V^2 in high-permittivity actuator materials such relaxor ferroelectrics such as lead magnesium niobate−lead titanate compositions. Large strains of the order of strains in ferroelectric piezoelectric materials, such as lead zirconate titanate, may be induced in these materials for similar fields. $\mathbf{Q}$ coefficients are defined in units of m^4/C.[2] Q values vary in an opposite way to M values. $\mathbf{Q}$ ranges from 10^{-3} m^4/C^2 in relaxor ferroelectrics to greater than the order of 10^3 m^4/C^2 in polyurethane films.

Fourth rank electrostriction tensors may also be expressed in collapsed Voigt notation as $\mathbf{M}_{ij}$ or $\mathbf{Q}_{ij}$. Expressing these tensors in matrix form illustrates the effects of point group symmetry on this tensor, as applied through Neumann's

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TABLE 1: List of Dielectric Constants, Elastic Constants, and Electrostriction Coefficients of Comon Dielectrics

materials	K	S ($\times 10^{-12}$) (m²/N)	$S/K\epsilon_0$ ($\times 10^{-4}$) (m/FN)	Q_h (m⁴/C²)	ref
relaxor ferroelectric					
PLZT (11/65/35)	5900	9.50	1.82	0.007	9, 10, 11
BaTi$_x$Sn$_{1-x}$O₃ ($x = 0.38$)	10300	8.90	1.01	0.0099	
BaSr$_x$Ti$_{1-x}$O₃ ($x = 0.35$)	25000	4.55	0.206	0.0069	
La/PMN-PT (1/93/97)	13000	16.42	1.43	0.006	
Perovskite ferroelectric					
SrTiO₃	450	1.82	4.57	0.07	11
PbTiO₃	270	7.81	32.6	0.03	
BaTiO₃	1070	6.02	6.36	0.03	
Pb(Ti$_{1-x}$Zr$_x$)O₃	1700	1.52	1.01	0.018	
glass ceramics					
Corning 888VE	300	7.25	27.31	0.079	9
Corning 888YT	370	5.85	17.87	0.055	
Corning 888ZF	440	4.93	12.66	0.064	
linear dielectrics					
single crystals					
CaF₂	6.8	6.92	1150	0.47	13, 4
BaF₂	7.4	15.3	2342	0.33	
KMnF₃	9.8	9.72	1121	0.24	
MgO	9.8	4.03	465	0.18	
ceramics					
MgO-doped Al₂O₃	10.5	2.90	312	1.58	this work
AlN	9.5	3.03	360	0.318	
Si₃N₄	8.7	3.13	406	1.06	
glasses					
Na−aluminosilicate	10.2	15.3	1696	0.519	12, 14
fused SiO₂	3.8	14.0	4163	0.37	this work
Na₂O·3SiO₂	11.3	16.3	1629	0.765	
spodumene glass	7.9	1.18	169	0.43	
polymers					15, 16
PVDF	16	420	29660	2.4	
VDF/TrFE	11	400	41090	2.5	this work
PVC	3.4	333	110700	10.1	
polyurethane	6.5	25000	4346000	850	

principle. For example, the electrostriction matrix for cubic materials (point group $m3m$) is

$$\begin{matrix} Q_{11} & Q_{12} & Q_{12} & 0 & 0 & 0 \\ Q_{12} & Q_{11} & Q_{12} & 0 & 0 & 0 \\ Q_{12} & Q_{12} & Q_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & Q_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & Q_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & Q_{44} \end{matrix}$$

while the matrix for isotropic materials such as unoriented ceramics, glasses, or polymers (Curie groups $\infty\infty m$ and $\infty\infty$) would be of the form

$$\begin{matrix} Q_{11} & Q_{12} & Q_{12} & 0 & 0 & 0 \\ Q_{12} & Q_{11} & Q_{12} & 0 & 0 & 0 \\ Q_{12} & Q_{12} & Q_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & 2(Q_{11}-Q_{12}) & 0 & 0 \\ 0 & 0 & 0 & 0 & 2(Q_{11}-Q_{12}) & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(Q_{11}-Q_{12}) \end{matrix}$$

It is also useful to define a hydrostatic electrostriction coefficient Q_h, as the variation of susceptibility with applied hydrostatic pressure. This coefficient can be useful in comparing electrostrictive effects in materials with different anisotropy characteristics. Since applied compressive stress is by convention negative, Q_h values are positive for ceramic materials, indicating the decrease of inverse dielectric susceptibility (χ) with applied pressure.

$Q_h = 0.5(d\chi/dp) = Q_{11} + 2Q_{12}$ (for materials with cubic or isotropic symmetry).

The Q_h, dielectric permittivity, and elastic compliance values for some common dielectric materials[9−16] are listed in Table 1.

As a consequence of the quadratic nature of the electrostriction effect, the sign of the strain produced in the material is independent of the polarity of the field. This is in contrast with linear piezoelectricity where reversing the direction of the field would cause a change in the sign of the strain. Another consequence is that electrostrictive strain occurs at twice the frequency of an applied ac field. In acentric materials where both piezoelectric and electrostrictive strains may be observed, this fact is very useful in separating the strains arising from piezoelectricity and from electrostriction.

The electrostriction tensor can also be treated as a complex quantity, similar to the dielectric and the piezoelectric tensors. The imaginary part of the electrostriction is also a fourth-rank tensor. Such a treatment could be very useful in providing a better understanding at electromechanical energy conversion in materials with relaxation mechanisms such as glasses containing alkali ions[7] or polymeric materials.[8] In this review, though, the discussion is confined to the real part of the electrostriction tensor.

Also, electrostriction in liquid and gaseous dielectrics has been studied since late in the 19th century, when studies by Roentgen[17] showed that all liquids expanded when an electric field was applied to them. In liquids, electrostriction is observed mainly as the contraction of a solvent around solute ions. Similar to solids, the electrostrictive effect in liquids is observed to be proportional to the square of the charge of the ions, inversely proportional to the ionic radius, and proportional to the value of K^{-2} dK/dP for the solute.[18] Our discussion, however, is confined to solid dielectrics.

