AD-A279 235 N PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
February 1994

3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE
New Materials for Large Strain Actuator Applications

5. FUNDING NUMBERS
PE - 61153N
WU - RR011
TA - DN580-030

2

6. AUTHOR(S)
Dr. K.M. Rittenmyer and Dr. R.Y. Ting

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
NAVAL RESEARCH LABORATORY
Underwater Sound Reference Detachment
P.O. Box 568337
Orlando, FL 32837

DTIC
ELECTE
MAY 17 1994
S F D

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND AD…(ES)
OFFICE OF NAVAL RESEARCH
800 N. Quincy Street
Arlington, VA 2217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published as Proceedings Reprint of SPIE - The International Society of Optical Engineering, Smart Structures and Materials 1994, 14-16 Feb 1994, Orlando, FL, Volume 2189, pp. 1-13.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Several new materials capable of generating large strains under an electric field are being developed for applications as actuators and high-drive sonar projectors. These materials are capable of generating strains which are several times larger than those produced by conventional lead zirconate-titanate ceramics. The first group of materials are the class of lead magnesium niobate-lead titanate (PMNPT) ceramics. These materials are electrostrictive and, therefore, are operated under dc bias fields. The largest strains are obtained when the temperature is maintained in the region of the order-disorder phase transition of the material. This, however, makes the properties of the material temperature dependent. An alternative material is the family of lanthanum-modified lead zirconate-titanate (PLZT) ceramics. These materials have been developed extensively for electrooptic applications. They can generate even higher levels of strain compared with the PMNPT ceramics with less temperature dependence. They, however, suffer from higher dielectric hysteresis and are more suitable for actuator applications because of dielectric heating. Results are presented for measurements on several compositions of PMNPT and PLZT.

14. SUBJECT TERMS
Lead Magnesium-Lead Titanate
Actuator
Transducer
Lead Lanthanum
Zirconate-Titanate
Electrostriction

15. NUMBER OF PAGES

16. PRICE CODE
13

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

GENERAL INSTRUCTIONS FOR COMPLETING SF 298

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to *stay within the lines* to meet ***optical scanning requirements***.

Block 1. Agency Use Only *(Leave blank)*.

Block 2. Report Date. Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least the year.

Block 3. Type of Report and Dates Covered. State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10 Jun 87 - 30 Jun 88).

Block 4. Title and Subtitle. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses.

Block 5. Funding Numbers. To include contract and grant numbers; may include program element number(s), project number(s), task number(s), and work unit number(s). Use the following labels:

C - Contract
G - Grant
PE - Program Element
PR - Project
TA - Task
WU - Work Unit Accession No.

Block 6. Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s).

Block 7. Performing Organization Name(s) and Address(es). Self-explanatory.

Block 8. Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report.

Block 9. Sponsoring/Monitoring Agency Name(s) and Address(es). Self-explanatory.

Block 10. Sponsoring/Monitoring Agency Report Number. *(If known)*

Block 11. Supplementary Notes. Enter information not included elsewhere such as: Prepared in cooperation with...; Trans. of...; To be published in.... When a report is revised, include a statement whether the new report supersedes or supplements the older report.

Block 12a. Distribution/Availability Statement. Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NOFORN, REL, ITAR).

DOD - See DoDD 5230.24, "Distribution Statements on Technical Documents."
DOE - See authorities.
NASA - See Handbook NHB 2200.2.
NTIS - Leave blank.

Block 12b. Distribution Code.

DOD - Leave blank.
DOE - Enter DOE distribution categories from the Standard Distribution for Unclassified Scientific and Technical Reports.
NASA - Leave blank.
NTIS - Leave blank.

Block 13. Abstract. Include a brief *(Maximum 200 words)* factual summary of the most significant information contained in the report.

Block 14. Subject Terms. Keywords or phrases identifying major subjects in the report.

Block 15. Number of Pages. Enter the total number of pages.

Block 16. Price Code. Enter appropriate price code *(NTIS only)*.

Blocks 17. - 19. Security Classifications. Self-explanatory. Enter U.S. Security Classification in accordance with U.S. Security Regulations (i.e., UNCLASSIFIED). If form contains classified information, stamp classification on the top and bottom of the page.

Block 20. Limitation of Abstract. This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited.

PROCEEDINGS REPRINT

SPIE–The International Society for Optical Engineering

Reprinted from

Smart Structures and Materials 1994

Smart Materials

14–16 February 1994
Orlando, Florida

Accesion For		
NTIS CRA&I		☑
DTIC TAB		☐
Unannounced		☐
Justification		
By		
Distribution /		
Availability Codes		
Dist	Avail and / or Special	
A-1	20	

Volume 2189

Box 10, Bellingham, Washington 98227 USA. Telephone 206/676-3290.

New Materials for Large Strain Actuator Applications

Kurt M. Rittenmyer and Robert Y. Ting

U.S. Naval Research Laboratory
Undewater Sound Reference Detachment
P.O. Box 568337
Orlando, Florida 32856-8337

ABSTRACT

Several new materials capable of generating large strains under an electric field are being developed for applications as actuators and high-drive sonar projectors. These materials are capable of generating strains which are several times larger than those produced by conventional lead zirconate-titanate ceramics. The first group of materials are the class of lead magnesium niobate-lead titanate (PMNPT) ceramics. These materials are electrostrictive and, therefore, are operated under dc bias fields. The largest strains are obtained when the temperature is maintained in the region of the order-disorder phase transition of the material. This, however, makes the properties of the material temperature dependent. An alternative material is the family of lanthanum-modified lead zirconate-titanate (PLZT) ceramics. These materials have been developed extensively for electrooptic applications. They can generate even higher levels of strain compared with the PMNPT ceramics with less temperature dependence. They, however, suffer from higher dielectric hysteresis and are more suitable for actuator applications because of dielectric heating. Results are presented for measurements on several compositions of PMNPT and PLZT.

