# Stress Sensitivity of Piezoelectric Ceramics: Part 2.
## Heat Treatment

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The large rise in permittivity experienced by transducer ceramics when subjected to stress parallel to the polar axis can reduce the utility of these materials. Measurements are described on PZT-4 and PZT-8 representative of ceramics useful for high-power high-stress applications, for which a stabilizing heat treatment has reduced the change in permittivity. It is shown that the stabilizing effect is permanent. Several stress cycles to 10 or 20 kpsi also stabilize these ceramics. It is shown that the stabilization with stress for stress cycles to 10 kpsi is not permanent. Measurements were made over an aging range from one day to six months.

**INTRODUCTION**

One of the major problems in transducer design for operation over wide stress limits is the large change in permittivity of piezoelectric transducer ceramics due to changes in static stress. This is shown in Part 1 and in the references cited there. To a certain extent changes in permittivity are reduced by “stress stabilization” as shown in Part 1. The object of this report is to discuss heat treatment as another, more effective, method of reducing variations of permittivity and piezoelectric constants for PZT-4 and PZT-8 (see references of Part 1 for descriptions of these ceramics), materials particularly well suited for high-power radiating transducers. Stress stabilization can be effective, as shown by Nishi in reducing variations in permittivity and tan∂ at 10 kpsi and up to 3 kV/cm driving field, if the stress is maintained for very long time periods. For some permanent installations at great depths, this is a practical procedure. For applications requiring relatively fast and frequent stress cycling, the heat treatment can reduce the severity of the problem in one step that could be incorporated into the ceramic production technique.

Graphs are presented illustrating effects of static stress parallel to the polar axis on permittivity, tan∂, and $d_{33}$ of normal and heat-treated PZT-4 and PZT-8.

The vital question remains: “Is the effect permanent?” Another experiment that answers that question affirmatively is described.

**I. EXPERIMENTAL RESULTS**

Measurement techniques were identical to those de scribed in some detail in the Appendix to Part 1. Briefly, pairs of 1/2-in. cubes were placed mechanically in series and driven electrically in parallel but out of phase so as not to drive the press used for stressing. $\varepsilon_{33}^{T}$ and tan∂ were measured at low electric field; $d_{33}$ was measured using a strain-gauge technique, driving the cubes at 100 Hz with 500 V rms (about 0.4-kV/cm rms) and measuring the resulting dynamic strain.

The heat-stabilizing treatment consisted simply of immersing the specimens in 200°C oil for 1 h. Other related treatments have also been used successfully, but no real optimization study has yet been made. Under these conditions, the easy relaxation of those domains under greatest internal stress (these are presumably most sensitive to temperature or stress) can take place readily. The compositions considered here are of tetragonal symmetry; with these domain reorientation is by 90°. Further perturbation by temperature or stress will not affect these domains, and they will therefore not contribute to increased permittivity or loss through further reorientation.

**A. Changes Induced by Heat Treatment without Stress**

A short auxiliary experiment was performed to indicate the magnitude of the changes produced by the heat treatment exclusive of stress effects. For simplicity, disks were used. Measurements were made of permittivity, planar coupling factor, frequency constant perpendicular to the poling direction, $d_{33}$ (with a calibrated 100-Hz dynamic force), and the resistance at resonance, from which (with the above) the mechanical Q can be calculated. The first three of these are measured to accuracies well within 1%; but the latter have considerably poorer accuracy, estimated at 5% —15%. Four groups of two disks each were used. Group I was a control group not treated. Group II was exposed to the 200°C, 1 h heat treatment about one day after poling and after initial measurements had been made. Groups III and IV were given

