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PROPERTIES OF MORGAN ELECTRO CERAMIC CERAMICS

by

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INTRODUCTION

The purpose of this memorandum is to summarize as completely as is presently possible the important properties of Vernitron piezoelectric ceramics. Data are included for all compositions commercially available from Morgan Electro Ceramics Piezoelectric Division. These include Ceramic B, PZT-2, PZT-4, PZT-5A, PZT-5H, and PZT-8.

The first section of this memorandum consists of a short general discussion of the most important properties of each ceramic composition, with recommendations for particular applications. The following section lists the symbols and units used in the section to follow.

The third section summarizes room temperature low signal data in a form as nearly complete as possible. Complete sets of elastic, piezoelectric and dielectric constants are listed. These properties are subject to fluctuations from element to element or from batch to batch, and the anisotropy ratios (s_{11}/s_{33} , s_{12}/s_{13} , s_{44}/s_{66} , $\epsilon_{11}/\epsilon_{33}$) vary drastically with thoroughness of poling. The sets presented here are self-consistent and hold for the level of poling suggested by the coupling factors listed.

The fourth section gives data relating to temperature and time stability. Data for the former are for samples subjected to an appropriate temperature stabilizing treatment.* This treatment reduces markedly temperature hysteresis effects and causes a relatively small decrease in piezoelectric coupling and increase in dielectric constant. Temperature hysteresis about the orthorhombic-tetragonal transition of Ceramic B is) however, not eliminated by any known stabilizing treatment. Data shown for Ceramic B are for increasing temperature only, and changes at the transition are more extreme with decreasing temperature.

Aging data are listed as change per time decade. These changes tend to be linear as function of the log of time, but there are significant deviations from this behaviour. The aging rates are usually a little higher than

listed when the element has piezoelectric properties stronger than those listed in Section III, and they are somewhat lower if piezoelectric properties are weaker.

Section V lists high signal properties, including data for both mechanical and electric driving conditions. These data allow comparison of the several compositions with respect to use in acoustic radiating transducers or in high voltage electrical generating systems. For acoustic radiating transducers important criteria are values of $\tan\delta$ with electric drive, change of permittivity and sensitivity with mechanical bias, allowable mechanical bias, dynamic strength, and dependence of mechanical Q on dynamic stress. For electrical generating systems the limiting factor is the maximum compressive stress (cycled) which may be maintained without significant degradation.

With acoustic receivers, even though these are not high signal devices, several properties listed in Section V are significant, since hydrophones are often operated at great depth in the ocean and there is therefore a significant mechanical bias stress. Cycling effects may be important if the hydrophone is to be submerged repeatedly.

Section VI lists data related to thermal effects, including pyroelectric constants, thermal expansion, thermal conductivity) and heat capacity. The pronounced effects of temperature stabilization on thermal expansion and pyroelectric constants are shown

The graphs at the end of this report show variation of ϵ_{33}^T , k_p , s_{31} , d_{31} , N_1 , and Q_m with temperature for the various ceramics. The curves for PZT-5A and PZT-4 hold only after temperature stabilization.

* This treatment is not ordinarily applied to production specimens, and is actually recommended only for PZT-4 and PZT-5A. With the former it consists of a one-hour soak at 200°C. The stabilizing treatment for PZT-5A consists of a 15-second soak at 250°C in oil followed by a 60-second soak in room temperature oil, with the process repeated at least five times. The respective changes in k and ϵ_{33}^T/ϵ are approximately -10% and +10% for PZT-4 and -9% and 5% for PZT-5A. Changes in N_1 are generally less than 1%. Stabilization to lower peak temperature can be accomplished by reducing the temperature of the soak. This will also reduce the changes in parameters. With large PZT-5A specimens the soak times must be increased so that the entire specimen reaches the soak temperature.

GENERAL COMPARISON

Ceramic B is a modified barium titanate which offers improved temperature stability and lower aging in comparison with unmodified barium titanate.

PZT -2 may be used for requirements of low dielectric constant but it is otherwise inferior in nearly all respects to PZT-4 or PZT-5A.

PZT-4 is recommended for high power acoustic radiating transducers because of its high resistance to depolarization and low dielectric losses under high electric drive. Its high resistance to depolarization under mechanical stress makes it suitable for use in deep-submersion acoustic transducers and as the active element in electrical power generating systems.

PZT-5A is recommended for hydrophones or instrument applications because of its high resistivity at elevated temperatures, high sensitivity, and high time stability.

PZT-5H has even higher sensitivity and permittivity than PZT-5A, and is in most other respects similar to PZT-5A. Its markedly lower Curie point, however, limits the working temperature range and leads to lower temperature stability.