Direct and Converse Electrostriction Effects

The electrostriction effect defined in the previous section, which relates the quadratic dependence of strain on applied field or induced polarization may be termed the direct electrostrictive effect.

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$$\mathbf{Q}_{ijmn} = (\mathrm{d}^2\mathbf{x}_{ij}/\mathrm{d}\mathbf{P}_m\,\mathrm{d}\mathbf{P}_n) = (\mathrm{d}^3\mathbf{G}/\mathrm{d}\mathbf{X}_{ij}\,\mathrm{d}\mathbf{P}_m\,\mathrm{d}\mathbf{P}_n)$$

or

$$\mathbf{M}_{ijmn} = (\mathrm{d}^2\mathbf{x}_{ij}/\mathrm{d}\mathbf{E}_m\mathrm{d}\mathbf{E}_n) = (\mathrm{d}^3\mathbf{G}/\mathrm{d}\mathbf{X}_{ij}\,\mathrm{d}\mathbf{E}_m\,\mathrm{d}\mathbf{E}_n)$$

By changing the order of differentiation in the free energy term, we may derive an equivalent converse effect of electrostriction as

$$\mathbf{Q}_{ijmn} = -{}^1\!/_2\,(\mathrm{d}\chi_{ij}/\mathrm{d}\mathbf{X}_{mn}) = (\mathrm{d}^3\mathbf{G}/\mathrm{d}\mathbf{P}_i\,\mathrm{d}\mathbf{P}_j\,\mathrm{d}\mathbf{X}_{mn})$$

or

$$\mathbf{M}_{ijmn} = {}^1\!/_2\,(\mathrm{d}\eta_{ij}/\mathrm{d}\mathbf{X}_{mn}) = (\mathrm{d}^3\mathbf{G}/\mathrm{d}\mathbf{E}_i\,\mathrm{d}\mathbf{E}_j\,\mathrm{d}\mathbf{X}_{mn})$$

which is the variation of the inverse dielectric susceptibility or the dielectric susceptibility with applied stress. It is also possible to define a second converse effect, in which electrostriction is defined as the variation of the piezoelectric voltage coefficient g_{ijk} with the induced polarization.

$$\mathbf{Q}_{ijkl} = -{}^1\!/_2\,(\mathrm{d}g_{ijk}/\mathrm{d}\mathbf{P}_l)$$

Electrostriction in Relation To Other Anharmonic Material Properties

It is necessary to model anharmonic behavior to describe some macroscopic properties that cannot be modeled using the harmonic approximation in solid state theory. Some of these properties are the thermal expansion coefficient, the isothermal compressibility, its pressure coefficient, and electrostriction, all of which contribute to the macroscopic Gibbs free energy and are typically defined like compliance coefficients.

Modeling anharmonic properties from first principles involves much effort in computational theoretical physics. However, simpler atomistic models, in combination with empirical correlations, can provide some understanding of electrostriction in relation with other anharmonic properties.

Under the action of an applied electric field, the cations and anions in a crystal structure are displaced in opposite directions by an amount Δr. This displacement is responsible for the electric polarization, the dielectric constant, and the electrostrictive strain.[3] To a first approximation, we may express the relation between these as

$$Q = x/P^2 \sim (\Delta r)/(\Delta r)^2 = 1/\Delta r \sim 1/K$$

Plotting Q_h as a function of the dielectric permittivity (Figure 6) reveals two distinct trends, one for materials with cubic perovskite structures and another for other materials. Perovskite materials of comparable compliances follow the $Q \sim 1/K$ relation. However, linear dielectric with a large range of compliances and a small range of dielectric constants do not follow this relationship. For example, diamond is a very covalent material with a very low complaince and has a $Q_h \sim 0.02$. Introducing a larger compliance range by including soft polymer dielectrics can further dilute this relationship.

Large strains in compliant solids such as polymers can introduce large changes in the dielectric stiffness and in anharmonic potentials. Electrostrictive strain is displacive and acts against the elastic forces in a material. Introducing the elastic compliance s into the Q vs K relationship can better express the correlation between these properties. Through the first converse effect, electrostriction is proportional to the change of dielectric stiffness β with stress X, which may be expressed as
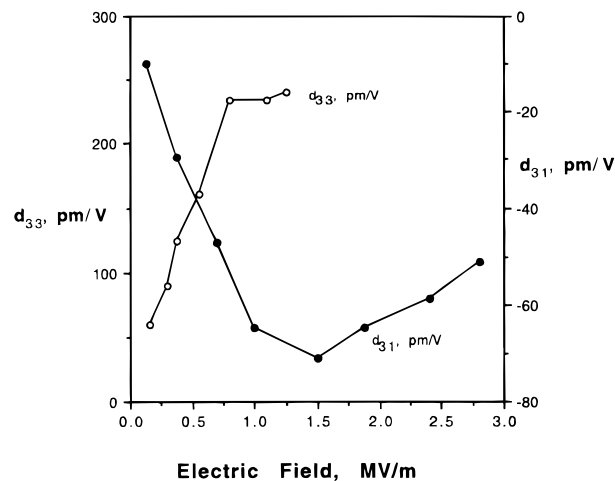

Figure 5. Variation of longitudinal and transverse d coefficients with applied electric field for electrostrictive PMN, 18 °C (ref 1).
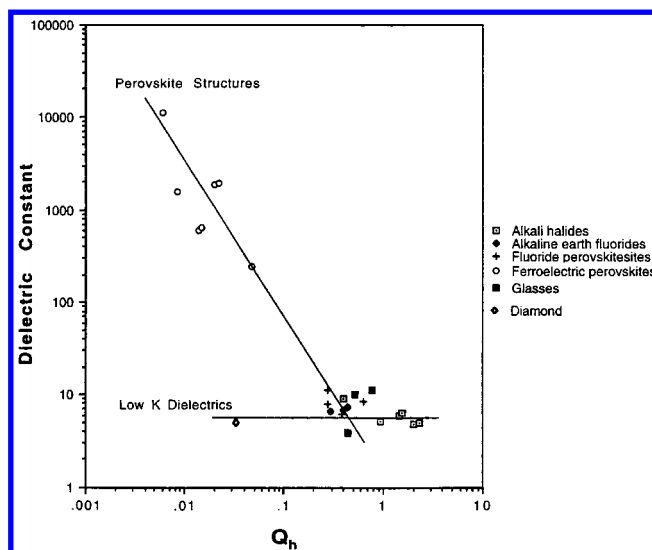