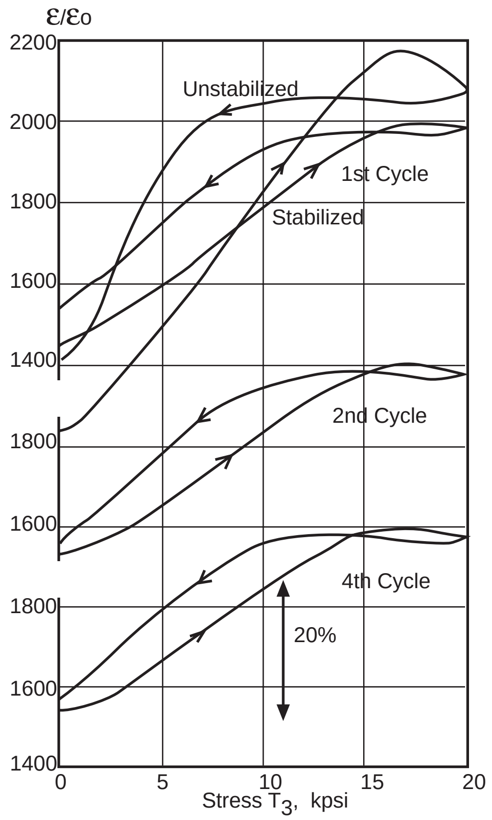


FIG. 1. $\varepsilon_{33}^{T}/\varepsilon_{o}$ vs parallel stress T2 for stabilized PZT-4; firstsecond, and fourth cycles. Comparison with normal PZT-4 for first stress cycle.

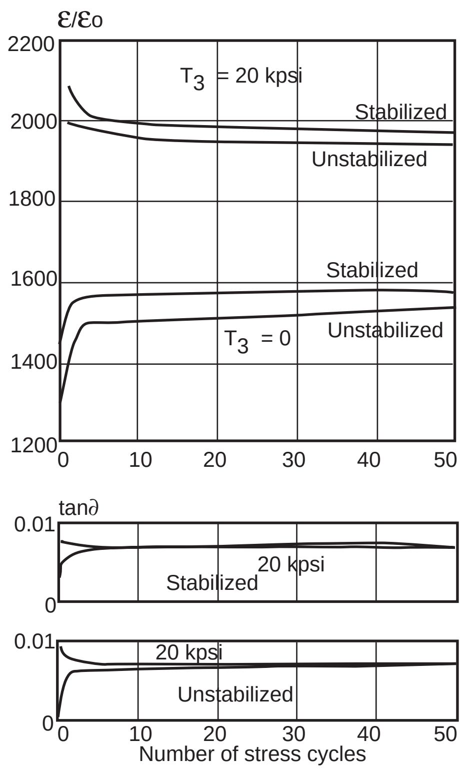


FIG. 2. $\varepsilon_{33}^{T}/\varepsilon_{o}$ and tan∂ vs number of stress cycles for peakstress of 20 kpsi. Stabilized and unstabilized PZT-4.

the heat treatment 13 days and 35 days after poling, respectively. All specimens were measured one, two, 14, and 36 days after poling. Average values are listed in Table I. Group I data for the successive measurements should represent normal aging. The first two points of Group III and the first three points of Group IV also represent normal aging, since heat treatment was done later. Examination of these three sets indicates good agreement, showing satisfactory sample-to-sample uniformity.

The changes in properties due to the heat treatment vary with the time of treatment after poling. Thus, for PZT-4, $\varepsilon_{33}^{T}/\varepsilon_{o}$ jumps (103.2-98.1)/98.1 = +5.2%, measured one day after heat treatment compared with the same time measurement for the control specimen. The jump for Group IV (treated 35 days after poling) relative to Group I was (101.4 -87.2)/87.2=+16.3%. Reduction of piezoelectric coupling is perhaps the most serious change that heat treatment produces. Compar ing Groups II, III, and IV with Group I shows reductions of -12.6%, -9.6% and -9.8%, respectively. The data of Table I(a) show that an early heat treatment raises the frequency constant Nl (Groups II and III), whereas a late treatment produces scarcely a change. The mechanical Q consistently is reduced by the heat treatment. The piezoelectric constant $d_{33}$ is reduced also, although the data are not sufficiently accurate for certain judgment on this point. The drop with treatment appears consistently to decrease with later treatment times.