PZT-8 is similar to PZT-4, but has even lower dielectric and mechanical losses under high electric drive. It is recommended for applications requiring higher power handling capability than is suitable for PZT-4.

Comparison of the above materials at room temperature may be made roughly using the table below, with the material with the highest value rated 100% and the others in proportion. For more exact comparison refer to the tables in the following sections.

	Ceramic B	PZT-2	PZT-4	PZT-5A	PZT-5H	PZT-8
	% of Highest Rated Ceramic					
Coupling factor	51	72	89	92	100	8
Short circuit sensitivity (d)	26	26	50	64	100	38
Open circuit sensitivity (g)	37	100	68	65	50	69
Permittivity	35	13	38	50	100	29
Compliance	52	71	75	100	100	70
Relative coercive electric field	44	46	100	12	8	-
Relative strain at relative coercive electric field	23	24	100	15	16	-
Relative coercive mechanical stress (static)	25	-	100	25	19	-
Curie point	115°C	370°C	328°C	365°C	193°C	300°C

II UNITS AND DESCRIPTION OF SYMBOLS

ϵ^T/ϵ_0 = relative dielectric constant, free.

ϵ^S/ϵ_0 = relative dielectric constant, clamped.

$\tan \delta = 1/QE$ dissipation factor at 1 kHz. low electric field.

k_p = planar coupling factor.

k_{31} = transverse or lateral coupling factor.

k_{33} = longitudinal coupling factor.

$k_{iL} = k_{15}$ = shear coupling factor; invariant coupling factor with electric field perpendicular to polar axis.

k_t = thickness coupling factor (laterally clamped).

k_{i3} = invariant coupling factor with electric field parallel to polar axis.

In these ceramics k_{i3} is slightly higher than k_{33}

d = piezoelectric constant, strain/field at constant stress or charge density/stress at constant electric field, 10 meters/volt.

g = piezoelectric constant, electric field/stress at constant stress, 10⁻³ volt meters/newton.

e = piezoelectric constant, stress/electric field at constant strain or charge density/strain at constant electric field, coulomb/metre .

h = piezoelectric constant, electric field/strain at constant charge or stress/charge density at constant strain. 10 volt/meter-.

s^E = elastic compliance at constant electric field, 10⁻¹² meter² /newton

s^D = elastic compliance at constant charge density, 10⁻¹² meter² /newton

c^E, c^D = elastic stiffness, 10¹⁰ newton/meter².

Q_M = mechanical Q. This is dependent upon configuration, and is given here for a thin disc.

N_1 = frequency constant of a thin bar, $f_a \cdot l$, cycle meters/second.

N_{3a} = frequency constant of a cylinder electroded on ends. $f_a \cdot l$ cycle meters/second.

N_{3t} = frequency constant of a thin plate, $f_a \cdot t$ cycle meters/second.

v_3^D = velocity of a compressional wave parallel to polar axis ($c_{33}^D = (v_3^D)^2 \rho$) meters/second.

v_4^D = velocity of a shear wave perpendicular to polar axis with polarization parallel to polar axis ($c_{44}^D = (v_4^D)^2 \rho$), meters/second.

v_4^E = velocity of a shear wave parallel to polar axis, ($c_{44}^E = (v_4^E)^2 \rho$), meters/second.

ρ = density, 10³ kg/m³.

θ = temperature; °C

P = polarization, 10 coulomb/cm² (10⁻² coulomb/m²)