INTRODUCTION

Two new families of materials have been developed which are capable of generating strains that are several times larger than those of PZT ceramics. The first group of materials are the lead magnesium niobate-lead titanate (PMN-PT) ceramics[1-6]. The second family of ferroelectric materials is the lead lanthanum zironate-titanate (PLZT) ceramics[7,8]. These materials show promise for applications as actuators and in small reduced-weight sonar projectors because they exhibit large field-induced strain, low electromechanical hysteresis, high effective d_{33} and high energy density. The electromechanical properties of these materials are analagous to magnetostrictive materials such as Terfenol in that the strain and electric polarization (which is analagous to magnetization) are related quadratically . Both PMNPT and PLZT belong to a class of materials known as relaxor ferroelectrics[2] which are distinguished from normal ferroelectric materials by a ferroelectric phase transition from a nonpolar phase to a polar phase that occurs over a very broad range of temperature of up to 100°C or more. The phase transition is characterized by a high dielectric permittivity peak value which is dependent on frequency, and shifts in temperature as a function of frequency as shown in Fig. 1. Also shown is the behavior of the polarization which, unlike ordinary ferroelectrics, starts to decrease below the temperature of the maximum in the dielectric permittivity and tails off slowly toward zero rather than showing the usual abrupt drop to zero at the Curie temperature. The phase transition is also characterized by ferrolectric hysteresis

0-8194-1484-0/94/$6.00

loops which do not open abruptly at the Curie temperature but rather decay slowly into just nonlinear dielectric behavior over a range of temperature. In addition, X-ray diffraction patterns of the material shows no line splitting due to the loss of symmetry of the unit cell of the crystal lattice as the material is cooled through the ferroelectric phase transition temperature. Instead, the phase transition results from an ordering of some of the ions within the unit cell from a disordered state at high temperature. There are three distinct regions in the dielectric permittivity versus temperature curve (Fig. 1). Below T_d, the depolarization temperature, the material has large polarization and the material is piezoelectric (region I). Above the temperature of maximum dielectric pemittivity, T_m, purely electrostrictive behavior occurs (region III). In between T_m and T_d, the material shows a mixed behavior (region II). In region II, there is great potential for applications because of the large dielectric permittivity which induces large strains via the electrostrictive effect. Of course, for many applications, region I, where the material behaves as a normal piezoelectric, is of interest. Because the transition occurs at low temperatures and over such a broad range of temperature, and the properties of the material likewise vary slowly with temperature, it is possible, unlike ordinary ferroelctrics, to utilize relaxor ferroelectrics within the temperature region of their phase transition where the dielectric and piezoelectric properties of the materials are greatly enhanced. In the following, results of the investigation of the temperature-dependent piezoelectric properties of several compositions of PMNPT and PLZT which were chosen specifically for transducer applications are described.

EXPERIMENTAL

Sample Preparation

Pellets of each composition listed in Table 1 were processed by a modified columbite precursor technique[6] where MgO and Nb_2O_5 are reacted at 1100°C and then PbO is added and calcined at 800°C. After the powders are milled, they are pressed into pellets with a binder which is then burned out at 500°C. The pellets were then pressed at 300 MPa and fired at 1185°C for 3 hours.

The PLZT material $(Pb_{0.93}La_{0.07}(Zr_{0.58}Ti_{0.42})_{1-x}Nb_x^{5+}O_3$ was prepared by mixing PbO, TiO_2, ZrO_2 powders and calcining them at 700-800°C; the calcined materials were ball-milled in acetone to reduce the particle size to approximately 6 µm and the powders were cold-pressed into pellets and then hot forged at 1175-1200°C at pressures greater than 1000 psi in oxygen to over 98% of theoretical density. This particular composition of PLZT is piezoelectric. Therefore, it was poled at 20-25 kV/cm in a silicone oil bath.

Property Measurements

A laser Doppler vibrometer (Dantec model 55L) was used to measure the strain in the ceramic samples as a function of frequency, temperature and electric field. The range of frequency which can be measured is 0.1-100 kHz. The technique and experimental procedures have been described previously[9]. A diagram of the apparatus is shown in Fig. 2. The d_{33} coefficients were determined by measuring the longitudinal strain of a rectangular sample with nominal dimensions of 17x8x2 mm. For measurements of d_{31}, the sample was mounted on edge with epoxy and the laser was focused on the opposite edge. A variable dc bias voltage was applied to the sample through a 10-kΩ resistor using a power supply which is capable of supplying 0-10 kV dc. The power amplifier outputs an audio signal (0.1-10 kHz) of magnitude from 10-50 V_{rms} that is then applied to the sample through a blocking capacitor (0.2 μF) which protects the output of the of the signal amplifier from the large dc voltage but allows the ac signal to pass with minimal influence. The velocity amplitude of the vibrating sample surface is measured by the LDV system and the strain is calculated from the velocity. The appropriate piezoelectric coefficient (d_{33} or d_{31}) is then calculated from the measured strain and the ac-electric field. The dc-bias fields up to 10 kV/cm were applied to the samples. Silicone grease was used on the edges of the sample to prevent dielectric breakdown.

Table 1.

Compositions of PMN-PT investigated

%PMN	%PT	Dopant	%Dopant	Designation
92.5	7.5	Sr	2.5	S250075
91.0	9.0	Sr	2.5	S250090
91.0	9.0	Sr	4.0	S400090
90.0	10.0	Ba	3.0	B300100
90.0	10.0	Ba	5.0	B500100
88.0	12.0	Ba	2.0	B200120
85.9	14.1	Sr	2.5	S250141

The temperature dependence of the dielectric and piezoelectric properties of the materials was determined by placing the sample and holder in a liquid nitrogen-cooled environmental chamber equipped with a window through which the laser can be focused at a point on the sample surface. The temperature was varied in the range from 5°C to 60°C which covers the temperature range where the generated strains of the material are large. In some cases, this range was extended from -20°C to 90°C. The dielectric properties of relaxor ferroelectrics such as PMN and PMNPT are time-dependent in the region of the order-disorder phase transition. The values of the dielectric and piezoelectric properties are therefore dependent on the rate at which the sample is heated and cooled as well as the amount of time the sample is left to stabilize. The sample was therefore left to stabilize at least 20 mins after each temperature change. The change in the sample measurements after this time was fairly negligible.