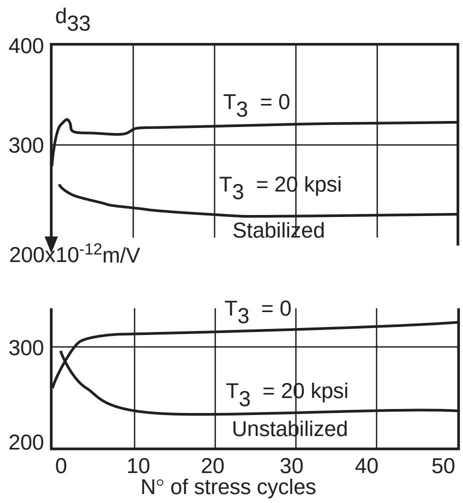


FIG. 4. $\varepsilon_{33}^{T}/\varepsilon_{o}$ vs number of Stresscycles for peak stress of 20 kpsi. Stabilized and Unstabilized PZT-4.

With PZT-8 [Table I(b)], increases in permittivity relative to Group I are +18%, +21%, and +23% respectively for Groups II, III, and IV one day after heat treatment. The planar coupling factor drops 5.2%, 3.9%, and 3.2% relative to Group I for the heat treated specimens of Groups II, III, and IV, respectively — changes less severe than for PZT-4. The frequency constant $N_1$ however, always drops with heat treatment for PZT-8, and increasingly for later treatment. $Q_M$ also drops, and $d_{33}$ rises a consistent trifle

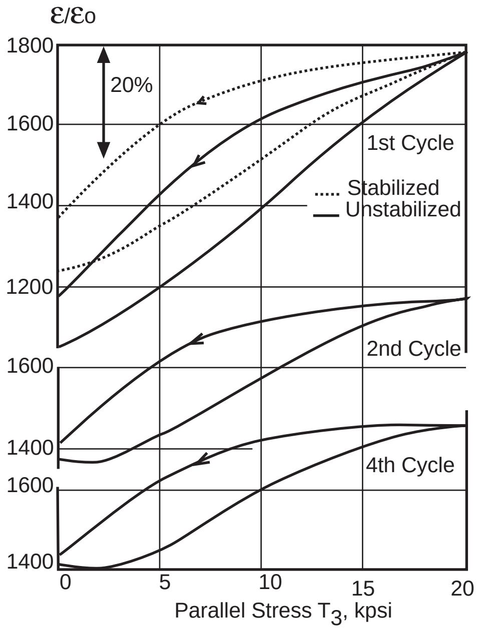


FIG 5, $\varepsilon_{33}^{T}/\varepsilon_o$ vs Parallel stress T3 for stabilized PZT-8, firstSecond, and fourth cycles. Comparison With normal PZT-8 for first Stress cycle.

(this measurement has poor accuracy). (The fact that the treated specimens of Figs. 7 and 8 have lower d constants than the untreated specimens is due to sample variability.) PZT-8 responds to the heat treatment as a de-aging process to a greater extent than PZT-4. All the properties tested here with the exception of kp revert to values they might have experienced earlier in time. For PZT-4, $d_{33}$ and $N_1$ are aged further, and the coupling factor drops a greater amount than for PZT-8.

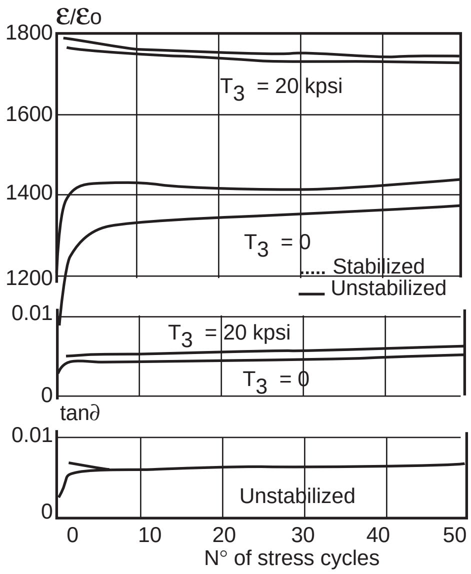


FIG. 6. $\varepsilon_{33}^{T}/\varepsilon_o$ and tan∂ vs number of stress cycles for peak stress of 20 kpsi. Stabilized and unstabilized PZT-8.