α = thermal expansion, 10⁻⁶ °C

III. TYPICAL ROOM TEMPERATURE DATA (Low signal)

	Ceramic B	PZT-2	PZT-4	PZT-5A	PZT-5H	PZT-8
$\epsilon_{33}^T/\epsilon_o(K_{33}^T)$	1200	450	1300	1700	3400	1000
$\epsilon_{33}^S/\epsilon_o$	910	260	635	830	1470	600
$\epsilon_{11}^T/\epsilon_o$	1300	990	1475	1730	3130	1290
$\epsilon_{11}^S/\epsilon_o$	1000	504	730	916	1700	900
$\tan\delta$	0.006	0.005	0.004	0.02	0.02	0.004
k_p	-.33	-.47	-.58	-.60	-.65	-.51
k_{31}	-.194	-.28	-.334	-.344	-.388	-.30
k_{33}	.48	.626	.70	.705	.752	.64
$k_{15}=k_{ii}$.48	.701	.71	.685	.675	.55
k_t	.384	.508	.513	.486	.505	.48
k_{i3}	.491	.650	.715	.715	.754	.63
d_{31}	-58	-60.2	-123	-171	-274	-37
d_{33}	149	152	289	374	593	225
d_{15}	242	440	496	584	741	330
d_h	33	32	43	32	45	31
g_{31}	-5.5	-15.1	-11.1	-11.4	-9.11	-10.9
g_{33}	14.1	38.1	26.1	24.8	19.7	25.4
g_{15}	21.0	50.3	39.4	38.2	26.8	28.9
g_h	3.1	7.9	3.9	2.0	1.5	3.6
$d_h g_h$	102	253	168	64	68	112
h_{31}	-3.8	-8.1	-9.2	-7.3	-5.05	-7.7
h_{33}	16.7	39.2	26.8	21.5	18.0	26.4
h_{is}	12.3	21.9	19.7	15.2	11.3	12.9
e_{31}	-3.1	-1.86	-5.2	-5.4	-6.55	-4.1
e_{33}	13.5	9.0	15.1	15.8	23.3	14.0
e_{15}	10.9	9.8	12.7	12.3	17.0	10.3
s_{11}^E	8.6	11.6	12.3	16.4	16.5	11.5
s_{33}^E	9.1	14.8	15.5	18.8	20.7	13.5
s_{44}^E	22.2	45.0	39.0	47.5	43.5	31.9
s_{66}^E	22.4	29.9	32.7	44.3	42.6	30.4
s_{12}^E	-2.6	-3.33	-4.05	-5.74	-4.78	-3.7
s_{13}^E	-2.7	-4.97	-5.31	-7.22	-8.45	-4.8
s_{11}^D	8.3	10.7	10.9	14.4	14.05	10.1
s_{33}^D	7.0	9.0	7.90	9.46	8.9	8.5
s_{44}^D	17.1	22.9	19.3	25.2	23.7	22.6
s_{12}^D	-2.9	-4.24	-5.42	-7.71	-7.27	-4.5
s_{13}^D	-1.9	-2.68	-2.10	-2.98	-3.05	-2.5

For PZT-5A the dielectric constants decrease about 2.4 decade of frequency to at least 20 mcps and increase 2.4%/decade of frequency below 1 kcps to at least 1 cps. For PZT-4 T_{33} decreases about 1.0% decade of frequency to a least 1 mcps and increases 1.0%/decade of frequency below 1 kcps to at least 1 cps.

III. TYPICAL ROOM TEMPERATURE DATA (Low Signal)

	Ceramic B	KT-2	PZT-4	HT-SA	PZT-SH	PZT-8
C_{11}^E	15.8	13.5	13.9	12.1	12.6	14.9
C_{33}^E	15.0	11.3	11.5	11.1	11.7	13.2
C_{44}^E	4.5	2.22	2.56	2.11	2.30	3.13
C_{66}^E	4.5	3.34	3.06	2.26	2.35	3.40
C_{12}^E	6.9	6.79	7.78	7.54	7.95	8.11
C_{13}^E	6.75	6.81	7.43	7.52	8.41	8.11
C_{11}^D	15.9	13.6	14.5	12.6	13.0	15.2
C_{33}^D	17.7	14.8	15.9	14.7	15.7	16.9
C_{44}^D	5.85	4.37	5.18	3.97	4.22	4.46
C_{12}^D	7.0	6.93	8.39	8.09	8.28	8.41
C_{13}^D	6.2	6.12	6.09	6.52	7.22	7.03
Q_M	400	680	500	75	65	1000
Q_E	170	200	250	50	so	250
N_1	2290	1680	1650	1400	1420	1700
N_{3t}	2740	2090	2000	1890	2000	2070
N_{3a}	2530	1910	2060	1845	1930	2000
v_3^D	5640	4410	4600	4350	4560	4720
v_4^D	3240	2400	2630	2260	2375	2420
v_4^E	2850	1670	1850	1650	1750	2030
density	5.55	7.6	7.5	7.75	7.5	7.6
Curie Point	115°C	370°C	328°C	365°C	193°C	300°C