RESULTS

Results of the laser Doppler measurements of d_{33} for a sample of composition S250075 are shown in Fig. 3. The d_{33} coefficient increases monotonically with applied electric field up to 10 kV/cm and is seen to be strongly dependent on temperature. The highest d_{33} values of 500×10^{-12} m/V are observed at the lowest measured temperature and the highest field used. The values are seen to decrease steadily with increasing temperature. At 60°C, the highest observed value of d_{33} is 170×10^{-12} m/V at 10 kV/cm. The d_{31} coefficient was measured and has a field and temperature dependence similar to that of the d_{33} coefficient. The ratio of d_{31} to d_{33} is fairly constant with values between 0.33 and 0.37 and is independent of the applied field.

Results of the d_{33} measurement for S250090, which has 1.5% higher $PbTiO_3$ content is shown in Fig. 4. At 5-10°C, a maximum of 550×10^{-12} m/V in the d_{33} is observed at an applied field of about 7 kV/cm. This maximum shifts to higher fields as the temperature increases. The d_{33} value decreases steadily as the temperature is increased and above 20°C, no maximum is observed as a function of field. Unlike S250075, the ratio of d_{31} to d_{33} is observed to decrease steadily from 0.42 to 0.26 as the temperature is raised (Fig. 5). This implies that d_{31} is falling more rapidly with temperature compared with d_{33}.

Increasing the level of Sr doping from 2.5% to 4.0% shifts the peaks in the d_{33} versus E curves to higher field levels and decreases the d_{33} values as shown in Fig. 6 for S400090 where the peak d_{33} value is about 440×10^{-12}m/V at 5°C. The maximum d_{33} was measured at the lowest temperature and steadily decreases with temperature. The ratio of d_{31} to d_{33} decreases slightly with temperature.

The d_{33} values of S250141 are plotted in Fig. 7 as a function of electric field and temperature. Maximums in d_{33} are observed at nearly all measured temperatures. The maximum is observed to shift with electric field at 15°C per kilovolt for this composition and the highest d_{33} of 650×10^{-12} m/V is observed in the range of temperature 20-30°C. The ratio, $-d_{31}/d_{33}$, was found to be independent of temperature with a value of 0.38.

For the Ba-doped material, B500100, the maximum d_{33} value of about 310×10^{-12} m/V is observed (Fig. 8). The d_{31}/d_{33} ratio varies from 0.38 at 60°C to near 0.6 at 5°C. The composition B200120 exhibits the highest d_{33} coefficients of any of the compositions examined (Fig. 9) with a maximum effective d_{33} of about 800×10^{-12} m/V. The peak, however, shifts fairly drastically with field and temperature. Destruction of the sample prevented determination of d_{31}.

The results of the d_{33} measurement for the piezoelectric PLZT sample are shown in Fig. 10. It is seen to be somewhat temperature dependent but less so than the PMN-PT material. Values of d_{33} range from 650×10^{-12} m/V at 10°C to nearly 900×10^{-12} m/V at 60°C. The values are not strongly dependent on field if the field is applied in the direction of polarization. The polarization however is easily reversed in the material. It can be stabilized by applying a dc-bias field of the correct polarity to the material.

Table 2. Summary of Results for PMN-PT materials at peak values of d_{33}

Sample E_o,T_o	max d_{33} (pm/V)	at field, E_o (kV/cm)	at Temp, T_o (deg C)	$-d_{33}/d_{33}$ (pm/V)	d_h at (pm/V)
S250075	500	9.0	5^+	0.34	160
S250090	550	7.5	5^+	0.26-0.41	100
S400090	440	10.0*	5^+	0.36	120
S250141	700	7.0	20	0.38	170
B300100	480	7.8	10	0.45	50
B500100	310	10.0*	10^+	0.57	20
B200120	800	4.4	30	---	---

*-indicates maximum electric field tested.
$^+$- indicates minimum temperature tested.

DISCUSSION

The results show that all the tested PMN-PT materials generate substantial piezoelectric effects under moderate dc field levels, but the materials with higher PT/PMN ratios yield higher piezoelectric coefficents at least up to the highest ratio (14%) tested. The materials generally show maximums in their field-dependent effective d_{33} values so that, to achieve maximum sensitivity, a particular bias field must be applied. This is shown in Table 2. Comparison of the two 9% PT materials (S250090 and S400090, Figs. 4-6) show that small differences in doping change the behavior of the material fairly drastically although the peak obtainable d_{33} values are within 10% of each other. The decrease in the d_{31} value relative to d_{33} (Fig. 5) for S250090 is interesting for academic reasons because it implies that at high temperature (60°C), the d_h value should increase since

$$d_h = d_{33}\left(1 + \frac{2d_{31}}{d_{33}}\right) \tag{1}$$

and the ratio of d_{31} to d_{33} is negative. Unfortunately, d_{33} decreases with temperature also and at 60°C and a bias field of 10 kV/cm, d_{33} is only about 175×10^{-12} m/V. However, the possibility of finding a material with low d_{31} and consequently high d_h even over a limited temperature range is intriging. The material itself has reasonably high effective piezoelectric coefficients and could be a useful material.

The Ba-doped material appears to be strongly affected by small changes in composition. Comparison of the results for B300100 , B500100 (Fig. 8), and B200120 (Fig. 9) demonstrate this.