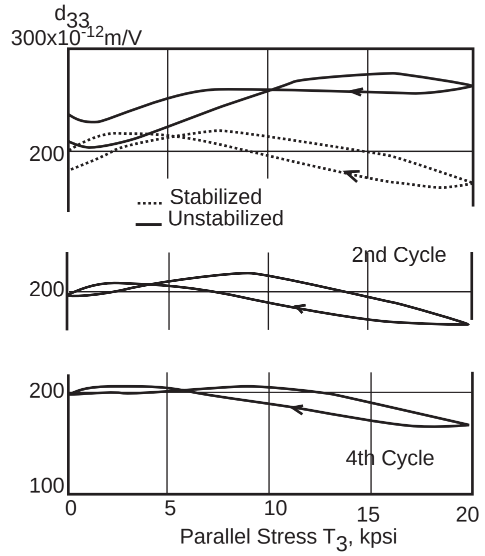


FIG. 7. $d_{33}$, vs parallel stress $T_3$ for stabilized PZT-8, first, second,and fourth cycles. Comparison with normal PZT-8 for first stress cycle.

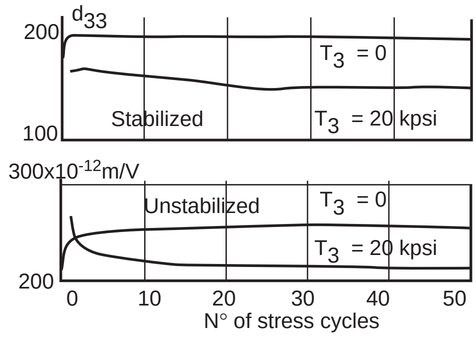


FIG. 8. $d_{33}$, vs number of stress cycles for peak stress of 20 kpsi. Stabilized and unstabilized PZT-8.

**B. Effects of Stress after Heat Treatment**

Figure 1 shows $\varepsilon_{33}^{T}/\varepsilon_o$ vs longitudinal stress ($T_3$) for the first, second, and fourth stress cycles to 20 kpsi. The heat treatment raised the initial relative permittivity to over 1400 and reduced the rise with stress, so that the maximum excursion is (1995-1535)/1445=37% as compared to 76% for the first stress cycle of unstabilized PZT-4. Some stress stabilization continues to take place for the heat-stabilized PZT-4, since the fourth cycle has a maximum excursion of (1990-1535)/1535=30%, and after 50 stress cycles to 20 kpsi the end points (Fig. 2) are different by only 24%. Since unstabilized PZT-4 has end points 29% different after 50 cycles, it is seen that stress cycling will stabilize; but the process is awkward and expensive as a production process. Also, no information is yet available on the permanence of the effect (see Sec. C). Heat stabilization is relatively inexpensive, and one treatment cuts the permittivity rise for PZT-4 by one-half for 20-kpsi maximum stress.

The same sort of effect occurs with the piezoelectric constant, $d_{33}$. Figure 3 shows $d_{33}$ vs longitudinal stress for the first stress cycle comparing stabilized and normal PZT-4. Figure 4 has the comparison as a function of number of stress cycles; and in this case, results are virtually identical, with the stabilized specimens at 20 kpsi on the first cycle being at the level of the fourth cycle at 20 kpsi for the unstabilized pair. The major improvement, then, is seen to accrue over the first few stress cycles where the changes due to stress are most severe.