Figure 6. Variation of Q_h (m⁴/C²) with dielectric constant for various materials.

$$Q \sim (\Delta\beta)/(X) \sim x/(x/s) \sim s$$

Empirically, $\log(Q_h)$ is seen to vary nearly linearly with $\log(s/\epsilon_0 K)$ (Figure 7). This combination of the compliance and the deielectric properties of a materials may be used as a predictor of the size of electrostriction effects in insulators.

Electrostrictive coefficients have also been related to other anharmonic properties such as the thermal expansion coefficient, the isothermal volume compressibility, and the pressure derivative of the volume compressibility with comparable levels of correlation. More complicated shell models and quasiharmonic models have also been attempted for electrostriction.[19−21] An a priori model to accurately predict electrostriction in linear dielectrics is held back in part by the lack of reliable and accurate measurements of electrostriction in these materials and also by the complexity of the problem.

Electrostriction in Antiferroelectric and Ferroelectric Materials

In a ferroelectric material, that exhibits both spontaneous and induced polarizations, $\mathbf{P}^F_i$ and $\mathbf{P}^i_j$, the strains arising from spontaneous polarizations, piezoelectricity, and electrostriction may be formulated as

$$\mathbf{x}_{ij} = \mathbf{Q}_{ijkl}\,\mathbf{P}^F_k\mathbf{P}^F_l + 2\mathbf{Q}_{ijkl}\mathbf{P}^F_k\mathbf{P}^i_l + \mathbf{Q}_{ijkl}\mathbf{P}^i_k\mathbf{P}^i_l$$

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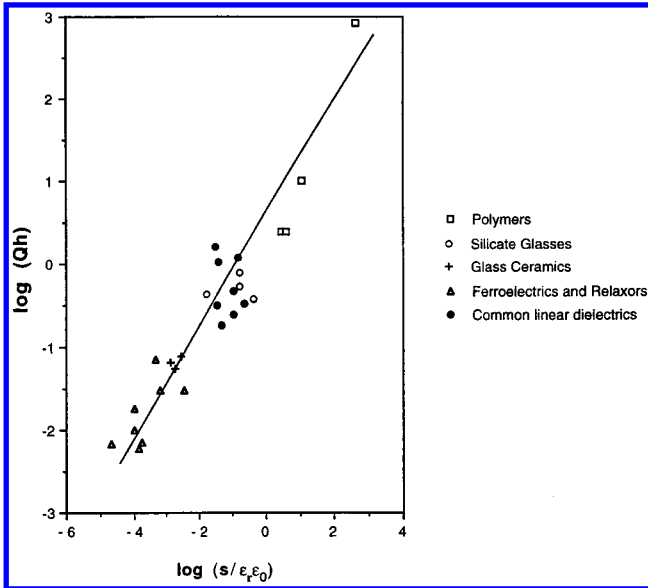*J. Phys. Chem. B, Vol. 101, No. 48, 1997* **10145**

Figure 7. Variation of log Q_h (m^4/C^2) with log(s/ϵ_oK) for various materials inluding polymers shows a near linear relationship.

Leaving out the negligibly small pure electrostrictive contribution in the ferroelectric state, we may express the piezo-electric voltage coefficient g_{ijk} as

$$g_{ijk} = \mathrm{d}\mathbf{x}_{ij}/\mathrm{d}\mathbf{P}^i_l = 2\mathbf{Q}_{ijkl}\mathbf{P}^F_k$$

Electrostriction has been shown to be the origin of piezo-electricity in ferroelectric materials in conventional ceramic ferroelectrics, such as barium titanate, as well as in organic polymer ferroelectrics such as vinylidene fluoride copolymers (PVDF).[15] This origin of piezoelectricity in electrostriction provides us an avenue into nonlinearity. The piezoelectric coefficient and the dielectric behavior of a transducer can be tuned to desired values. The piezoelectric coefficient varies with the polarization induced in the material and may be controlled by an applied electric field (Figure 5). The electrostrictive element may be tuned from an inactive to a highly active state. The electrical impedance of the element may be tuned by exploiting the dependence of permittivity on the biasing field for these materials, and the saturation of polarization under high fields.[3,21]

Electrostrictive coupling between sublattices has also been proposed as a mechanism to explain piezoelectric anisotropy in antiferroelectric ceramics.[22] In a two-sublattice model, if $\mathbf{Q}_{ij}$ denotes the conventional electrostriction tensor, and q_{ij} the corresponding intersublattice coupling parameters, then the strains arising from spontaneous polarizations and induced polarizations $\mathbf{P}^F_k$ and $\mathbf{P}^i_k$, in the ferroelectric state may be written in Voigt notation as

$$x_k = (\mathbf{Q}_{kl} + q_{kl})(\mathbf{P}^F_k)^2 + 2(\mathbf{Q}_{kl} + q_{kl})\mathbf{P}^F_k\mathbf{P}^i_k + $$
$$(\mathbf{Q}_{kl} + q_{kl})(\mathbf{P}^i_k)^2$$

When a spontaneous polarization is induced, the pure electrostrictive contribution from induced polarizations alone is negligible, and we may express the piezoelectric coefficient d_{kl} as

$$d_{kl} = \mathrm{d}\mathbf{x}_k/\mathrm{d}\mathbf{P}^i_k = 2(\mathbf{Q}_{kl} + q_{kl})\mathbf{P}^F_k$$