The latter material shows the highest d_{33} coefficent of any of the materials at a bias field of 4 kV/cm and a temperature of 30°C with a value of about 800×10^{-12} m/V.

The PLZT material appears to be an interesting material for actuator applications. Its high d_{33} and lower dependence on temperature possibly make it an attractive alternative to the PMN-based materials. The polarization, however, was observed to reverse slowly with time but at low applied fields. This will generate significant hysteresis. The material is therefore not suitable for sonar transducer application.

From the standpoint of piezoelectric properties, the material S250141 appears to be very attractive. The peaks in the d_{33} coefficient occurs at 25°C which is around room temperature for many applications. For most underwater applications, the material could be thermally stabilized at 25°C. The effective d_{33} of the material at a field of 7 kV/cm was about 650×10^{-12} which is almost a factor of three larger than that of the Navy type III lead zirconate-titanate ceramic commonly used in sonar projectors. However, the high-field dielectric and electromechanical losses hve not been considered yet. These must be considered for a high-drive sonar material before any conclusions can be drawn. The other materials considered still have high effective d_{33} coefficients relative to PZT materials and remain viable candidates depending on whether their high-field dielectric losses are sufficiently small. All of the materials could have application in actuators where electromechanical losses are not as deleterious to performance.

ACKNOWLEDGEMENTS

This work was funded by the Office of Naval Research.

REFERENCES

1. K. Uchino, "Electrostrictive Actuators: Materials and Applications," *Ceramic Bulletin*, vol. 65, pp. 647-654, 1986.

2. L.E. Cross, "Relaxor Ferroelectrics,"*Ferroelectrics*, vol.76, pp. 241-267, 1987.

3. Q. Zhang, W. Pan, A. Bhalla, and L.E. Cross, "Electrostrictive Response in Lead Magnesium Niobate-Lead Titanate (0.9PMN-0.1PT) and Lead Lanthanum Zirconate Titanate (PLZT 9.5/65/35) Under Variation of Temperature and Electric Field", *J. Am. Cer. Soc.*, vol. 72, pp. 599-604, 1989.

4. W.Y. Pan, W.Y. Gu, D.J. Taylor, and L.E. Cross, "Large Piezoelectric Effect Induced by Direct Current Bias in PMN:PT Relaxor Ferroelectric Ceramics," *Jpn. J. Appl. Phys.*, vol. 28, pp. 653-661, 1989.

5. S.M. Pilgrim, M. Massuda, J.D. Prodey and A.P. Ritter, "Electromechanical Properties of Some $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$-$(Ba,Sr)TiO_3$ Ceramics: I," *J. Am. Cer. Soc.*, vol. 75, pp. 1964-1969, 1992.

6. S.L. Swartz and T.R. Shrout, "Fabrication of Perovskite Lead Magnesium Niobate," *Mat. Res. Bull.*, vol. 17, pp. 1245-1250, 1982.

7. G.H. Haertling and C.E. Land, "Hot-pressed (Pb,La)(Zr,Ti)O_3 ferroelectric ceramics for electrooptic applications," *J. Am. Cer. Soc.*, vol. 54, pp. 1-11, 1971.

8. G.H. Haertling, "Improved hot-pressed electrooptic ceramics in the (Pb,La)(Zr,Ti)O_3 system," *J. Am. Cer. Soc.*, vol.54, pp. 303-309, 1971.

9. K.M. Rittenmyer, "Direct Measurement of the temperature-dependent piezoelectric coefficients of composite materials by laser Doppler vibrometry," *J. Acoust. Soc. Am.*, vol 91, pp. 2254-2260, 1992.

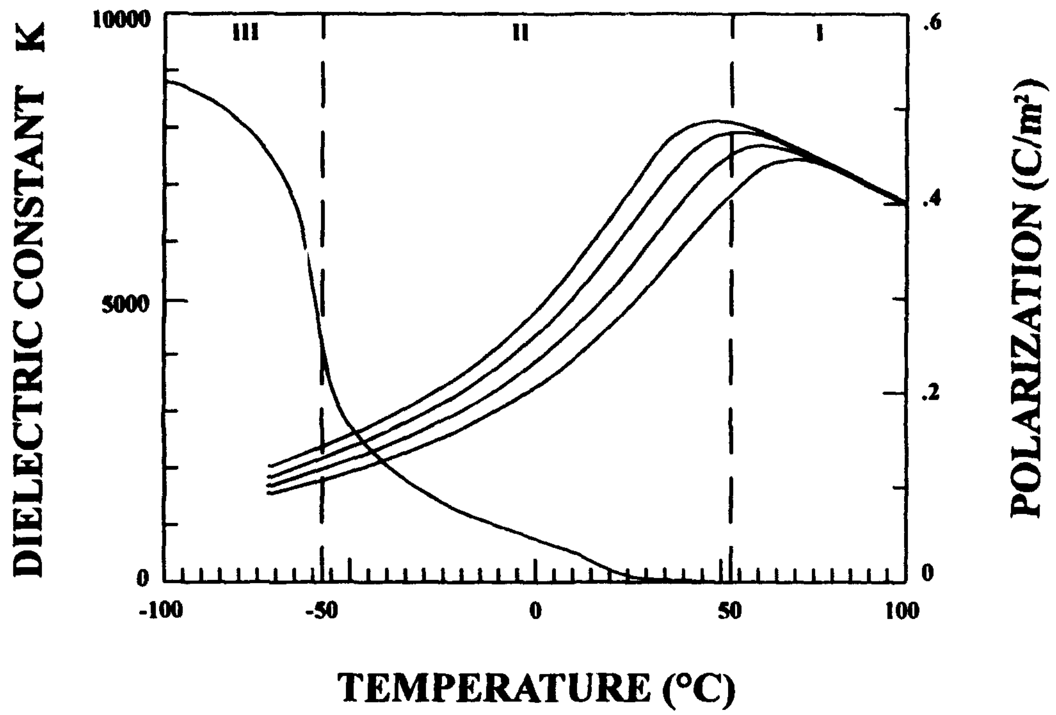

Fig. 1. Dielectric permittivity of a relaxor ferroelectric material versus temperature for several frequencies.