**2. PZT-8**

The variation of $\varepsilon_{33}^{T}/\varepsilon_{o}$ with longitudinal stress $T_3$ for PZT-8 (after the 200°C, 1-h heat treatment) is shown in Fig. 5 for the first, second, and fourth cycles to 20 kpsi. Data for untreated PZT-8 for the first cycle are also shown. Again the improvement is noteworthy: Permittivity rose 43% for the stabilized again for the unstabilized PZT-8. The major stress stabilization has occurred by the fourth cycle (Fig. 6) figures for rise in

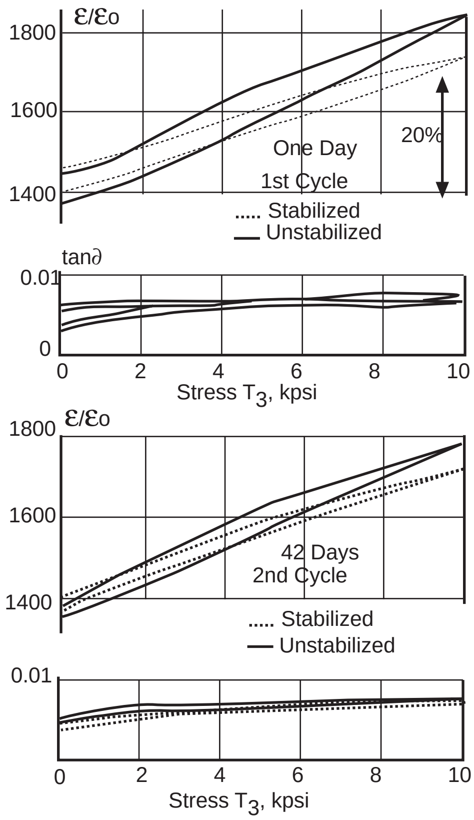


FIG. 9. Representative detail runs from aging study of stabilizing treatment. Upper Curve: $\varepsilon_{33}^{T}/\varepsilon_{o}$ and tan∂ vs parallel stress $T_3$ for stabilized and unstabilized PZT-4, first stress cycle, one day after poling. Lower curve: $\varepsilon_{33}^{T}/\varepsilon_{o}$ and tan∂ vs parallel stress T, for specimens of PZT-4 stabilized but not stressed until 42 days after poling; compared with unstabilized PZT-4 specimens that had been stressed at each previous measurement date. See text.

permittivity are 23%, and 37% specimens with and without heat stabilization, respectively. Stress stabilization continues for the unstabilized PZT-8 with stress cycling, so that the change of permittivity for the 50th cycle is 20% for the stabilized and 27% for the unstabilized PZT-8. These results are marginally better than those for PZT-4. The curves of $d_{33}$ vs longitudinal stress Tl (Fig. 7) show less total variation with heat-stabilized PZT-8. As a function of the number of stress cycles (Fig. 8), $d_{33}$ again has been stress stabilized so that, after the second stress cycle, $d_{33}$ is stable with $T_3$=O, whereas this requires three or four cycles for the untreated ceramic. The changes in $d_{33}$ for heat-stabilized PZT-8, at stress, are greater than for the unstabilized ceramic. This is to be expected when the permittivity rise is reduced, for the differential of the defining piezoelectric equation is

$$\Delta d_{33}/d_{33}=\Delta k_{33}/k_{33}+1/2\Delta\varepsilon_{33}T/\varepsilon_{33}T+1/2\Delta s_{33}^{E}/s_{33}^{E}.$$

**C. Permanence of Changes Induced by Heat Treatment**

To check the permanence of the reduction in stress sensitivity induced by the stabilizing heat treatment, an experiment was performed over a period of six months comparing permittivity and tan∂ for stabilized and normal PZT-4 cubes during stress runs to 10 kpsi. One control pair of cubes was not treated. Four pairs were stabilized by 200°C heat treatment for 1 h. The first pair and the control were given detail stress runs (Point by point) for the first, second, and fourth stress cycles one day after heat treatment, one week after, six weeks after, and six months after heat treatment. The second treated pair was put through the same stress schedule with the omission of the set applied one day after stabilizing. Similarly, the third was not stressed until six weeks after treatment and then again after six months, while the fourth was only stressed at the six-month aging date.