The strains $\mathbf{x}^{AF}_k$ associated with the field-induced transition from antiferroelectric to ferroelectric states and spontaneous strains $\mathbf{x}^{PF}_k$ observed at the transition from paraelectric to antiferroelectric states can be expressed in terms of the

spontaneous polarization in the ferroelectric state, $\mathbf{P}^F_k$, and $\mathbf{P}^A_k$, the spontaneous polarization in the antiferroelectric state as

$$\mathbf{x}^{AF}_k = 2q_{lk}(\mathbf{P}^F_k)^2 \qquad \text{and} \qquad \mathbf{x}^{PF}_k = (\mathbf{Q}_{kl} - q_{kl})(\mathbf{P}^A_k)^2$$

The piezoelectric anisotropy factor d_{ij}/d_{ik} may then be calculated as

$$d_{ij}/d_{ik} = (\mathbf{Q}_{ij} + q_{ij})/(\mathbf{Q}_{ik} + q_{ik})$$

Estimations of q_{ij} ($\sim$0.01 m^4/C^2) show in antiferroelectric materials show that they are comparable to but smaller than $\mathbf{Q}_{ij}$ ($\sim$0.06 m^4/C^2) values.

Some Applications of Electrostriction

Despite the fact that electrostriction was initially relegated to the role of an esoteric, and at best secondary effect, the number of applications of the phenomenon, both theoretical and practical, has been increasing significantly since the introduction of PMN as a prototype electrostrictive material.[1] Most applications take advantage of the electrostrictor as an actuator, exploiting the anhysteretic, tunable nature of the electro-mechanical response. Mechanical applications range from stacked actuators, through inchworms, microangle-adjusting devices, and oil pressure servo valves.[23,24] These are in the main servo-transducers, deployed as micropositioning devices, featuring a reproducible, nonhysteretic deformation response on the application of an electric signal of suitable magnitude.

The advantages that electrostrictors have over other actuator materials include low hysteresis of the strain-field response, no remanent strain (walk off), reduced aging and creep effects, a high-response speed (<10ms), and strain values (>0.03%) achievable at realizable electric fields. Displacement ranges of several tens of microns may be achieved with ±0.01 μm reproducibility. Most actuator applications of electrostrictors as servo transducers and micropositioning devices take advantage of these characteristics. Mechanical applications range from stacked actuators through inchworms, microangle adjusting devices, and oil pressure servo valves. Multilayer actuators produce large displacements and high forces at low drive voltages. The linear change in capacitance with applied stress of an electrostrictor can be used as a capacitive stress gage.[25] Electrostrictors may also be used as used in field tunable piezoelectric transducers. Recently, electrostrictive materials have been integrated into ultrasonic motors and novel flexten-sional transducers.

Electrostrictors have also been integrated into "smart" optical systems such as bistable optical devices, interferometric dilatometers, and deformable mirrors. Electrostrictive correction of optical aberrations is a significant tool in active optics. Electrostrictors also find applications in "very smart" systems such as sensor-actuator active vibration suppression elements. A shape memory effect arising from inverse hysteretic behavior and electrostriction in PZT family antiferroelectrics is also of interest.

In selecting electrostrictive relaxor ferroelectrics for actuator and sensor applications, the following criteria are commonly used. A large dielectric constant and field stability in the *K* vs **E** relations are useful in achieving large electrostrictive strains. These criteria also lead to large induced polarizations and large induced piezoelectric coefficients through the second converse effect. Broad dielectric transitions allow for a large operating temperature range. Minimal **E**−**P** hysteresis and no remanent polarization are useful in achieving a low loss material that is not susceptible to Joule heating effects. These factors are listed in Table 2. As a fundamental effect, electrostriction may prove to be an important factor in the design of submicron electronic
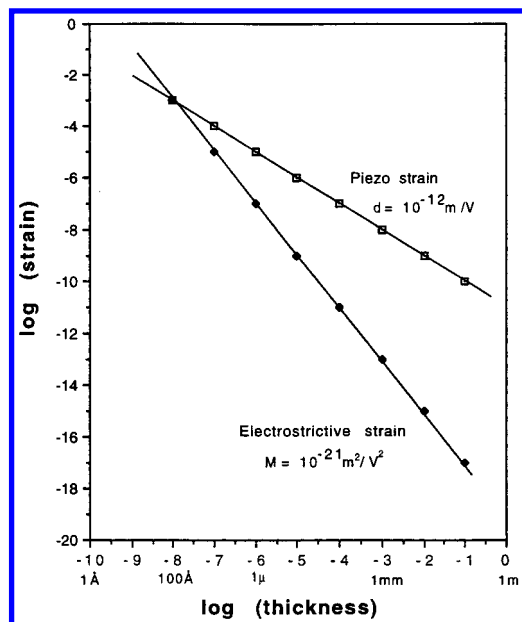
Figure 8. Strains from piezoelectric quartz and electrostrictive amorphous silica glass for devices of varying thickness, with a voltage of 10 V across the device. A typical $d \approx 10^{-12}$ m/V and $M \approx 10^{-21}$ m²/V² were assumed.

TABLE 2: Selection Critera for Ceramics for Electrostrictive Devices

desirable properties	material behavior
• large strain, induced polarization, and induced piezoelectricity	• large dielectric constants
• large operating temperature range	• broad dielectric transition
• low loss, low joule heating, minimal hysteresis, no remanent polarization	• operation in paraelectric regime ($T > T_{max}$)

devices. The present focus is on synthesis of materials with large electrostriction effects. The other extreme of the scale may prove to be of interest, too. As microelectronic devices are taken to smaller dimensions, the increased field levels on the materials can cause quadratic electrostrictive effects ($x\alpha E^2 \sim 1/t^2$) to predominate over inear piezoelectric effects ($x\alpha E \sim 1/t$). This effect is illustrated for silica, using the piezoelectric d coefficients of quartz ($d \approx 10^{-12}$ m/V) and electrostrictive $\mathbf{M}$ coefficients of silica glass ($M \approx 10^{-21}$ m²/V²) in Figure 8. An applied voltage of 10 V is assumed, and piezo and electrostrictive strains are plotted for devices of various thicknesses. Oxide layers in semiconductors are typically a few hundreds of angstroms thick. Around thicknesses of 100 Å, the electrostrictive strain can be larger than the piezoelectric contribution, and close to breakdown strains for ceramics. It is then tempting to consider designing a material with zero electrostriction coefficients for applications in areas where field induced damage is a significant risk. Other, more benign options are also offered by the effect in an increasing array of novel sensor and actuator applications that make it well worth further study.