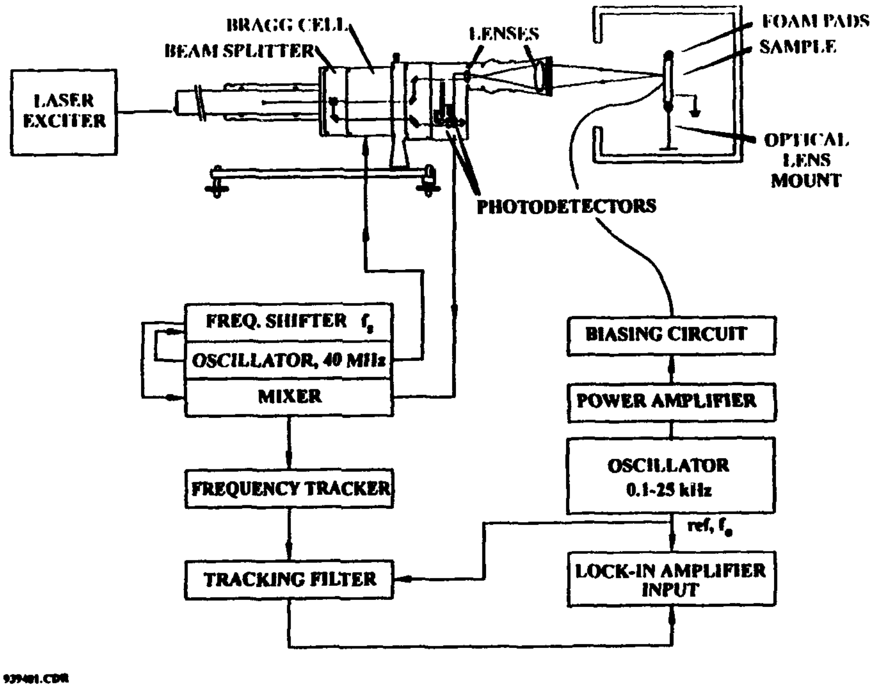

Fig. 2 Schematic diagram of laser Doppler vibrometer system used to measure strain produced in the piezoelectric and electrostrictive samples

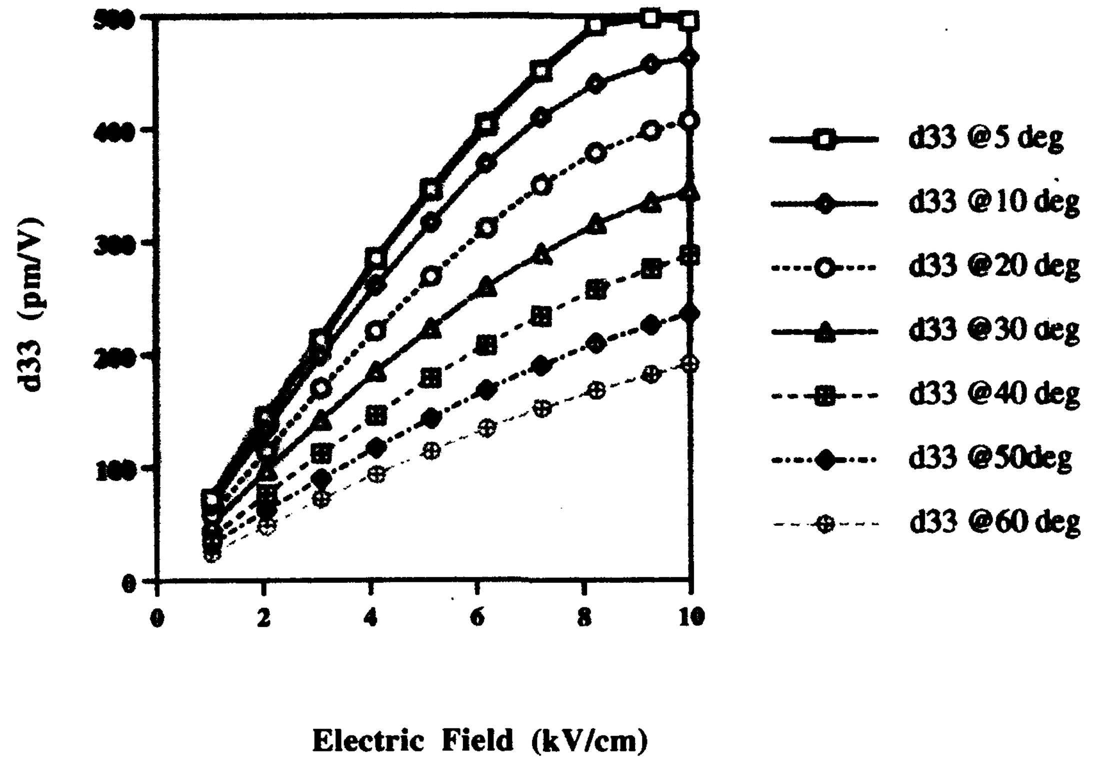

Fig. 3. Piezoelectric coefficient d_{33} for composition S250075 as a function of electric field for various temperatures.

