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New Piezoelectric Materials for Ultrasonic Transducers

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Two types of piezoelectric ceramics with large electromechanical anisotropies (planar coupling factor k_p is much less than thickness dilatational coupling factor k_t) have been developed for use as high-frequency ultrasonic transducer materials: modified lead titanate ceramics (Pb, Sm)(Ti, Mn)O_3 and ferroelectric PbZrO$_3$ ceramics modified by adding small amounts of Pb(Mn$_{1/3}$Nb$_{2/3}$)O$_3$ and PbTiO$_3$. These new ceramics have a large k_t and k_t/k_p. PZT/polymer piezoelectric composite sheets have also been developed for use in medical transducers. These composite sheets were fabricated using a "dicing and filling" technique. The resulting composites are highly flexible and show both a large k_t and a low acoustic impedance.

§1. Introduction

Various new piezoelectric materials for use in medical ultrasonic transducers have been developed in recent years. Conventional materials, such as PZT ceramics, show a high electromechanical coupling factor; however, they must be acoustically matched to tissue in order to facilitate efficient transmission and reception over a broad frequency band. Application of these ceramics in linear arrays entails additional complexity. Each element in an array must be subdiced into several subelements to suppress coupilng to unwanted lateral modes. This is due to PZT's large electromechanical coupling factor with regard to lateral (planar) modes, making it difficult for PZT cersmics to be used for high frequency array transducers.

Thus, piezoelectric ceramics with large electromechanical anisotropies (planar coupling factor k_p is much less than thickness dilatational coupling factor k_t) have recently come to be developed for use as high-frequency ultrasonic transducer materials.[1-6] In contrast to the case for PZT ceramics,[7] the width-to-thickness ratio, w/t, of a transducer element can be larger than unity (no need for subdicing). The authors have developed modified lead titanate ceramics (Pb, Sm)(Ti, Mn)O$_3$ and applied them to high-frequency ultrasonic probes for a medical diagnosis system.[4,6] Enhanced electromechanical anisotropy has also been found in ferroelectric PbZrO$_3$ ceramics modified by adding small amounts of Pb(Mn$_{1/3}$Nb$_{2/3}$)O$_3$ and PbTiO$_3$. These new piezoelectric ceramics have a large k_t and k_t/k_p.

Elimination of dicing altogether, and a much better matching to the acoustic impedance of tissue has been achieved with piezoelectric polymers such as PVDF and its copolymer.[8,9] However, the performance of such transducers is limited by a low electromechanical coupling factor. In this respect, intensive work has been carried out on PZT/polymer composites having a high electromechanical coupling factor and a low acoustic impedance.[10-12] The authors have developed high-frequency PZT/polymer composite sheets (PZT pillars embedded in a polymer matrix) and applied them to medical ultrasonic probes.[10]

This paper first describes the electromechanical properties of modified lead titanate ceramics (Pb, Sm)(Ti, Mn)O$_3$. It then presents the crystallographic and electromechanical properties of modified PbZrO$_3$ ceramics, and compares the two ceramic systems. Finally, it provides a description of PZT/polymer composites and their properties.

§2. Modified Lead Titanate Ceramics

The modified lead titanate ceramics that were investigated have the chemical formula (Pb$_{1-(3x/2)}$Ln$_x$)(Ti$_{1-y}$Mn$_y$)O$_3$ (Ln=rare-earth). These ceramics were prepared using conventional ceramic fabrication techniques, and poled in silicone oil at 150°C for 10 min. The poling field dependence of the electromechanical properties was examined carefully The planar coupling factor, k_p, and thickness dilatational coupling factor, k_t, are shown as functions of the poling field, E_p, in Fig. 1. Here, Ln=La, Nd, Sm, or Gd and the composition was fixed at $x=0.08$ and $y=0.02$.