Measuring a Range of Electrostrictive Effects

A variety of experimental methods have been employed to measure a wide range of electrostrictive effects in dielectric materials. The direct and converse electrostriction effects are of importance in that they offer two independent and equivalent techniques of measuring electrostriction in a material: (a) by measuring the strains induced in materials in response to applied fields or induced polarizations, using the direct effect, and (b) measuring the change in permittivity (via the change in capacitance) under an appropriate stress using the converse effect.
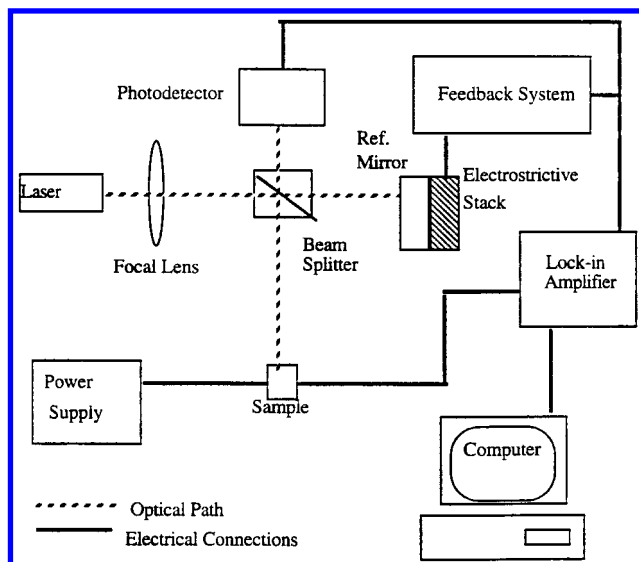

Figure 9. Schematic of a typical interferometric ultradilatometer, showing system components, optical paths, and electrical connections (ref 33)

The detection of small electrostrictive strains and the accurate evaluation of electrostrictive properties in most low-permittivity materials is a necessarily intricate process. For a field strength of 10^6 V/m, the typical induced strain in a centric ionic material is of the order of 10^{-9}. This translates into a displacement of 10^{-12} m, or 0.01 Å, for a sample 1 mm thick.. However, experiments to measure electrostrictive effects have been carried out since the turn of the 20th century. An early review of electrostriction by Cady[26] cites several measurements of electrostriction in insulators such as gases, oils, rubbers, glasses, and cements. These effects were measured by evaluating the expansion or the contraction of a condenser—probably a Leyden jar in the case of early measurements.

Widely used experimental techniques include the strain gauge method in which the output from a strain gage (usually pasted on the displacing sample) is used to measure the displacement in a given direction. The increased sensitivity and available in linear voltage displacement transformers (LVDTs) and potentiometers have made them another tool to measure displacements in electrostrictive materials.[25] The strain gage and LVDT techniques are typically used for materials with larger strains, typically of the order of 10^{-4} or greater. The technique of capacitance dilatometry involves measuring the change in capacitance arising from the electrostrictive displacement of one face of a parallel plate capacitor. The accuracy of early capacitance dilatometry measurements may have been limited by the unavailability of phase locking and sophisticated electronic feedback loops incorporated into the system to compensate for thermal drift.[28,29] Homodyne and heterodyne laser ultradilatometers based on Michelson interferometers have been used since the 1930s to measure very small displacements.[30-33] These instruments detect the shifts in interference fringes caused by changes in path length of two laser beams, one of which is reflected from the surface of a sample under an ac field. Using phase locking and feedback loops to stabilize the system, interferometers are capable of resolutions of 10^{-3}Å or better and are usually operating in the range of $1-100$ kHz (Figure 9). Typical results from interferometry measurements for MgO and spodumene glass are shown in Figure 3.

Recently, a bimorph based dilatometer similar in principle to an atomic force microscope has been introduced. This instrument is capable of measuring displacements of the order of 0.01 Å in a frequency range of $1-100$ kHz and is useful in studying electrostriction in thin films (Figure 10).[34] In most
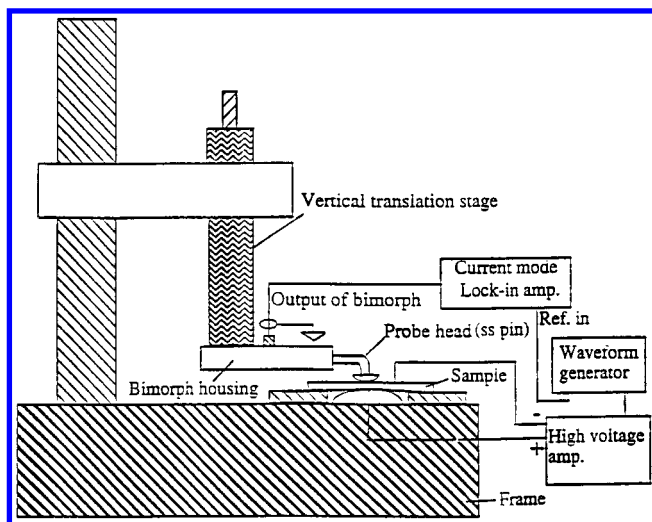
Solid Dielectrics

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Figure 10. Schematic of the bimorph dilatometer for measuring electromechanical response in polymer thin films (ref 34).