This checked the effects of aging alone and the effects of aging with occasional stress cycles. Permittivity and loss were measured because the changes in permittivity are most difficult for projector designers to design around; piezoelectric measurements were not made. Longitudinal stress of 10 kpsi was chosen since it is a stress level PZT-4 is entirely capable of handling (see Part 1) and one that could be encountered in practice. Figure 9 gives examples of the detail runs made. The first cycle for both the control and the stabilized pair than was stressed through each cycle with the control are shown in the upper set of curves. The lower set of curves is for the second cycle after 42 days of aging for the control (actually the ninth stress cycle for the control pair) compared to the second cycle for a pair heat treated 42 days previously, but not stressed until that set of four stress cycles. The stabilizing effect is evident. After one day, the permittivity rise is (1850-1370)/1370=35% on the first stress cycle for normal PZT-4 compared to (1740-1406)/1406=24% for stabilized PZT-4. Curves of tan∂ may not be significantly different, but the stabilized specimens have consistently lower loss. After six weeks, the difference is not as great largely because of the stabilization due to the first stress cycle (not shown). The numbers are (1770-1346)/1346 = 31.5% rise for unstabilized PZT-4 and (1720-1355)/1355= 27% permittivity rise for heat-

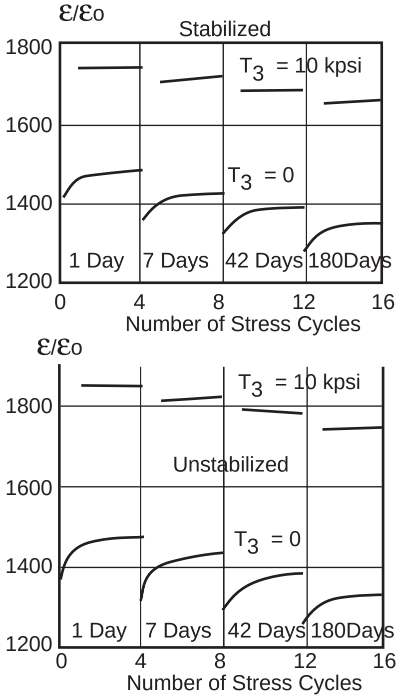


FIG. 10. $\varepsilon_{33}^{T}/\varepsilon_o$ as function of number of stress cycles for each measurement date. Comparison of stabilized and unstabilized specimens of PZT-4.

treated specimens. The end-point information is plotted in Fig. 10 for the unstabilized specimens and the stabilized pair subjected to all the stresses with those specimens. Several points are of interest. There is a gradual divergence of the $T_3$= 10 kpsi and $T_3$= 0 curves for both sets of cubes, and for both e and tan∂ (tan∂ is not shown in Fig. 10). Table II summarizes this divergence. The large percentage changes in tan∂ are not considered particularly detrimental since the loss factors remain below 1%; and in the comparison of the two groups, in spite of greater loss changes, tan∂ is always less for the stabilized pair of cubes. Another interesting feature of the curves of Fig. 10 is the impermanence of the stress stabilization. After a period of relative peace, the first disturbance (in this case, a stress cycle to 10 kpsi) results in larger changes in e and tan∂ than the cycle preceding (which was the last of a set of four). Finally, Fig. 10 and Table II show the permanence of the effect of heat treatment in reducing the permittivity rise due to stress in PZT-4. This fact is further illustrated in Fig. 11, where the same two pairs of cubes are compared on a log time plot using fourth-cycle end points for $\varepsilon_{33}^{T}/\varepsilon_o$ and tan∂. On the same log time plot, the control pair of cubes that had been exposed to four stress cycles on each measurement day was compared to stabilized pairs that had not been stressed previous to that day (the second, third, and fourth pairs of cubes described above). Except for slight experimental scatter, this set of curves was identical with Fig. 11, and therefore is not shown. Again this shows that stress stabilizing is impermanent (at least for stress to 10 kpsi). Effects of the stabilizing heat treatment are, however, permanent, since the rise in permittivity remains less for the stabilized specimens.

