

# Dielectric and piezoelectric properties of modified lead titanate zirconate ceramics from 4.2 to 300K

X. L. ZHANG, Z. X. CHEN, L. E. CROSS, W. A. SCHULZE

*Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802, USA*

The dielectric and piezoelectric properties (d-p properties) of four kinds of doped lead titanate zirconate piezoelectric ceramics (PZTs) have been measured from 4.2 to 300 K. The d-p properties of the materials converge with decreasing temperature down to liquid helium temperature, even though the properties have large differences at room temperature. The values of mechanical and electrical quality factors,  $Q_m$ ,  $Q_e$ , and of the frequency constant,  $N$ , of the materials increased at low temperature. It is evident from the freeze out in  $K'$  and the associate temperature: frequency-dependent maxima in  $\tan \delta$  that the relaxation processes including ferroelectric domain wall motion and thermal defect motion contribute to the d-p properties. The Navy type-III composition has a minimum temperature coefficient of d-p parameters and it is evident that PZT ceramics modified with  $Fe_2O_3$  can provide good stability and also give the strongest piezoelectric response at liquid helium temperature.

## 1. Introduction

PZT ceramics with composition close to the morphotropic phase boundary (MPB) have increased d-p properties [1, 2]. However, most of the practical PZT ceramics are modified by adding different dopants to maximize specific properties. These dopants can be divided into two groups as follows [3]:

(1) "softeners": which cause a decrease in the coercive field, electric and mechanical quality factors, while increasing the dielectric constant and piezoelectric coupling factors. The typical softeners are  $La_2O_3$ ,  $Nb_2O_5$ ,  $Ta_2O_5$  and  $Sb_2O_3$ ;

(2) "hardeners": which cause an increase in the coercive field and quality factors, and a decrease in dielectric constant. The typical hardeners are  $Fe_2O_3$ ,  $MgO$  and  $Sc_2O_3$ .

The mechanisms by which these modifiers act upon the properties are rather complex, but basically, their effects can be explained by the theory of vacancy compensation in the lattice of PZT [4] and of space charge effects [5].

Investigating the d-p properties of modified

PZT ceramics in a wide temperature range should provide some additional information about the mechanisms by which the dopants effect the properties of PZT ceramics and also some information about phase transitions in the PZT system.

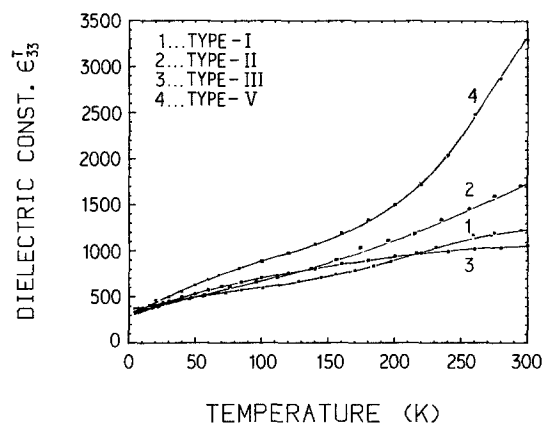


Figure 1 A plot of dielectric constant,  $\epsilon_{33}^T$ , against temperature measured at a frequency of 1 kHz, and electric field strength of  $10 \text{ V cm}^{-1}$  for four types of doped PZT ceramics.

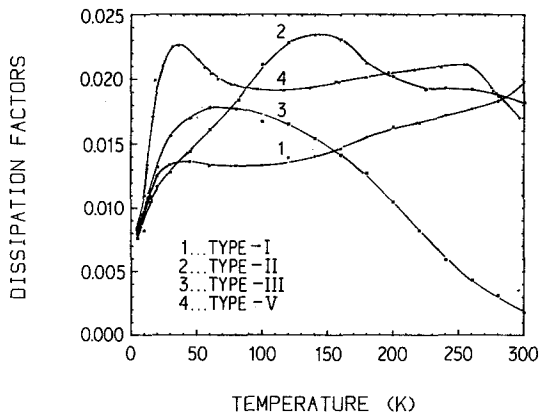


Figure 2 A plot of dissipation factor against temperature measured at a frequency of 1 kHz field strength,  $E_3$ , of  $10 \text{ V cm}^{-1}$  for four types of ceramics.