Figure 11. (a) Schematic of a converse method measurement system. The sample is shown shaded (ref 48). (b) Compressometery results for ceramic alumina, aluminum, and silicon nitride.

direct effect measurements, the electrostatic attractive stress between opposite charged faces of a dielectric material can contribute to the dimensional change. This stress is called the Maxwell stress, and the corresponding strain x_M is dependent on the dielectric and elastic properties of the material. With all quantities being measured in the direction of the field, x_M is given by[35]

$$x^M = -0.5\epsilon_0\epsilon_r sE^2$$

This correction is significant mainly in the case of low-permittivity materials where very small strains are observed and for elastically soft polymers.

Techniques for measuring the converse effect call for precision evaluation of dielectric properties. Small capacitance changes of the order of $10^{-16} - 10^{-15}$ F need to be resolved for applied stresses of the order of 0.1 MPa for low permittivity ceramic materials. Other requirements are stable temperature control and the establishment of "true" stress systems−completely hydrostatic if the hydrostatic Q_h coefficients are being measured and truly uniaxial stresses in compressometry (Figure 11a).[7,36] Modifications to compressometric systems are aimed mainly at improving sensitivity or uniaxiality for accurate evaluation of the separated components of the electrostriction tensor.[37,38] A correction corresponding the capacitance change due to the geometric shape change of the dielectric from elastic strain has to be performed to calculate accurate $\mathbf{Q}_{ij}$ values in low-permittivity dielectrics when the converse method is used. Results from compressometry measurements for some common ceramics are illustrated in Figure 11b. In the case of low-permittivity materials, it is necessary to measure electrostriction by both direct and converse methods to calculate reliable and accurate $\mathbf{Q}$ or $\mathbf{M}$ values (Table 3).

Some recent studies on quartz have used the change in resonant frequency of the vibration modes of the material caused by a dc field,[39] or the dc-field-induced variations in the transit times of ultrasonic pulses in the material.[40] These methods are used to calculate combinations of the electroelastic and the electrostrictive constants of quartz, as well as the nonlinear piezoelectricity and the permittivity tensors. While the method yields accurate results for the piezostriction, the electrostriction values show poorer agreement with values in the literature.

Electrostriction and Polarization Mechanisms

The basic mechanisms contributing to the polarization in dielectric materials have been identified and treated exten-
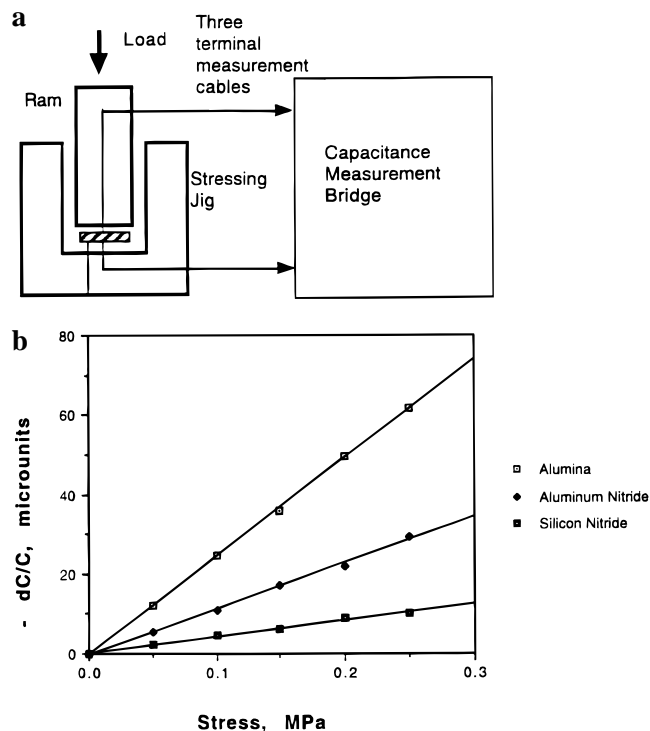
TABLE 3: Comparison of Direct and Converse Method Measurement Results for a Variety of Dielectric Materials[a]

material	direct Q_{11} (m⁴/C²)	converse Q_{11} (m⁴/C²)
BaF$_2$		
Q_{11}	−0.33	−0.31
Q_{12}	−0.29	−0.29
Q_{44}	1.46	1.48
spodumene glass (Li$_2$O·Al$_2$O$_3$·4SiO$_2$)	0.43	0.46
KMnF$_3$		
Q_{11}	0.51	0.49
Q_{12}	−0.09	−0.10
Q_{44}	1.16	1.15
CaF$_2$		
Q_{11}	−0.48	−0.49
Q_{12}	−0.48	−0.48
Q_{44}	1.99	2.01
LiF	0.79	0.57
888 VE Corning glass ceramic	0.081	0.079
MgO	0.33	0.34
BeO	1.45	1.48
SrF$_2$		
Q_{11}	−0.33	−0.33
Q_{12}	0.38	0.39
Q_{44}	2.01	1.90
3% Ca/PMN-PT	0.00289	0.00333
calcite	1.20	1.19

[a] These values agree to within ±5% (refs 4 and 12).

sively.[41] Electrostriction is a polarization related effect defined as $\mathbf{x}_{ij} = \mathbf{Q}_{ijkl}\mathbf{P}_k\mathbf{P}_l$. An understanding of the mechanisms of polarization, especially the ionic and electronic, can offer further insight into the underlying mechanisms and is useful in discerning trends in the electrostrictive behavior, especially in low permittivity linear dielectrics. Electrostriction measurements on most crystalline materials have been performed only over limited frequency ranges (10^5 Hz and below). Little variation of the $\mathbf{Q}$ coefficients with the frequency of measurement is seen for most crystalline ionic solids. Measurements over wider ranges of frequencies may be necessary to directly study the frequency dependence of electrostriction.

