

# Pyroelectric Activity of Ferroelectric PT/PVDF-TRFE

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## ABSTRACT

This paper studies the pyroelectric coefficient of 0-3 composites consisting of 27%vol lead titanate (PT) powder embedded in a vinylidene fluoride-trifluoroethylene copolymer (PVDF-TRFE) matrix. The constituent phases of the composites have been polarized in four possible ways: only the copolymer polarized; only the ceramic polarized; the copolymer and ceramic phases polarized in the same direction; the two phases polarized in opposite directions. The pyroelectric coefficient was measured by a dynamic method at 5 mHz within the temperature range 20 to 90°C (which covers the ferroelectric to paraelectric phase transition temperature of the copolymer matrix). The composite with the copolymer and ceramic phases polarized in the same direction exhibits strong pyroelectric but relatively weak piezoelectric activity, and *vice versa* when the constituent phases are oppositely polarized. A theoretical model is used to analyze the pyroelectric coefficient of the composites in terms of the pyroelectric and dielectric properties of the copolymer matrix as determined from experiment, and those of the ceramic particles which are assumed to be temperature independent. The pyroelectric coefficient and dielectric permittivity of the ceramic particles are obtained as fitting parameters. The theoretical prediction is found to agree well with the experimental data.

## 1 INTRODUCTION

COMBINING ferroelectric ceramic particles and a polymer matrix to form composites can give advantages of mechanical flexibility and low acoustic impedance while retaining useful pyroelectric and piezoelectric properties. Such materials have a considerable potential in sensor and transducer applications, due especially to the possibility of tailoring its properties to specifications by a judicious selection of constituent components and of their volume ratio. An additional degree of freedom is made available by employing a polymer matrix that is also ferroelectric, in which case the state of its polarization may be manipulated by poling techniques.

For the present study we choose lead titanate (PT) powder as inclusion and vinylidene fluoride-trifluoroethylene copolymer (PVDF-TRFE) of VDF to TRFE molar ratio 56/44 as the matrix material. Using a special poling method [1, 2] composites in the following four different polarization states have been prepared: only the matrix polarized, only the inclusions polarized, the two phases polarized in parallel directions and the two phases polarized in antiparallel directions. The directions of the polarization vectors of the matrix and the inclusions in these different polarization states are schematically illustrated in Figure 1. The pyroelectric coefficients of these composites and the dielectric permittivity have been measured from 20 to 90°C. These experimental data

are used for a theoretical modeling of the pyroelectric coefficient of the composites.

## 2 THEORY

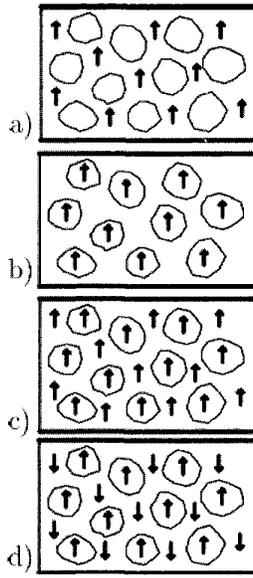
Compared to the large amount of theoretical work on the dielectric properties of composites, there are relatively few theories describing the effective pyroelectric coefficient of composites consisting of pyroelectric inclusions in a pyroelectric matrix. The pyroelectric coefficient  $p$  of composites with a non-pyroelectric matrix is commonly described as a product of the volume fraction of the inclusions  $v$ , the local field coefficient  $L_E$  with respect to the electric field and the pyroelectric coefficient of the inclusions  $p_i$  [3, 4].

$$p = vL_E p_i \quad (1)$$

A similar formula was also proposed by Furukawa *et al.* [5, 6] for the effective piezoelectric coefficient  $d$  of a composite of incompressible piezoelectric inclusions in an incompressible non-piezoelectric matrix (*i.e.* both the inclusions and matrix have a Poisson's ratio  $\nu = 0.5$ )

$$d = vL_T L_E d_i \quad (2)$$

where  $L_T$  is the local field coefficient with respect to the stress and  $d_i$  is the piezoelectric coefficient of the inclusions. To extend Equation (2) to the case where the matrix is also piezoelectric, transformation rules for  $v$ ,  $L_E$ ,  $L_T$  and  $d_i$  have been suggested to obtain the matrix contribution to  $d$  [5]. Applying the same transformation rules for extending



**Figure 1.** Schematic view of a composite indicating the directions of the polarizations in the polymer matrix and ceramic inclusions. (a) only the copolymer matrix polarized, (b) only the ceramic inclusions polarized, (c) both phases polarized in parallel directions, (d) two phases polarized in antiparallel directions.

to the case of a pyroelectric matrix, Equation (1) becomes

$$p = vL_E p_i + (1 - vL_E)p_m \quad (3)$$

where  $p_m$  is the pyroelectric coefficient of the matrix. The following expression for  $L_E$  was derived [7] from the Maxwell-Wagner model, assuming that the inclusions are spherical and of low volume fraction

$$L_E = \frac{3\varepsilon_m}{(2 + v)\varepsilon_m + (1 - v)\varepsilon_i} \quad (4)$$

where  $\varepsilon_i$  and  $\varepsilon_m$  are the dielectric permittivities of the inclusions and the matrix, respectively.