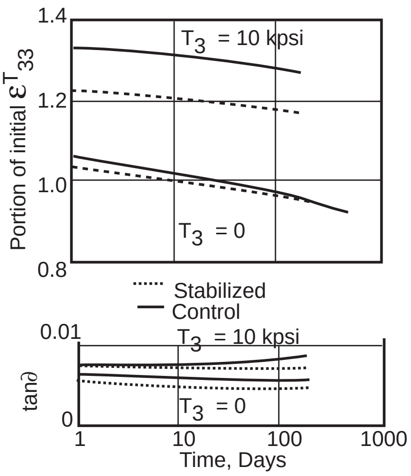


FIG. 11. Portion of initial permittivity and tan∂ for fourth stress cycle as function of time after poling; stabilized and un stabilized PZT-4. Data from Fig. 10.

## II. SUMMARY

Two piezoelectric ceramics widely used for high power high-efficiency underwater sound projectors, PZT-4 and PZT-8, were heat treated to minimize the rise in permittivity with stress. This was found to be a moderately successful procedure when ceramics so treated were compared to unstabilized ceramics for stress cycling to 20 kpsi. After several stress cycles, stress stabilization was also effective in reducing the permittivity rise. During a six-month aging study using stress cycles to 10 kpsi, it was found that the heat stabilizing treatment has permanent beneficial effect, whereas the stress stabilization with stress of 10 kpsi is transitory.

## ACKNOWLEDGMENTS

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TABLE I. Measurements of PZT-4 & PZT-8 discs showing effect on properties of heat treatment time