IV. TEMPERATURE & TIME STABILITY

	Ceramic B	PZT-2	PZT-4	PZT-5A	PZT-5H	PZT-8
Change in k_p /time decade	-1.8%	-1.8%	-1.7	-0.0%	-0.2%	-1.7%
Change in ϵ_{33}^T /time decade	-0.8%	-2.8%	-2.5%	-0.9%	-0.6%	-4%
Change in N_1 /time decade	+0.5%	+0.6%	+0.8%	+0.1%	+0.3%	+0.9%
Change in D_{33} /time decade	-3.4%	-2.97.	-3.9%	-6.3%		
a) Change in k_p						
0 to 40°C	44% (b)	2.4%	4.9%	2.5%	3.2%	-
-60 to + 85°C	130%	10%	9.5%	9.0%	12%	-
-60 to + 150°C	-	11%	9.5%	9.0%	21%	-
4°K to + 200°C	-	-	27%	55%	-	-
a) Change in K_{33}^T						
0 to 40°C	20%	10%	2.7%	16%	33%	-
-60 to + 85°C	50% (b)	29%	9.4%	52%	86%	-
-60 to + 150°C	-	91%	31%	76%	-	-
4°K to + 200°C	-	-	130%	147%	-	-
a) Change in N_1						
0 to 40°C	4% (b)	0.4%	1.7%	0.8%	2.9%	-
-60 to + 85°C	18%	1.5%	4.8%	2.6%	9%	-
-60 to + 150°C	-	3.4%	7.3%	2.6%	9%	-
4°K to + 200°C	-	-	13%	17%	-	-
Volume resistivity in ohm meters						
25°C	$>10^{10}$	$>10^{10}$	$>10^{10}$	$>10^{11}$	$>10^{11}$	$>10^{10}$
100°C	$10^{7.5}$	$10^{8.5}$	$10^{8.5}$	10^{11}	10^{11}	$>10^{8.5}$
200°C	10^5	$10^{6.5}$	$10^{6.5}$	10^{10}	10^{10}	
Time constant, seconds						
25°C	>100	>100	>100	>2000	>2000	2100
100°C	≈ 0.3	≈ 2	≈ 5	≈ 1800	2000	≈ 2
200°C	≈ 0.002	≈ 0.03	≈ 0.07	≈ 250	1000	-

a) After stabilizing treatment for PTZ-4 and PTZ-5A. All changes relative to value at 25°C; with PTZ-4, PTZ-5A and PZT-5H data include temperature hysteresis. With Ceramic B and PZT-2 the data are for increasing temperature only.

b) Includes hysteresis about orthorhombic-tetragonal transition near -30°C.

V. HIGH SIGNAL PROPERTIES (In this Table units of electric field are kv/cm or 105 volts/m and stress in psi)

	Ceramic B	PZT-2	PZT-4	PZT-5A	PZT-5R	PZT-8
AC depoling field	3.5	>10	>10	7	~4	15
AC field for $\tan\delta=0.04$, 25°C ^{a)}	1.7	1.8	3.9	0.45	0.3	10
% increase of k_{33}^T at above electric field	-	-	17	11	5.3	10
AC field for $\tan\delta = 0.04$, 100°C	1.0 at 75°C	1.6	3.3	0.45	0.2	-
Maximum rated static compressive 25°C stress (maintained) parallel to polar axis.	2,000	-	1000	3 000 or 2,000	1,500 or 1,500c	12,000
100°C	1000 at 75°C	-	6,000	3,000	1,000 or 1,500c	-
% change of k_{33}^T with stress increase to rated maximum compressive stress at 25°C.b)	-	-	+25%	-3%d)	--4%e)	+18%
% change of d_{33} with stress increase to rated maximum compressive stress at 25°C.	-	-	115%	-0% at 3,000 -13% at 5,000	-5% at 1,500 -7% at 2,000	+6% 12,000
Maximum rated compressive stress 25°C (cycled) parallel to polar axis	2,000	-	12,000	3,000	2,500	-
100°C	1,000 at 750C	-	6,000	3,000	2,000	-
Maximum rated static compressive 25% stress (Maintained). perpendicular to polar axis	2,000	-	8,000	2,000	1,500	8,000
100°C	1,000 at 75°C	-	4,000	2,000	1,000	-
% change of k_{33}^T with stress increase to rated maximum compressive stress at 25°C. b)	-	-	+10%	-	-	~2 %
2 change of d_{31} with stress increase to rated maximum compressive stress at 25°C.	-	-	-10%f	-	-	-10%
Maximum rated hydrostatic pressure	20,000	50,000	50,000	20,000	20,000	>50,000
Ccompressive strength	>50,000	> 75,000	>75,000	>75,000	>75,000	>75,000
Tensile strength, static	7,500	11,000	11,000	11,000	11,000	11,000
Tensile strength, dynamic (peak) ^{g)}	3,000	3,500	3,500	4,000	4,000	5,000
Mechanical Q at 0 psi	400	680	500	75	65	1,000
Mechanical Q at 1,000 psi	- 140	-	- 180	- 25	-	- 800
Mechanical Q at 2,000 psi	85	-	~ 110	~ 25	-	~ 500
% increase in s_{11}^E at 1,000 psi	1.7	~1.7	10.5	-	~ 0.1	-
% increase in s_{11}^E at 2,000 psi	-	3.7	~3.7	17	-	-0.2
Polarization	8 H coul/cm ²	40	30	38	33	25
25°	-	-	-	-	-	-
Coercive Field	~ 5	h)	h)	12	6.5	h)

a) The value of $\tan\delta$ at a given electric field is a function of time after poling or after any major disturbance such as exposure to an elevated temperature.