TABLE 4: $1/\epsilon_r(dn^2/dp)$ and $1/\epsilon_r(d\epsilon_r/dp)$ for Some Oxides and Fluorides

material	$1/\epsilon_r(d\epsilon_r/dp)$ (m²/N)	$1/\epsilon_r(dn^2/dp)$ (m²/N)
KMnF$_3$	-4.39×10^{-11}	8.79×10^{-13}
CaF$_2$	-3.42×10^{-11}	1.5×10^{-12}
BaF$_2$	-4.29×10^{-11}	3.8×10^{-12}
LiF	-5.08×10^{-11}	4.2×10^{-13}
MgO	-2.58×10^{-11}	-9.5×10^{-13}
KTaO$_3$	-1.38×10^{-10}	-6.7×10^{-14}
SrTiO$_3$	-2.74×10^{-10}	-2.9×10^{-14}
silica glass	-1.5×10^{-11}	1.03×10^{-13}

The variation of the low-frequency dielectric constants with temperature and pressure has been a subject for analysis by physicists for several decades.[42,20] Several studies review the changes in refractive index of solids with pressure and attempt to explain these changes in terms of the polarizabilities of ions.[43,44] These two sets of data may be combined to analyze the electronic and ionic contributions to electrostriction. The electronic and ionic contributions to electrostriction may be compared for some well characterized oxide and fluoride materials. Results from studies on hydrostatic Q_h electrostriction coefficients of low-permittivity fluorides[45] are used in this analysis, along with measurements of the change of refractive index of solids with pressure.[46,47]

The electrostrictive contribution from both ionic and electronic polarization mechanisms at low frequencies is proportional to the ratio $1/\epsilon_r(d\epsilon_r/dp)$. Using the approximation $n^2 \sim \epsilon_e$, where n is the refractive index of the material and ϵ_e the electronic or high-frequency dielectric constant, we may calculate $1/\epsilon_r(d\epsilon_e/dp) \sim 1/\epsilon_r(dn^2/dp)$ from the dn/dp data. To compare the relative contributions of the electronic and ionic polarizations at low frequencies, the same low-frequency (1 kHz) value for ϵ_r was used in both $1/\epsilon_r(d\epsilon_e/dp)$ and $1/\epsilon_r(d\epsilon_r/dp)$ ratios. The data used here was measured at pressures of 1 kbar and less so that no nonlinearity was apparent in dn/dp or $d\epsilon_r/dp$. The results are listed in Table 3 for eight oxide and fluoride materials.

It may be seen that most of the oxides in this analysis show a decrease in refractive index with pressure. This is true also for α-Al$_2$O$_3$, ZnO, stoichiometric and nonstoichiometric MgAl$_2$O$_4$ spinels, α-ZnS, and α-CdS.[44] Most fluorides on the other hand show an increase in n with pressure. Low-frequency dielectric constants decrease with pressure for both oxide and fluoride materials. The differing behaviors at different frequencies are caused by the relative magnitude of the electronic and ionic polarizations to electrostriction. In general the ionic contribution to electrostriction is at least 2 orders of magnitude greater than the electronic contribution, neglecting sign. The polarization effects caused by the relative shifting of the anion sublattice with respect to the cation sublattice in the crystal dominates the change in electronic polarizabilities of the various ions with pressure.

Both positive and negative values of dn/dp are observed. This holds out the tantalizing possibility of manipulating electrostriction values. By choosing materials with predominantly electronic polarizability contributions, and probably combining or doping them, it may be possible to achieve specific (especially zero) electrostrictive responses in materials. This would involve further research into the variaion of electrostrictive effects with frequency, and possible mixing rules for electrostriction. The possibility of achieving zero electrostriction through the manipulation of crystal anisotropy has been discussed in an earlier work.[48]

Electrostriction in Polymer Dielectrics

Piezoelectric and electromechanical coupling properties have been well characterized for ferroelectric polyvinylidene fluoride
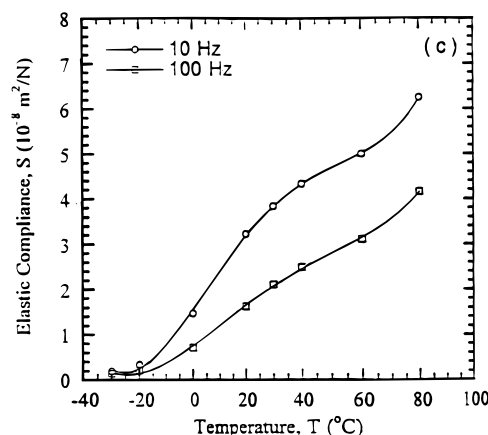
Figure 12. Elastic compliance vs temperature curves for Dow 2105-80AE polyurethane elastomer at 10 and 100 Hz (ref 50).

(PVDF) and its copolymers with trifluoroethylene (TRFE). Their applications have been limited mainly by their lower electromechanical activity when compared to conventional ceramic actuator materials. Recently, there has been renewed interest in nonferroelectric polyurethane elastomers because of their large field induced strain response, which is primarily electrostrictive. These materials could have promising applications in sensor, actuator and microelectromechanical systems technology.[8,27,49]

Some unusual effects have been observed in these polymer electrostrictors. The first is the large strain response. Strains of the order of 0.25% have reproducibly been achieved in these polymer systems for fields of the order of 1 MV/m. In discussing these materials, it may be more practical to define an effective field-induced strain coefficient R_e to calculate the large strains achieved in these materials.

$$x = R_e E_*^2$$

A strong temperature effect is observed, as may be expected from the nonlinear temperature dependence of the compliance of this polymer (Figure 12). The Maxwell stress induced strain in these materials is given by

$$x_M = -0.5s\epsilon_0 K E^2$$

A Maxwell strain coefficient R_m, similar to R_e, can be defined to calculate the percentage of Maxwell stress contribution. Below the glass transition temperature T_g, the Maxwell stress contributions are fairly small ($\sim$10%) while above T_g, the Maxwell stress contribution to the field-induced strain response increases to about 35−50%. A strong frequency effect is also observed (Figure 13a).

One effect that may help explain the large field induced strain in these materials is the thickness dependence of R_e. The induced strain and correspondingly, R_e, initially increased with increasing thickness and then decreases (Figure 13b). Experiments with different electrode materials and thermally stimulated discharging current measurements support the hypothesis that effects related to charge injection, or interfacial charge may cause these dependencies.