The study of commercial PZT will also give the application engineers a data base from which to choose PZT types for low-temperature applications.

## 2. Experimental procedure

The samples used in this study were a family of commercial PZT from one manufacturer that are categorized as Navy-type I, II, III, and V. The main compositions of the ceramics is lead titanate zirconate and each type is modified by different dopants. The samples were received in the form of prepoled and silvered discs. When possible, measurements were made on the undisturbed discs, but it was necessary to cut and repole bar-shaped specimens to fill the dimensional requirements of the IRE standards on piezoelectric crystals [6]. When the ceramics were reshaped,

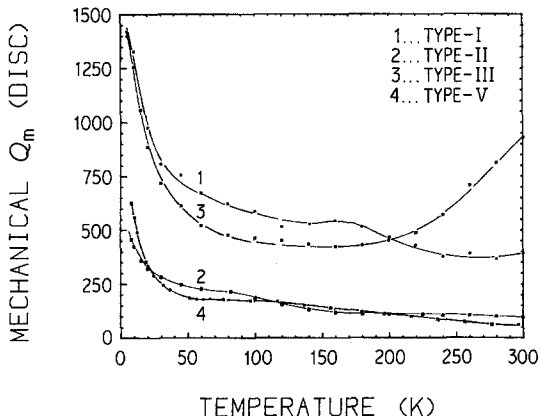


Figure 3 Mechanical  $Q_m$ -temperature dependence for four types of doped PZT ceramics.

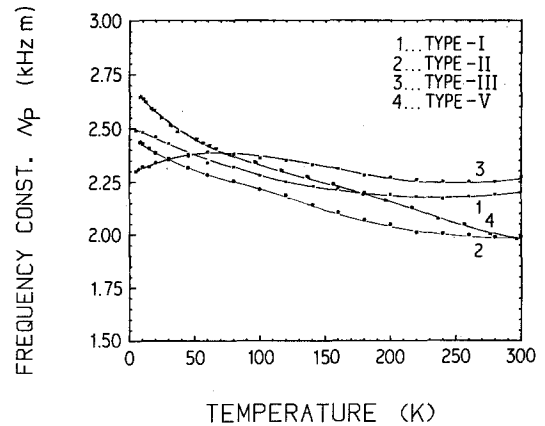


Figure 4 A plot of frequency constant,  $N_p$ , against temperature for four types of PZT ceramics.

fired or sputtered on silver or gold, electrodes were used. All shapes met the dimensional requirements of the standard and were suspended in vacuum by fine Cu or Ag wire.

The resonance measurements were made on a Hewlett Packard spectrum analyser model 3595A and dielectric measurements were made on an automatic capacitance bridge Hewlett Packard Model 4270 or 4275.

## 3. Results and discussion

Figs. 1 and 2 show the temperature dependences of the dielectric constant  $\epsilon_{33}^T$  and dissipation factor in the range 4.2 to 300 K. The  $\epsilon_{33}^T$  and  $\tan \delta$  decreased and converged at very low temperature. This shows that the base composition of the four kinds of ceramics is very close. At room temperature, the  $\epsilon_{33}^T$  were widely separated,

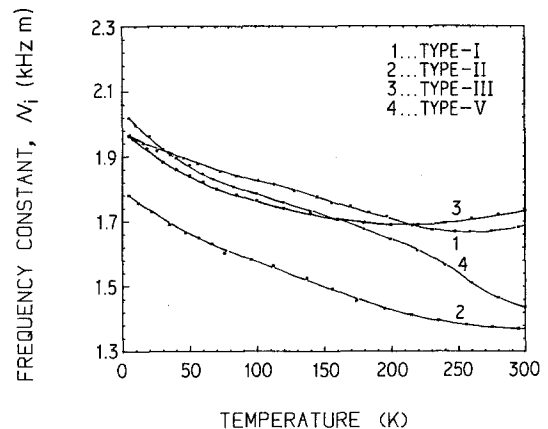


Figure 5 A plot of frequency constant,  $N_i$ , against temperature for four types of PZT ceramics.