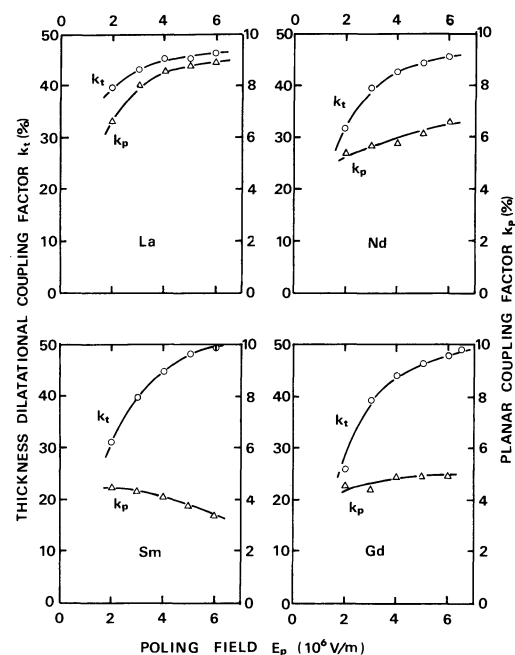It was found that the relationship of the coupling factor to the poling field had noticeably different features

Fig. 1. Planar coupling factor k_p and thickness dilatational coupling factor k_t for (Pb$_{0.88}$Ln$_{0.08}$)(Ti$_{0.98}$Mn$_{0.02}$)O$_3$ ceramics as a function of poling field (Ln=La, Nd, Sm or Gd) (reference 3).

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for various rare-earths. Particularly, the planar coupling factor, k_p, decreased gradually with an increase in the poling field $(2 \sim 6 \times 10^6$ V/m) for Ln=Sm. This unusual property caused exceptionally enhanced electromechanical coupling anisotropy in the $PbTiO_3$ ceramics. The same phenomenon is observed in the $(Pb_{1-x}Ca_x)[(Co_{1/2}W_{1/2})_y Ti_{1-y}]O_3 + MnO(NiO)$ ceramic system.[5]

Another aspect of Fig. 1 is that the poling field dependence curve for the coupling factor, k_t, becomes steeper as the rare-earth ionic radius decreases. This behavior is probably related to variations in the ferroelectric domain structure caused by changes in the tetragonality of the crystal lattice.

It was thus felt desirable to determine the electromechanical properties of the (Pb, Sm)(Ti, Mn)O_3 system in detail. In this connection, the electromechanical coupling factor ratio, k_t/k_p, is given as a function of Sm concentration in Fig. 2. Here, Mn concentration, y, was 0.02, and the poling field was fixed at $E_p = 6 \times 10^6$ V/m. This ratio, which indicates electromechanical anisotropy, produced a characteristic curve with a maximum at $x=0.08$.

The dependence of electromechanical properties on the Mn concentration was examined fixing Sm concentration at $x=0.08$. Results are shown in Fig. 3. The electromechanical coupling factor, k_t, did not noticeably depend on Mn concentration, where-as k_p had a minimum value at $y=0.015$. As a result, the greatest electromechanical anisotropy occured when $x=0.08$ and $y=0.015$ in a $(Pb_{1-(3x/2)}Sm_x)(Ti_{1-y}Mn_y)O_3$ ceramic system. The maximum value of k_t/k_p was 17.
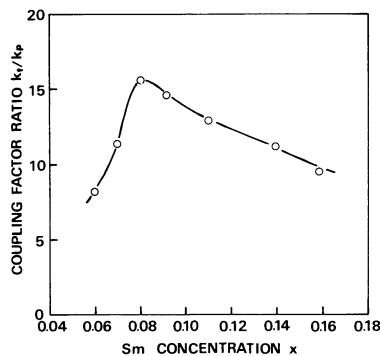
Yamashita *et al.* have suggested that infinite k_t/k_p

Fig. 2. Electromechanical coupling factor ratio k_t/k_p for $(Pb_{1-(3x/2)}Sm_x)(Ti_{0.98}Mn_{0.02})O_3$ as a function of Sm concentration (reference 6).
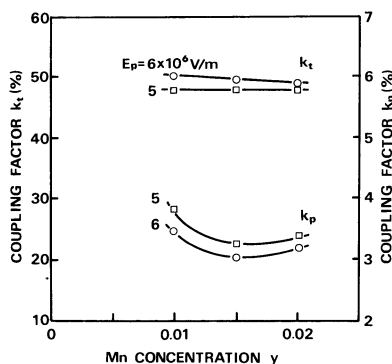
Fig. 3. Electromechanical coupling factors k_t and k_p for $(Pb_{0.88}Sm_{0.08})(Ti_{1-y}Mn_y)O_3$ as a function of Mn concentration.

could be attained in a $(Pb_{1-x}Ca_x)[(Co_{1/2}W_{1/2})_y Ti_{1-y}]O_3 + MnO(NiO)$ ceramic system because no planar resonant signals are observed at room temperature.[5] This same phenomenon also occurs in our ceramic system. In this case, however, we determined k_p by extrapolating the temperature characteristic curve to room temperature, since the resonant signal could often be observed around room temperature, even though it was very weak.