When a polymer dielectric with metal electrodes is subjected to a high voltage, charge injection can occur in this material. Injected charges can then be trapped in various sites such as defects, interfaces, etc., and their effects can show a strong thickness and frequency dependence. Filtering polyurethane polymers before solution casting markedly reduces the field-induced strain observed in these materials (Figure 13b) and the frequency dispersion as well, supporting the charge injection
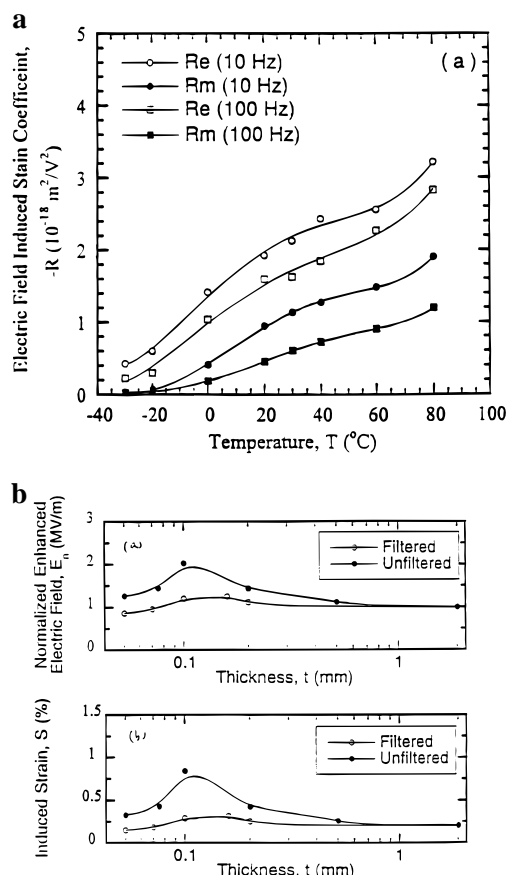
Figure 13. (a) Field induced strain coefficient R_e and maxwell strain coefficient R_m for unfiltered polyurethane thin films, at *RT*, 10 and 100 Hz, through the glass transition for Dow 2105-80AE polyurethane elastomer (ref 50). (b) Normalized enhanced elecric field and the corresponding induced strain as a function of thickness for filtered and unfiltered electrostrictive polyurethane thin films, at *RT*, 10 Hz (ref 50).

hypothesis. The dielectric and elastic properties are not significantly changed by filtering.

Injected charges can also cause enhanced nonuniform local electric fields, depending on the film thickness. The depth of the region of the polymer with enhanced local fields from charge injection is determined by the transport coefficients of the charges in the polymer film under an electric field. The volume fraction of the polymer with enhanced local fields increases with a decrease in sample thickness. After a critical thickness, though, charge neutralization and homogenization processes reduces the local field enhancement. The strain responses correspondingly decrease.[50]

The nonlinear compliance behavior of these polyolyurethane elastomers, combined with unusual polarization behavior from interfacial charge effects, can make for large induced strains that are thickness dependent. Further work in this area may identify the specific chemistry responsible for the large strains associated with charge injection and their applications in sensor and actuator areas.

Summary

As a summary, some common misconceptions about electrostriction to describe the key ideas set out in this paper are listed here.

Misconception 1. Electrostrictive Strain Is Proportional to the Square of the Applied Electric Field. For most low-permittivity dielectrics, **P** is proportional to the applied field **E**, and therefore this statement is true. However, for high fields, polarization can saturate for high-permittivity materials, espe-

cially in ferroelectric ceramics. A linear relationship is observed when strain is plotted as a function of the square of polarization for these materials, but not as a function of the electric field. So it is more accurate to say that electrostrictive strain is proportional to the square of the induced polarization.

Misconception 2. Large Voltages Are Required To Observe Electrostriction. Two factors have made this a misconception. The introduction of thick and thin film capacitors has enabled high-field levels to be achieved even in low-permittivity materials at low voltages. Also, the introduction of high dielectric constant relaxor ferroelectrics have raised polarization levels to new heights, further contributing to large electrostrictive strains with relatively modest voltages.

Misconception 3. Electrostriction Constants Are about the Same Size for All Materials, and Materials with Larger Electrostriction Coefficients Produce the Largest Strains. Q constants measured for solids vary from the order of 10^{-3} m^4/C^2 for relaxor ferroelectrics to 1 for low-permittivity insulators. Larger Q values have been observed for polymer materials. The induced electrostrictive strain is proportional to the square of the polarization, which implies the square of the relative permittivity is introduced in the strain−electric field relation. For similar electric fields, materials with large dielectric constants produce the larger starins.

Misconception 4. Thermal Expansion Effects Make Electrostrictive Microposiioners and Stress Gauges Impractical. This statement is true for low-permittivity oxide ceramics but not for relaxor ferroelectrics. For PMN-type ceramics, $Q \sim$ 0.01 m^4/C,[2] $K \sim$ 10 000, and the thermal expansion cofficient $\alpha \sim 10^{-6}\ K^{-1}$. The electrostrictive strain in these ceramics for a field around 1 MV/m is 10^{-3}, which corresponds to a 1000 °C change in temperature! Relaxor ferroelectrics can also have abnormally low thermal expansion coefficients near their diffuse phase transitions, where K values are quite large.

In conclusion, though electrostriction effects can be very small in common materials, experimental techniques using phase and frequency selection can help in achieving accurate and reliable measurements of **M** and **Q** coefficients. Being a nonlinear effect, electrostriction may be applied smart systems requiring tunable properties. Electrostriction is a significant electromechanical coupling mechanism in many high field situations. Investigating the variation of electrostriction with frequency can reveal the contributions of various polarization mechanisms to electrostrictive effects. In areas such as polymer thin films, the effects of charge injection and defects can produce anomalously large strains that are worth further investigation. Electrostriction still poses a range of problems and challenges in the areas of modeling and in terms of a fundamental understanding of a well-known effect.

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