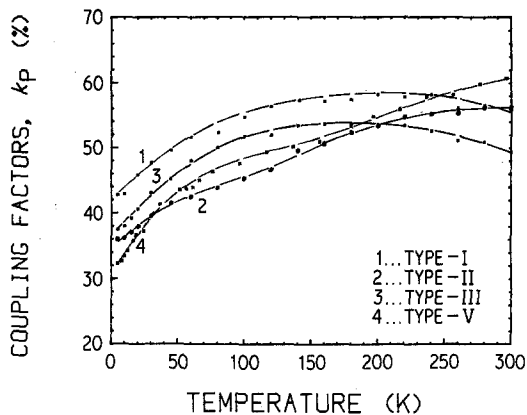


Figure 6 A plot of planar coupling factor,  $k_p$ , against temperature for four types of PZT ceramics.

clearly a result of the different dopants. For types I and III, which are the hard materials modified by hardeners NiO and  $Fe_2O_3$ , respectively, the permittivity is smaller. The soft materials, types II and IV, which were modified by softeners  $Nb_2O_5$  and  $Sb_2O_3$ , respectively, have higher permittivity. From Fig. 2 it can be seen that every sample has a characteristic  $\tan \delta$  peak; it suggested that there is at least one relaxation process for each sample in this range of temperature. The relaxation processes could be connected with the impurity ions and with domain walls or phase-boundary motion. At very low temperature, these thermally activated effects are "frozen" out which makes the  $\epsilon_{33}^T$  and  $\tan \delta$  converge to the average of the intrinsic single-domain properties.

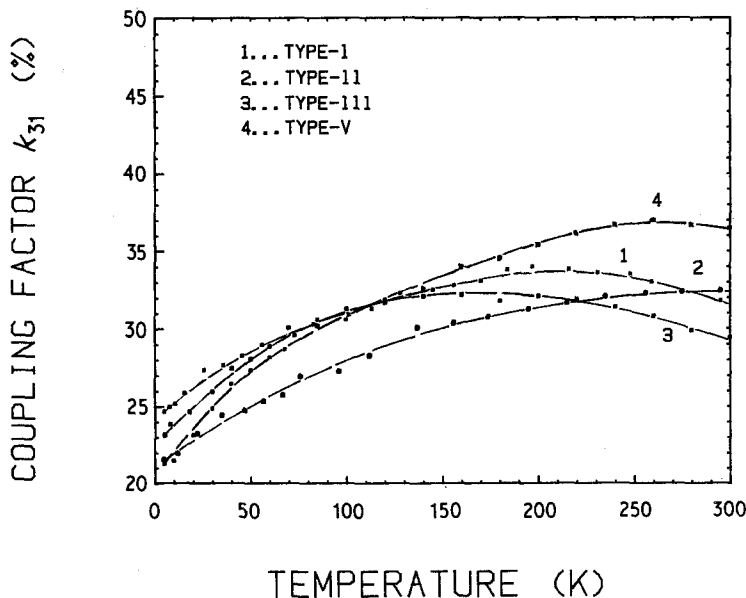


Figure 7 A plot of coupling factor,  $k_{31}$ , against temperature for four types of PZT ceramics.

Figs. 3 to 5 show the mechanical quality factor,  $Q_m$ , and frequency constant  $N_p$  (planar) and  $N_t$  (thickness). The  $Q_m$  of hard materials, types I and III, are much larger than those of the softer materials. Because the relaxation processes are "frozen" out,  $Q_m$  becomes very high for all of the samples at very low temperature. For hard materials I and III, the temperature coefficient of  $N_p$  and  $N_t$  are much smaller than for the softer materials. All of the frequency constants decreased with increasing temperature, except for type III; its  $N_p$  is anomalous in the 4.2 to 80 K range.