These are the results of the modification of $PbTiO_3$ ceramics already known to have relatively large electromechanical anisotropy.[13] Previously unknown results regarding $PbZrO_3$ are looked at in the next section.

§3. Modified Lead Zirconate Ceramics

Pure lead zirconate, $PbZrO_3$, is an anti-ferroelectric (orthorhombic) crystal having a Curie temperature of 230°C. Therefore, some modification is required to obtain piezoelectric $PbZrO_3$ ceramics. That is, it is necessary to induce a morphotropic phase transition to a ferroelectric phase by incorporating some additives. In the present work, $PbTiO_3$ and $Pb(Mn_{1/3}Nb_{2/3})O_3$ were used as additives. The phase diagram and electromechanical properties of the ternary system $PbZrO_3$–$PbTiO_3$–$Pb(Mn_{1/3}Nb_{2/3})O_3$ have already been reported on,[14] except near the anti-ferroelectric phase, Aα. In the authors' work, crystallographic and electromechanical properties for the $(1-x-y)PbZrO_3 + xPb(Mn_{1/3}Nb_{2/3})O_3 + yPbTiO_3$ system were determined in the ferroelectric rhombohedral phase near the anti-ferroelectric orthorhombic phase $(x, y < 0.2)$.

These modified $PbZrO_3$ ceramics were also prepared using conventional fabrication techniques. The final products were examined by X-ray diffraction using $CuK\alpha$ to determine crystallographic properties. Specimens were polished to a mirror finish, and annealed at 500°C for 1h to facilitate X-ray measurements. Poling was carried out at 100°C under a dc field of $4 \sim 6 \times 10^6$ V/m for 10 min to determine electromechanical properties.

Lattice parameters of the $(1-x-y)PbZrO_3 + xPb(Mn_{1/3}Nb_{2/3})O_3 + yPbTiO_3$ ceramic system are shown in Fig. 4 as a function of $PbTiO_3$ content, y. The $Pb(Mn_{1/3}Nb_{2/3})O_3$ content, $x=0.05$ and 0.10). The thickness the figure, lattice parameters for the rhombohedral phase(s) are shown. For example, the system is orthorhombic when $y=0.025$ for $x=0.025$. The lattice parameters (lattice constant, distortion angle, and unit cell volume) varied systematically with $PbTiO_3$ and $Pb(Mn_{1/3}Nb_{2/3})O_3$ content. This indicates that these additives were properly incorporated into the $PbZrO_3$ lattice.

Electromechanical coupling factor k_t and k_p are shown in Fig. 5 as a function of $PbTiO_3$ content, y ($Pb(Mn_{1/3}Nb_{2/3})O_3$ content, $x = 0.05$ and 0.10). The thickness dilatational coupling factor, k_t, did not noticeably change with $PbTiO_3$ content, and had a relatively large value (0.43 ~ 0.48). In contrast to k_t, the planar coupling factor, k_p, decreased notably with the decrease in $PbTiO_3$ content. Change was abrupt at $y=0.05$ for $x=0.05$, and $y=0.025$ for $x=0.10$. It should be noted that k_p is as low as 0.02 when $y=0$ and $x=0.05$. An electromechanical coupling factor ratio k_t/k_p of 24 was attained with this
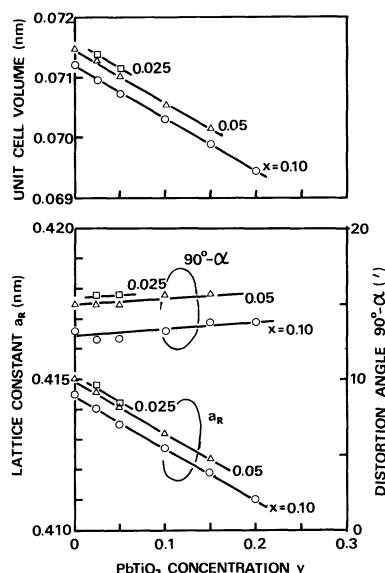
Fig. 4. Lattice parameters for $(1-x-y)\text{PbZrO}_3+x\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})$ $\text{O}_3+y\text{PbTiO}_3$ ceramics as functions of PbTiO_3 concentration.
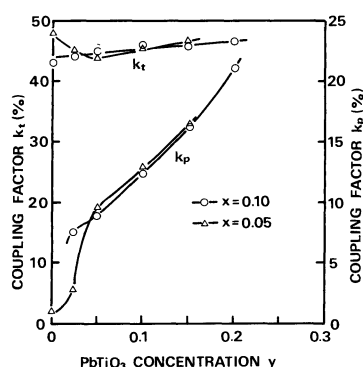