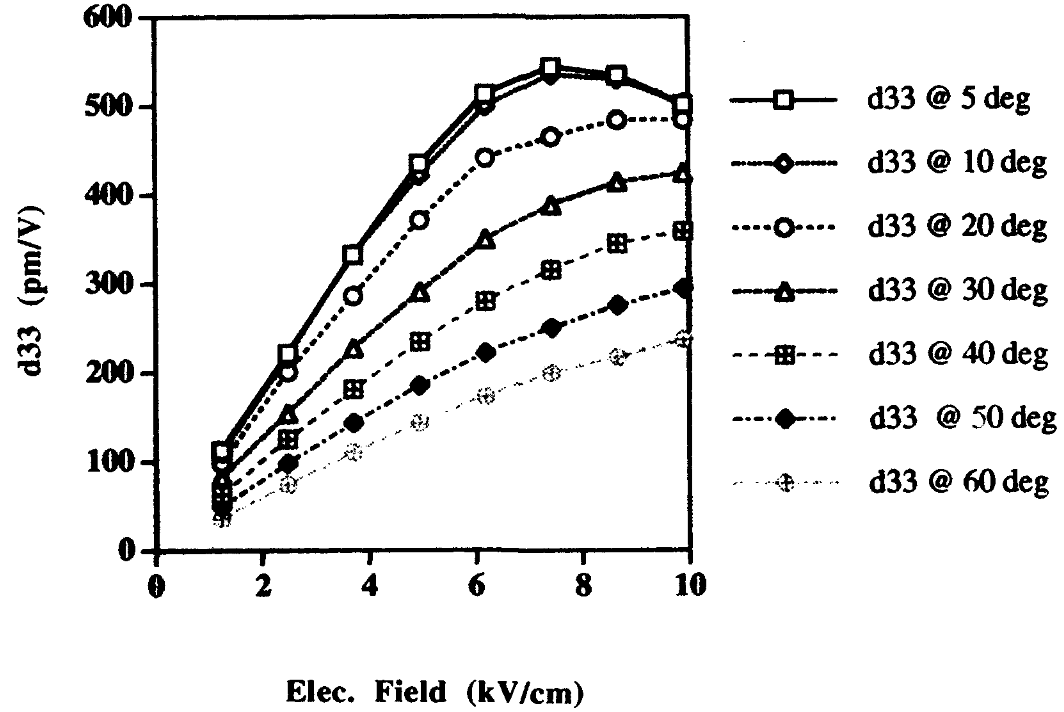

Fig. 4. Piezoelectric coefficient d_{33} for composition S250090 as a function of electric field for various temperatures.

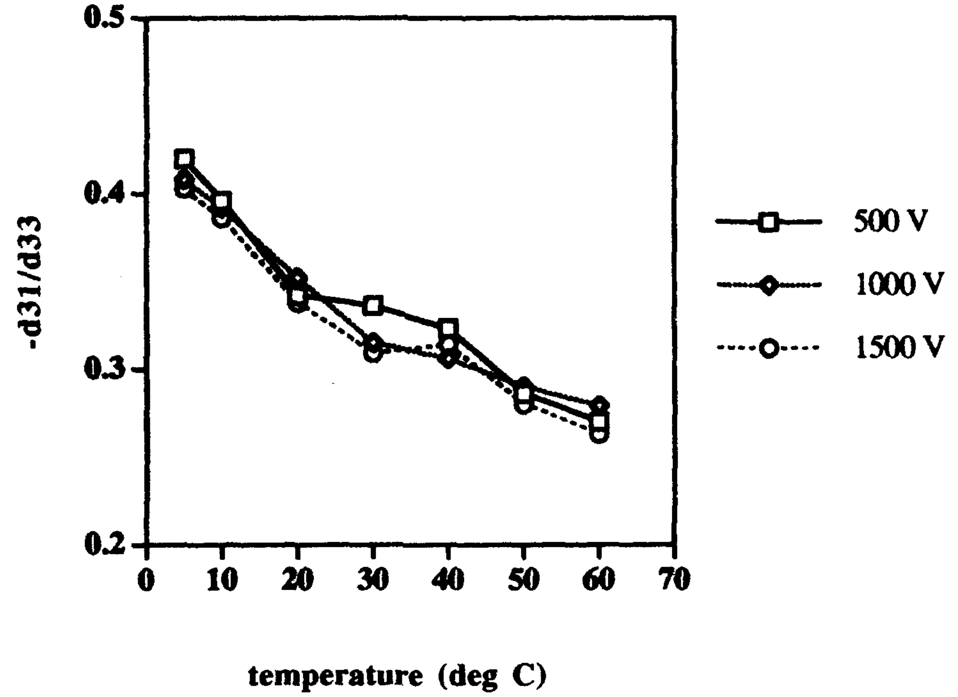

Fig. 5. Ratio of piezoelectric coefficents, $-d_{31}/d_{33}$, for composition S250090 as a function of temperature.