The PZT system has intrinsically p-type conductivity resulting from excess Pb vacancies [7]. If 5-valence ions replace  $Zr^{4+}$  or  $Ti^{4+}$ , or 3-valence ions replace  $Pb^{2+}$  (or vacancies of  $Pb^{2+}$ ), they behave as donors. The donors decrease the conductivity by electron-hole compensation. The aliovalent ions which enter the lattice and replace the  $Pb^{2+}$  or  $Zr^{4+}$  or  $Ti^{4+}$ , provide the relaxation ions that contribute to the dielectric polarization and piezoelectric properties. The motions of relaxing ions under stress is an intrinsically lossy process [8], and therefore reduces the electrical and mechanical quality factors,  $Q_e$  and  $Q_m$ , even though the d.c. resistivity is increased.

Because of additional polarizability associated with the defects, the "soft" materials have larger coupling factor values and piezoelectric constant values than "hard" materials at higher temperature, as can be seen in Figs. 6 to 10. "Hard" materials, types I and III, have smaller  $k$  and  $d$  values, and

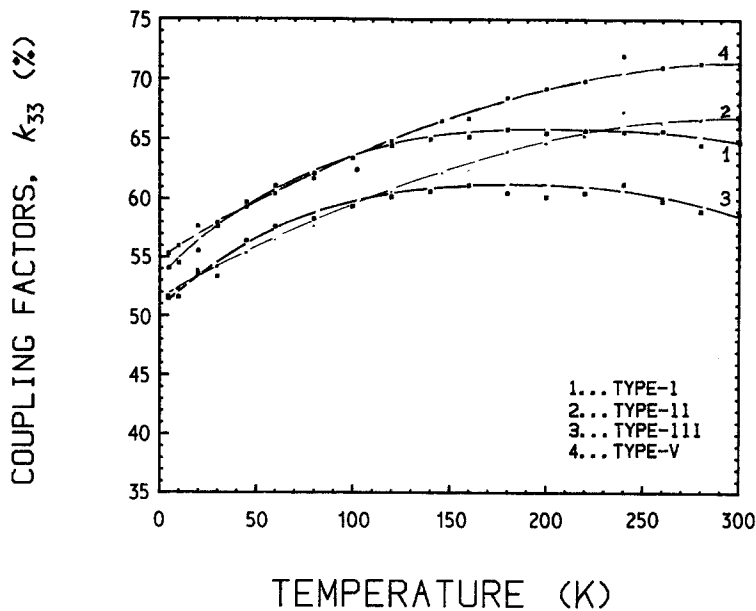


Figure 8 A plot of coupling factor,  $k_{33}$ , against temperature for four types of PZT ceramics.

also smaller temperature coefficient of  $\epsilon$ ,  $k$ , and  $d$  parameters. The effects of “hardeners” are in many ways opposite to that of the “softeners”. They behave as acceptors, not as donors. For example, the impurity ion of type III as  $\text{Fe}^{3+}$  (or  $\text{Fe}^{2+}$ ). Since its ionic radius is very close to the radius of  $\text{Zr}^{4+}$  or  $\text{Ti}^{4+}$ , the  $\text{Fe}^{3+}$  ion enters the  $\text{Pb}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  lattice to replace  $\text{Ti}^{4+}$  or  $\text{Zr}^{4+}$ . In this location it lacks an outer electron and acts as an acceptor to make the hole concentration increase, producing a more strongly p-type ceramic. The modification with  $\text{Fe}^{3+}$  creates oxygen vacancies and therefore tends to limit its own

solubility in the PZT lattice. Polarization stiffening has been postulated to occur by the orientation of slowly reorientable defect dipoles in the lattice and by space charge development at the grain boundary where the exsolved additional  $\text{Fe}^{3+}$  may be compensated by domain polarization or may give rise to a second phase. The acceptor dopant additions contribute little to the polarizability and actually stiffen out some of the extrinsic polarizability of the pure material. The limited stiffening of the hard material (types I and III) with reduced temperature is qualitatively explained by this effect.