b) After appropriate stabilizing treatment. This consists of the temperature stabilization discussed previously plus a few minutes soak at the appropriate static stress. The temperature stabilization is, however, more important than the stress soak.

c) The higher figure applies to a receiver, the lower to a radiator. The recommended use of PZT-5A or PZT-5H is the former.

d) In range to 10,000 psi.

e) In range to 5,000 psi.

f) The lateral d-constant perpendicular to the stress and polar axis is up about 20%.

g) These figures are dependent upon configuration and perfection of fabrication. The static tensile strength figures were obtained from bending tests on thin bimorph structures, while the dynamic tensile strength figures were obtained from measurements of high amplitude resonant vibration of rings. The latter tests are more sensitive to minor flaws.

h) Coercive field values for PZT-2 and PZT-4 are not well defined as values from hysteresis loops are time dependent and dependent on amplitude of peak electric field.

VI. THERMAL EFFECTS

Pyroelectric effects, $(\partial P/\partial \theta)T$ in 10^{-6} coul/CM²°C (10^{-2} coul/m²°C)

Temp, 0°C	Ceramic B ^(b) First Heating	PZT-4 First Heating	PZT-5A	
			First Heating	Subsequent Heatings
-196	-	-	-0.02	-0.02
-80	-0.025	-0.025	-0.03	-0.02
-60	-0.025	-0.025	-0.03	-0.02
0	-0.022	-0.025	-0.04	-0.02
30	-0.022	-0.028	-0.06	-0.02
60	-0.022	-0.026	-0.07	-0.02
80	(a)	-0.025	-0.09	-0.02
100	(a)	(a)	-0.11	-0.02
200	0	(a)	-0.17	-0.04
300	0	(a)	-0.23	-0.09

a) Above about 800°C the pyroelectric effect is marked by anomalous dielectric charges

b) Ceramic B has a very sharp peak in the pyroelectric constant at the orthorhombic - tetragonal phase transition near -30°C. The peak value is about 0.3 $\mu\text{coul}/\text{cm}^2 \text{ } ^\circ\text{C}$.

B. Thermal Expansion Coefficient (α in $10^{-6}/^\circ\text{C}$)

°C	Poled PZT-5A				Poled PZT-4			
	First Heating		Subsequent Heatings		First Heating		Subsequent Heatings	
	α_1	α_3	α_1	α_3	α_1	α_3	α_1	α_3
0	+1.5	+2	+1	+4	+1.5	+0.1	+3.8	+1.7
50	+1.5	+2	+1.4	+4	+4.5	-0.1	+3.8	+1.7
100	+6	-6	+2	+3	+5.8	-6	+3.8	-1
150	+6	-7	+2.7	+1	+6.4	-6	+3.8	-1.4
200	+5	-7	+3.3	-1.6	+5.4	-6.1	+3.4	-2.4
-250	+4.2	-6	+3.9	-4.2				

Virgin (Unpoled)			Ceramic B		
	PZT-5A	PZT-4	First Heating		
	α	α	°C	α_1	α_3
0	+2.5	+2.0	30		
50	+2.1	+1.8	40	+7.5	+4.7
100	+2.0	+1.5	50	+7.5	+4.7
150	+1.8	+1.1	60	+7.5	+4.7
200	+1.5	+1.0	70	+7.5	+4.3
250	+1.0	+0.3	80	+7.5	+3.2
300	+0.7	0.0	90	+7.5	+1.8
350	-3.0	+6.2	100	+7.5	0
400	+5	+7.8	Above 120°C		
500	+8.2	+8.2		$\alpha = +9$	

As noted above, thermal expansion of PZT-4 and PZT-5A is extremely anisotropic only on first heating, and on first heating only above about 50°C. With Ceramic B thermal expansion is markedly anisotropic only above about 800°C even on first heating.

C. Heat Capacity

PZT ~ 420 joules/kg°C (138 joules/°C mole)

Ceramic B ~ 500 joules/kg°C (117 joules/°C mole)

D. Thermal Conductivity

PZT ~ 1.25 Watts/metre°C

Ceramic B ~ 2.5 Watts/metre°C