| | Days after poling | $\varepsilon_{33}^T/\varepsilon_o$ | % | $k_p$ | % | N$_1$ Hz.m | % | $Q_M$ | % | $d_{33}$ ($\times 10^{-12}$m/V) | % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **Values for PZT-4** | | | | | |
| | PRE | 1183 | 87.9 | - | - | - | - | - | - | - | - |
| Group I | 1 | 1346 | 100 | 0.528 | 100 | 1599 | 100 | 340 | 100 | 278 | 100 |
| | 2 | 1321 | 98.1 | 0.525 | 99.4 | 1604 | 100.3 | 490 | 144 | 273 | 98 |
| | 14 | 1273 | 94.6 | 0.518 | 98.1 | 1617 | 101.1 | 590 | 174 | 258 | 93 |
| | 36 | 1174 | 87.2 | 0.514 | 97.3 | 1622 | 101.4 | 640 | 188 | 258 | 93 |
| | PRE | 1154 | 86.6 | - | - | - | - | - | - | - | - |
| Group II | 1 | 1333 | 100 | 0.540 | 100 | 1592 | 100 | 360 | 100 | 278 | 100 |
| | 2 | 1375 | 103.2 | 0.469 | 86.9 | 1614 | 101.4 | 470 | 131 | 236 | 85 |
| | 14 | 1304 | 97.8 | 0.460 | 85.2 | 1633 | 102.6 | 640 | 178 | 241 | 87 |
| | 36 | 1284 | 96.3 | 0.458 | 84.8 | 1639 | 103.0 | 720 | 200 | 233 | 84 |
| | PRE | 1182 | 86.0 | - | - | - | - | - | - | - | - |
| Group III | 1 | 1375 | 100 | 0.547 | 100 | 1590 | 100 | 370 | 100 | 281 | 100 |
| | 2 | 1350 | 98.2 | 0.545 | 99.6 | 1594 | 100.3 | 500 | 135 | 275 | 98 |
| Heat Treat 13 days | 14 | 1413 | 102.8 | 0.485 | 88.7 | 1609 | 101.2 | 530 | 143 | 252 | 90 |
| after poling | 36 | 1335 | 97.1 | 0.475 | 86.8 | 1629 | 102.5 | 700 | 189 | 245 | 87 |
| | PRE | 1216 | 87.1 | - | - | - | - | - | - | - | - |
| Group IV | 1 | 1396 | 100 | 0.543 | 100 | 1590 | 100 | 370 | 100 | 276 | 100 |
| | 2 | 1378 | 98.7 | 0.541 | 99.6 | 1597 | 100.4 | 490 | 132 | 276 | 100 |
| Heat Treat 35 days | 14 | 1321 | 94.6 | 0.535 | 98.5 | 1610 | 101.3 | 630 | 170 | 270 | 98 |
| after poling | 36 | 1416 | 101.4 | 0.477 | 87.8 | 1611 | 101.3 | 480 | 130 | 248 | 90 |
| | | | | | | **Values for PZT-8** | | | | | |
| | PRE | 919 | 100.2 | - | - | - | - | - | - | - | - |
| | 1 | 917 | 100 | 0.481 | 100 | 1690 | 100 | 1200 | 100 | 226 | 100 |
| | 2 | 907 | 98.9 | 0.480 | 99.8 | 1691 | 100.1 | 1240 | 103 | 216 | 96 |
| | 14 | 879 | 95.9 | 0.474 | 98.5 | 1701 | 100.7 | 1480 | 123 | 216 | 96 |
| | 36 | 874 | 95.3 | 0.472 | 98.1 | 1708 | 101.1 | 1590 | 133 | 207 | 92 |
| | PRE | 921 | 101.4 | - | - | - | - | - | - | - | - |
| | 1 | 908 | 100 | 0.478 | 100 | 1693 | 100 | 1160 | 100 | 221 | 100 |
| | 2 | 1062 | 17.0 | 0.452 | 94.6 | 1689 | 99.8 | 1240 | 107 | 211 | 95 |
| | 14 | 1012 | 111.5 | 0.444 | 92.9 | 1700 | 100.4 | 1470 | 127 | 224 | 101 |
| | 36 | 1007 | 110.9 | 0.443 | 92.7 | 1703 | 100.6 | 1610 | 139 | 232 | 105 |
| | PRE | 927 | 100.5 | - | - | - | - | - | - | - | - |
| | 1 | 922 | 100 | 0.490 | 100 | 1689 | 100 | 1130 | 100 | 224 | 100 |
| | 2 | 914 | 99.1 | 0.489 | 99.8 | 1691 | 100.1 | 1280 | 113 | 213 | 95 |
| | 14 | 1070 | 116.1 | 0.464 | 94.7 | 1681 | 99.5 | 1240 | 110 | 244 | 109 |
| | 36 | 1020 | 110.6 | 0.457 | 93.3 | 1696 | 100.4 | 1590 | 141 | 213 | 95 |
| | PRE | 932 | 100.4 | - | - | - | - | - | - | - | - |
| | 1 | 928 | 100 | 0.488 | 100 | 1688 | 100 | 1180 | 100 | 223 | 10 |
| | 2 | 921 | 99.2 | 0.487 | 99.8 | 1693 | 100.3 | 1260 | 107 | 211 | 95 |
| | 14 | 891 | 96.0 | 0.481 | 98.6 | 1700 | 100.7 | 1450 | 123 | 218 | 98 |
| | 36 | 1086 | 117.0 | 0.464 | 95.1 | 1683 | 99.7 | 1250 | 106 | 228 | 102 |

TABLE II. Percent rise in permittivity and tan∂ for PZT-4 at various aging times for the first and fourth stress cycles to 10kpsi

| | Time | 1 day | | 7 days | | 42 days | | 180 days | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1st | 4th | 1st | 4th | 1st | 4th | 1st | 4th |
| $\varepsilon_{33}^T/\varepsilon_o$ | Norma1 | 34.8 | 25 | 36.0 | 27 | 38.7 | 29 | 38.2 | 31 |
| | Stabilized | 23.8 | 17 | 25.2 | 20 | 27.0 | 21 | 28.6 | 23 |
| tan∂ | Normal | 120 | 18 | 163 | 30 | 192 | 43 | 158 | 53 |
| | Stabilized | 109 | 34 | 131 | 52 | 168 | 50 | 186 | 57 |