Fig. 5. Electromechanical coupling factors k_t and k_p for $(1-x-y)$ $\text{PbZrO}_3+x\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3+y\text{PbTiO}_3$ ceramics.
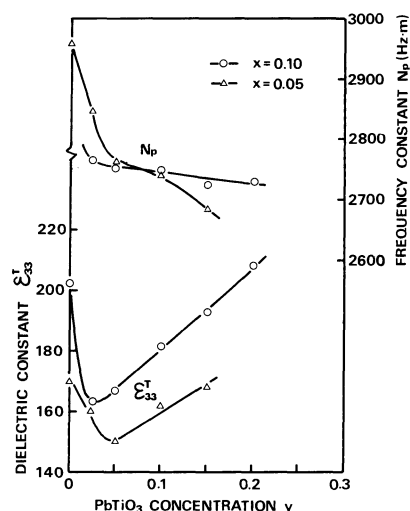

Fig. 6. Dielectric constant and frequency constant for $(1-x-y)$ $\text{PbZrO}_3+x\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3+y\text{PbTiO}_3$ ceramics.

composition.

Frequency constants for planar vibration, N_p, and dielectric constant, ε_{33}^T, are given in Fig. 6 as a function of PbTiO_3 content, y. The change in these material constants was also abrupt at $y=0.05$ for $x=0.05$, and $y=0.025$ for $x=0.10$. These results may be due to the

fact that there is a morphotropic phase boundary in the rhombohedral phase although no noticeable change could be observed in the lattice parameters. The existence of two rhombohedral phases (Fα, Fα') with similar crystal structure has already been reported in Pb(Zr, Ti) O$_3$[15] and (Pb, La)(Ti, Zr)O$_3$[16] systems.

It is concluded, therefore, that the electromechanical anisotropy of modified PbZrO$_3$ ceramics is extremely large in their rhombohedral Fα' phase especially at the boundary composition between Fα' and Aα.

§4. Comparison between Modified PbTiO$_3$ and PbZrO$_3$ Ceramics

The large degree of electromechanical anisotropy in modified PbTiO$_3$ ceramics may be partly due to large lattice anisotropy, c/a, of the tetragonal lattice. However, lattice anisotropy is small in modified PbZrO$_3$ ceramics (rhombohedral distortion angle is 15'). In this case, enhanced electromechanical anisotropy is considered to be related to elastic and dielectric anomalies in the morphotropic phase boundary (A$\alpha\leftrightarrow$Fα', F$\alpha'\leftrightarrow$Fα).

Electromechanical and dielectric properties of (Pb$_{0.88}$Sm$_{0.08}$) (Ti$_{0.985}$Mn$_{0.015}$)O$_3$ and 0.95PbZrO$_3$+0.05Pb (Mn$_{1/3}$Nb$_{2/3}$)O$_3$ ceramics are summarized in Table I. It is interesting that the modified ceramics of two end members of Pb(Zr, Ti)O$_3$ have similar electromechanical properties in spite of their different crystallographic properties.

The modified PbZrO$_3$ ceramics have a low dielectric loss and low Curie temperature compared to modified PbTiO$_3$ ceramics. This latter characteristic is a disadvantage in practical use. Despite this point, modified PbZrO$_3$ ceramics are also useful piezoelectric materials for high-frequency ultrasonic transducer applications.