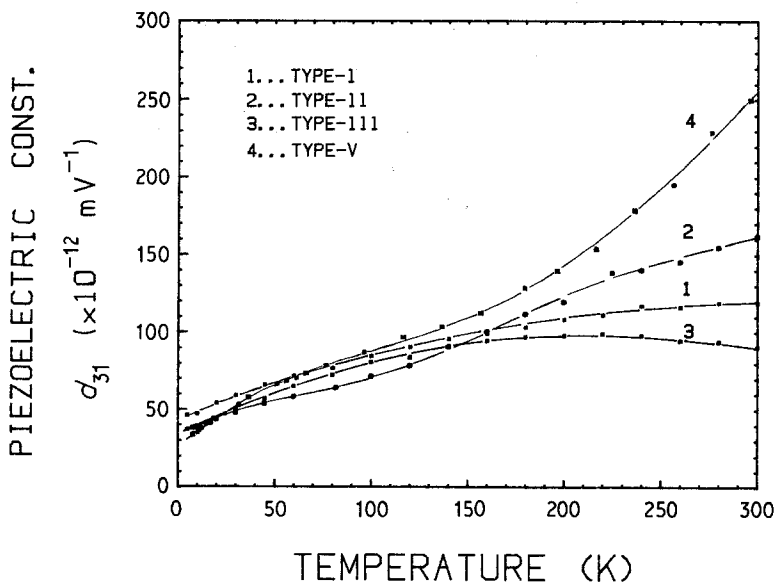


Figure 9 A plot of piezoelectric constant,  $d_{31}$ , against temperature for four types of PZT ceramics.

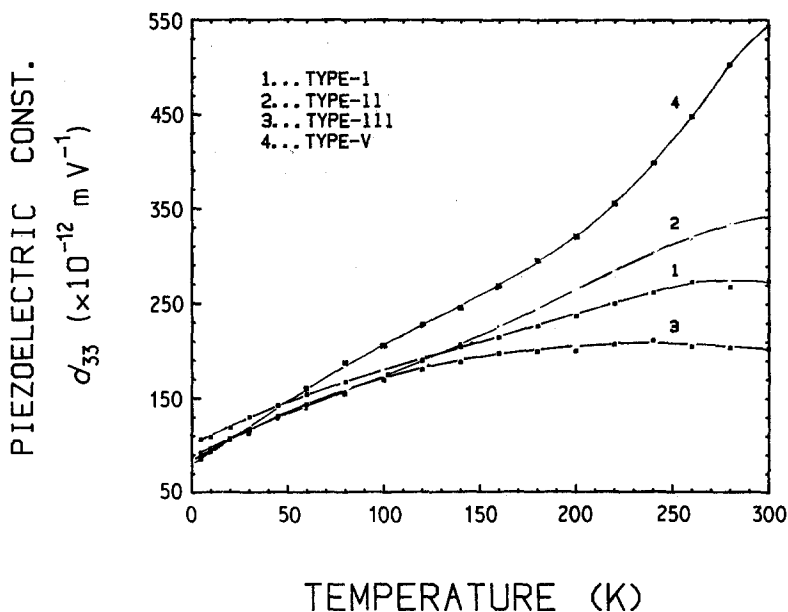


Figure 10 A plot of piezoelectric constant,  $d_{33}$ , against temperature for four types of PZT ceramics.

The second mechanism that may alter the d-p properties with reduced temperature is a change in phase content (tetragonal-rhombohedral) due to a finite temperature dependence of the morphotropic boundary. Some evidence for this shift may be contained in the temperature dependence of  $\tan \delta$ , but the maxima as observed in Fig. 2 could also be associated with minor dielectric relaxation processes.

#### 4. Conclusions

The main d-p properties of four kinds of doped PZT ceramics (two of them hard materials, another two soft materials) have been measured from 4.2 to 300 K. The hard materials (types I and III) have smaller dielectric and piezoelectric activities, but they also have smaller temperature coefficients of d-p parameters. For very low temperature application, they may, in fact, be preferable to the soft materials. In both types of doped materials, evi-

dence for dielectric relaxation mechanisms is given by the temperature-frequency course of the permittivity and  $\tan \delta$ , and it is clear that the processes are significantly different in the two cases.

#### References

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