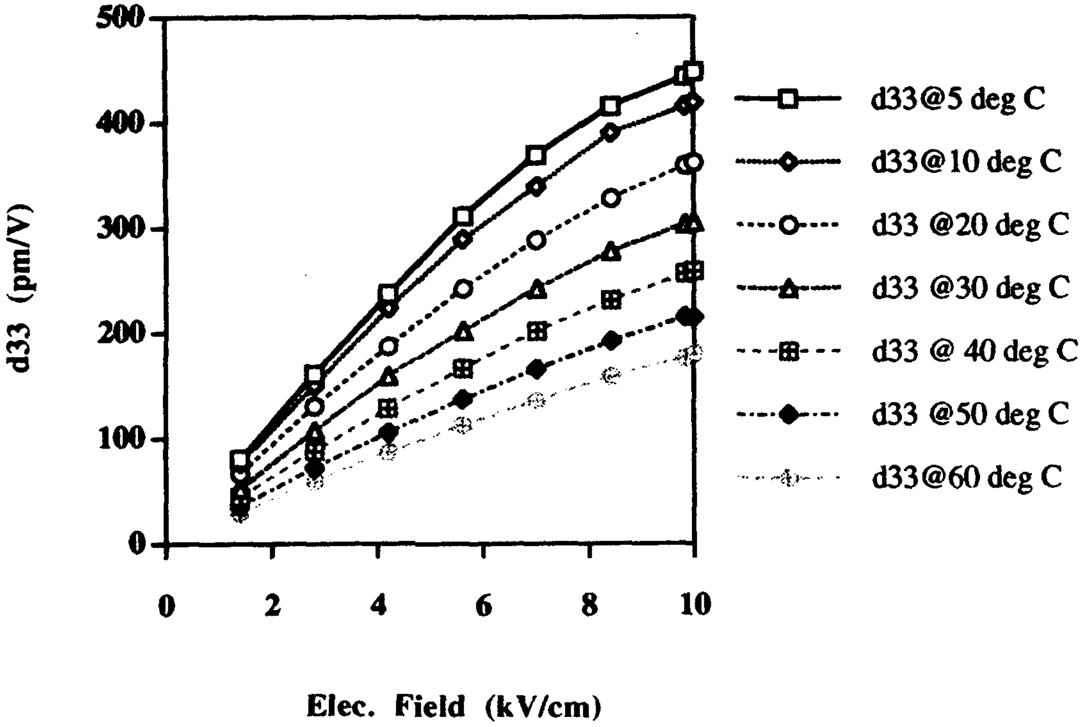

Fig. 6. Piezoelectric coefficient d_{33} for composition S400090 as a function of electric field for various temperatures.

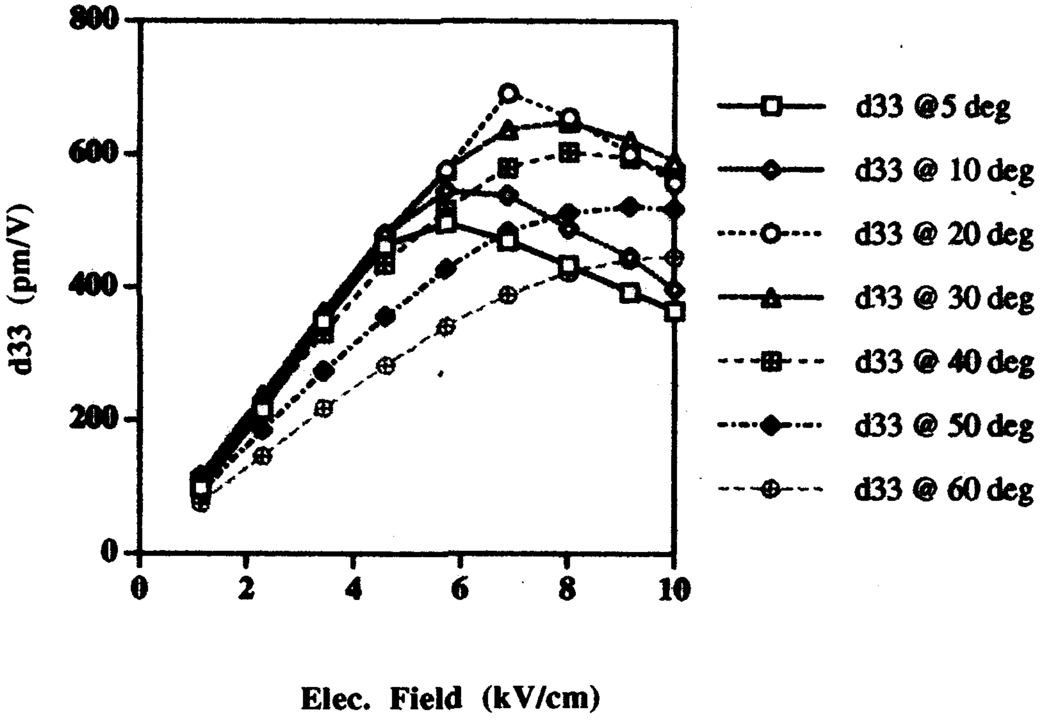

Fig. 7. Piezoelectric coefficient d_{33} for composition S250141 as a function of electric field for various temperatures.

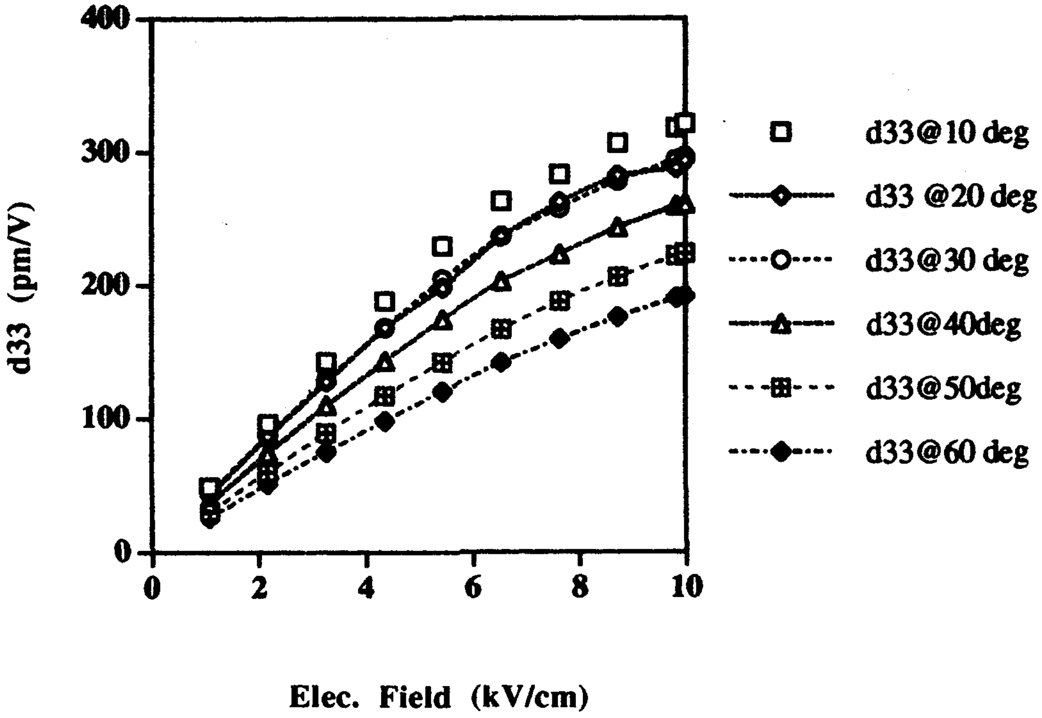

Fig. 8. Piezoelectric coefficient d_{33} for composition B500100 as a function of electric field for various temperatures.