§5. PZT/polymer Piezoelectric Composites

Recently, piezoelectric composites (PZT/polymer) having various structures have been intensively analyzed for ultrasonic transducer applications.[17] These composites can be classified according to Newnham's connectivity theory.[18] The 1–3 connectivity (PZT pillar embedded in a polymer matrix) is reported to be useful for high-frequency transducer applications.[19,20] Currently, intensive work has been carried out to obtain high-frequency 1–3 composites and apply them to medical ultrasonic probes.[10–12] Furthermore, the dynamic behavior of the thickness mode has been analyzed theoretically in 1–3 composites.[21,22]

In the present work, high-frequency PZT/polymer 1–3

Table I. Material Constants of Modified PbTiO$_3$ and PbZrO$_3$ Ceramics

Material Constant	PbTiO$_3$	PbZrO$_3$
k_t	0.50	0.48
k_p	0.03	0.02
k_t/k_p	17	24
ε_{33}^T	175	170
$\tan\delta$	0.002	0.0009
N_t	2200 Hz·m	2250 Hz·m
N_p	2690	2950
T_c	355°C	250°C

composite sheets were fabricated using a "dicing and filling" technique. Dielectric and electromechanical properties of the composites were then determined in detail as a function of the PZT volume fraction and PZT pillar shape. The fabrication procedure is described in the succeeding paragraph.

A poled PZT plate was attached to a ferrite substrate and diced into a large number of small pillars as shown in Fig. 7(a). The interpillar spaces were then filled with polyurethane. Following a 10h setting time at room temperature, the composite was stripped from the substrate (Fig. 7(b)). The PZT pillar size and volume fraction were varied by changing blade thickness and dicing pitch. Since PZT was already poled, poling was not required after preparation.

A number of composites with different PZT pillar shape and volume fractions were prepared according to this procedure. The resulting composites were highly flexible, as shown in Fig. 8. Finally, chromium-gold films were then deposited as electrodes onto both surfaces of the composites.

Typical 25%-PZT composite impedance characteristics are shown in Fig. 9. Here, the thickness of the composite is 0.4 mm. As a result of the polyurethane matrix damping effect, a single resonant curve with no observable spurious response was obtained. The mechanical quality factor, Q_m, determined from the resonant cuve was $10 \sim 20$ depending on the PZT pillar shape.[23]

The electromechanical coupling factor for thickness dilatational vibration, k_t, and the dielectric constant, ε_{33}^T, are demonstrated as a function of the PZT volume fraction, v_{PZT}, in Fig. 10. Here, PZT pillar shape is constant (width-to-thickness ratio $w/t = 0.5$). The dielectric constant decreased almost linearly with a decrease in v_{PZT}. On the other hand, the coupling factor, k_t, had a maximum value (0.75) at $v_{PZT} = 0.25$. The authors believe that such a systematic v_{PZT} dependence of k_t has not yet been explained. It is interesting to compare the result with the expected v_{PZT} dependence of d_h (hydrostatic piezoelectric
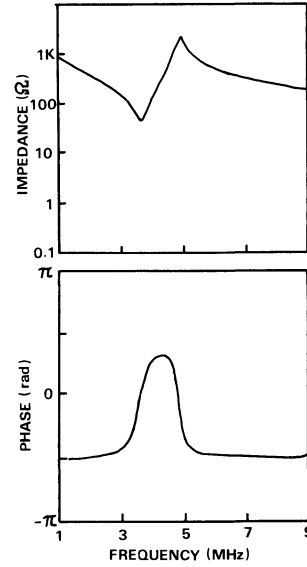
Fig. 9. Impedance and phase characteristics of 25%-PZT composite (thickness is 0.4 mm) (reference 10).
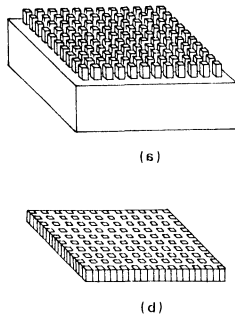
Fig. 7. Preparation process of PZT/polymer 1-3 composite sheets: (a) dicing process: (b) composite stripped from substrate.
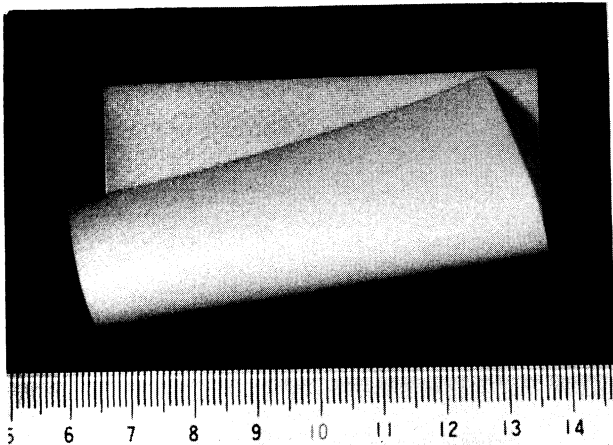
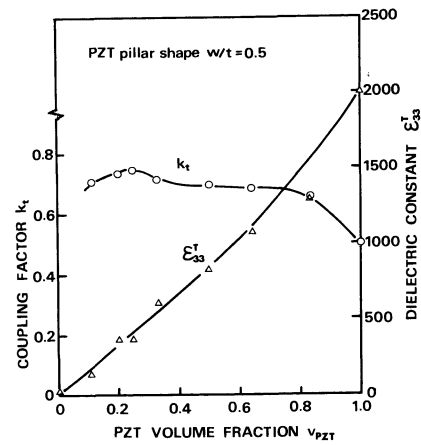Fig. 8. Typical PZT/polyurethane 1-3 composite sheet (25% PZT).

Fig. 10. Electromechanical coupling factor k_t and dielectric constant ε_{33}^T of composite as a function of PZT volume fraction (reference 10).
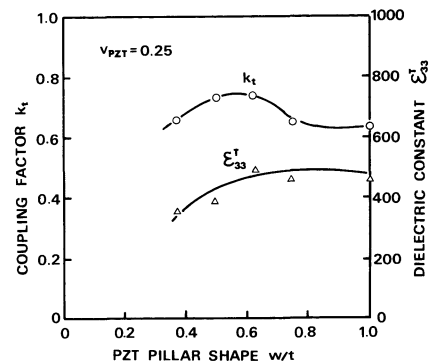
Fig. 11. Electromechanical coupling factor k_t and dielectric constant ε_{33}^T of composite as a function of PZT pillar shape (reference 10).

constant).[24] The value of d_h was also expected to be maximum at $v_{PZT}=0.25$.

The PZT pillar shape (w/t) dependence of k_t and ε_{33}^T is given in Fig. 11. In this case, v_{PZT} was constant (0.25). The dielectric constant, ε_{33}^T, had a tendency to decrease as the pillar shape factor, w/t, decreased. This result implies that the distribution of the electric flux changes with the w/t in PZT pillars and the polyurethane matrix. The coupling factor, k_t, reached a maximum at w/t $=0.5 \sim 0.6$. It should be noted that ε_{33}^T and k_t can not be determined solely from the PZT volume fraction.

These composites look to be very promising materials for medical ultrasonic probe application. They simultaneously offer both high electromechanical coupling, and low acoustic impedance.

§6. Summary

The authors have developed new piezoelectric materials for use in medical ultrasonic trsnsducers: two types of piezoelectric ceramics with a large electromechanical anisotropy, and PZT/polymer flexible composites with a high electromechanical coupling factor and low acoustic impedance. These are summarized below.

1) Electromechanical properties of modified lead titanate ceramics $(Pb_{1-(3x/2)}Ln_x)(Ti_{1-y}Mn_y)O_3$ (Ln=rare-earth) were determined placing emphasis on electromechanical anisotropy. It was found that Sm substitution for Pb dramatically increased the electromechanical coupling factor ratio, k_t/k_p. This is because the planar coupling factor, k_p, decreases gradually when the poling field is increased from 2×10^6 to 6×10^6 V/m, while the thickness dilatational coupling factor, k_t, increases normally. The k_t/k_p ratio was found to be as large as 17 when $x=0.08$ and $y=0.015$ for Ln=Sm.

2) Large electromechanical anisotropies were also found in ferroelectric $PbZrO_3$ ceramics modified by adding small amounts of $Pb(Mn_{1/3}Nb_{2/3})O_3$ and $PbTiO_3$. These ceramics, $(1-x-y)PbZrO_3+xPb(Mn_{1/3}Nb_{2/3})O_3+yPbTiO_3$, have exteremely large electromechanical anisotropies in the rhombohedral $F\alpha'$ phase. The k_t/k_p ratio is 24 for $x=0.05$ and $y=0$. This is a boundary composition between the anti-ferroelectric orthorhombic phase, $A\alpha$, and the $F\alpha'$ phase.

3) High-frequency PZT/polymer 1-3 composite sheets were fabricated using a "dicing and filling" technique. These composites are very flexible piezoelectric materials. It was found that dielectric and electromechanical properties depend not only on PZT volume fraction, v_{PZT}, but also on PZT pillar shape, w/t. The electromechanical coupling factor, k_t, was as high as 0.75 when v_{PZT} $=0.25$ and $w/t=0.5 \sim 0.6$ in the PZT/ polyurethane composite.

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