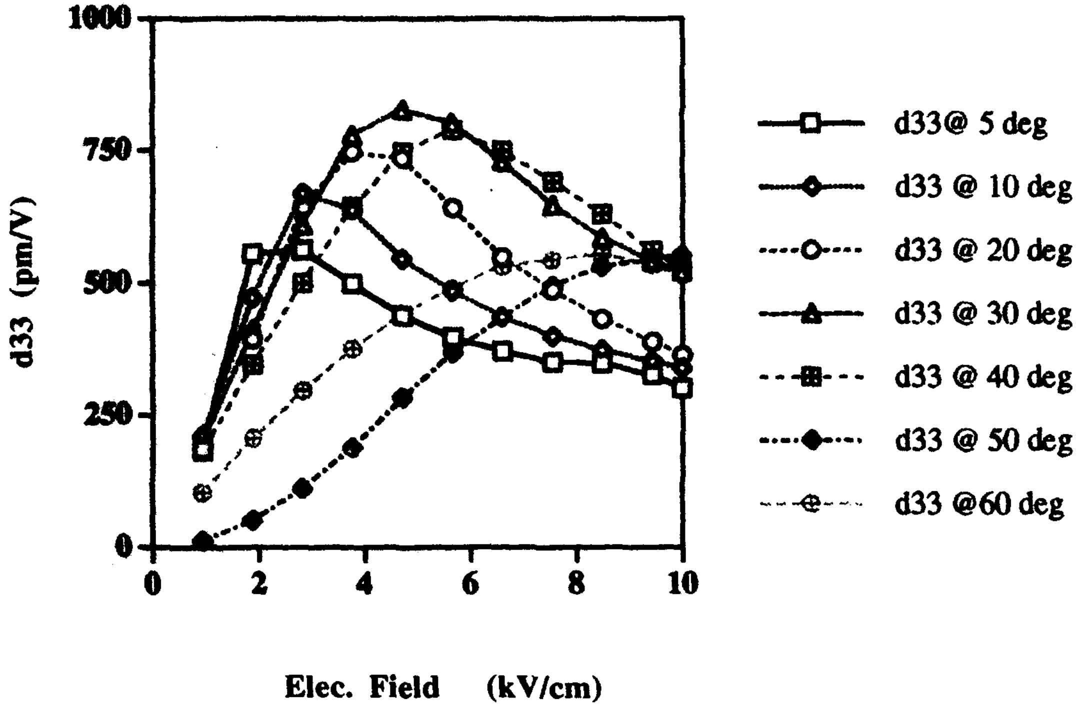

Fig. 9. Piezoelectric coefficient d_{33} for composition B2000120 as a function of electric field for various temperatures.

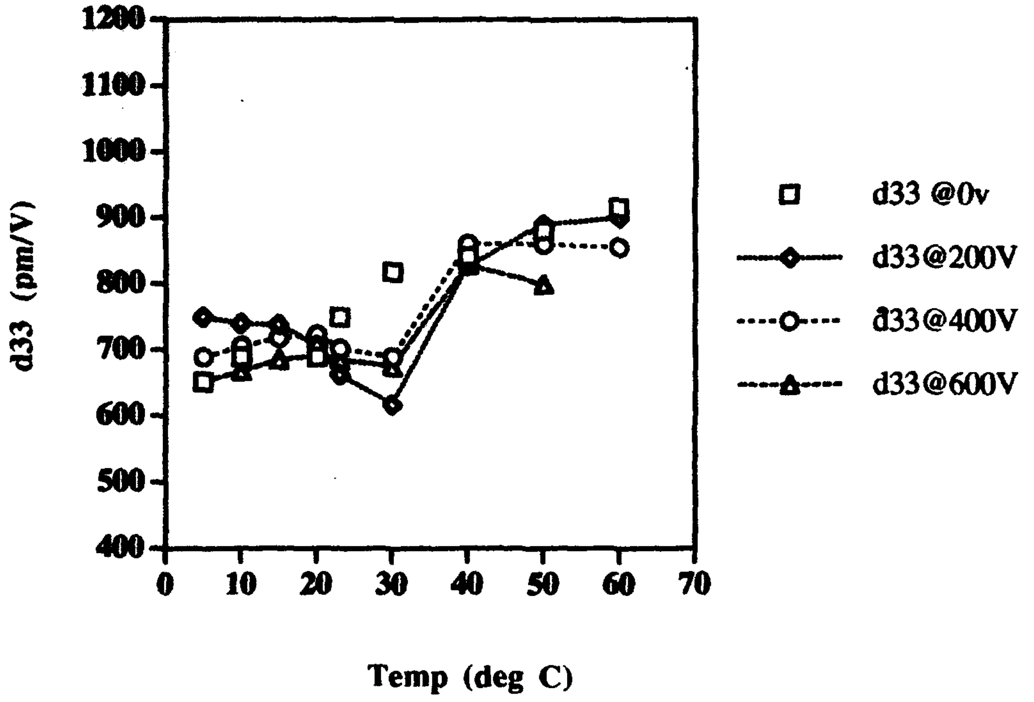

Fig. 10. Piezoelectric coefficient d_{33} for composition PLZT sample as a function of temperature.