For composites containing high volume fractions of inclusions or inclusions with size large compared to the sample thickness, some 1-3 connectivity is expected to come into play to complicate the original 0-3 geometry associated with low inclusion fractions. A cube model was proposed by Dias and Das-Gupta [8] to treat this case of mixed connectivity.

We have investigated the problem of spherical pyroelectric inclusions embedded in a pyroelectric matrix with 0-3 connectivity. For the case where the difference in the polarizations of the two phases is completely compensated by charges at the matrix-inclusion interfaces we derived the relation

$$p = \frac{\varepsilon - \varepsilon_m}{\varepsilon_i - \varepsilon_m} p_i + \frac{\varepsilon_i - \varepsilon}{\varepsilon_i - \varepsilon_m} p_m \quad (5)$$

where  $\varepsilon$  is the effective dielectric permittivity of the composite. In comparison to Equation (3) with  $L_E$  given by Equation (4), Equation (5) should be a more accurate expression for  $v$  larger than (say)  $\approx 15\%$ , below which they give approximately the same answers. The derivation of Equation (5) will be given in detail in a subsequent paper.

For 0-3 composites with spherical inclusions  $\varepsilon$  may be calculated

from the Bruggeman formula [9]

$$\frac{\varepsilon_i - \varepsilon}{\varepsilon^{1/3}} = (1 - v) \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_m^{1/3}} \quad (6)$$

### 3 EXPERIMENTAL

Roughly spherical particles of PT [10] of size  $\sim 100$  nm have been embedded in PVDF-TRFE 56/44 mol-% copolymer to form a 0-3 composite with 27%vol ceramic. The copolymer was dissolved first in methylethylketone. Then the ceramic powder was added to the copolymer solution and dispersed by ultrasonic agitation. After the solvent had evaporated, the composite was placed between two stainless steel plates covered with aluminum foil and a  $30 \mu\text{m}$  thick film was prepared by compression molding at  $220^\circ\text{C}$ . Gold electrodes were deposited on the top and bottom surfaces of the film. For the characterization of the pyroelectric coefficient and dielectric permittivity of the matrix material, a PVDF-TRFE 56/44 mol-% copolymer film was also prepared in a similar way.

The poling procedures which have been developed are based on the following considerations:

1. When an electric field is applied to the 0-3 composite for a duration which is substantially shorter than the dielectric relaxation time of charge in both components, then the divergence of the electric displacement at the internal interfaces is zero. The maximum achievable polarization of PVDF-TRFE is substantially lower than the remanent polarization of PT. Therefore, it is expected that the polarization state of the inclusions remains essentially unchanged while the matrix is fully polarized if the field is of an appropriate magnitude. At room temperature the dielectric relaxation time in PVDF-TRFE is  $>1000$  s. Therefore, poling durations  $<1$  s should fulfil this condition, even when the injection of charge from the electrodes is taken into account.

2. On the other hand, the ceramic particles can only be poled efficiently under conditions which allow a substantial transport of charge within the material, *i.e.* at high temperatures and for a long poling time.

In the experiments the following poling conditions were selected:

1. At room temperature several cycles of a sinusoidal electric field with frequency  $f = 10$  Hz and amplitude  $E_{\text{rms}} = 80 \text{ V}/\mu\text{m}$  were applied to the sample.
2. At  $100^\circ\text{C}$ , *i.e.*, when the copolymer matrix is in the paraelectric phase, a dc electric field of  $55 \text{ V}/\mu\text{m}$  is applied for one hour. Then the field was turned off and the sample was cooled to room temperature.

Although a short dc-pulse would serve more or less the same purpose as condition (1), a sinusoidal electric field has been used in this work because the electric displacement can be measured simultaneously with a Sawyer-Tower circuit, thus allowing monitoring of the remanent polarization.

When a sample is poled under condition (2), charge is injected from the electrodes into the material and the existing charge is rearranged. Therefore, an internal field in the material still persists after the external field has been removed. This results in an enhanced pyroelectric activity. For this reason, pyroelectric coefficient measurements were performed after the samples had been stored at room temperature for

several days during which the pyroelectric coefficient decreased to a steady value.

The polarization state of the matrix and inclusions was characterized by the measurement of the pyroelectric coefficient of the composite as a function of temperature between 20°C and 90°C, covering the ferroelectric as well as the paraelectric state of the copolymer matrix.

The Curie temperature of PT is substantially above this range, so the inclusions remain ferroelectric over the entire investigated temperature range. A comparison of the pyroelectric coefficient before and after thermal depolarization of the matrix allows the characterization of the polarization state of both the ceramic inclusions and the copolymer matrix.

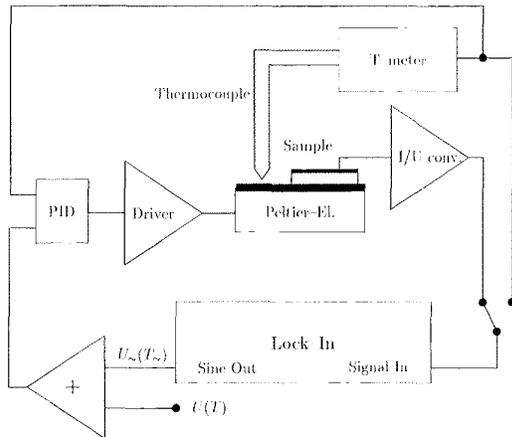


Figure 2. Experimental setup for the dynamic measurement of pyroelectric coefficient. The sinusoidal output voltage  $U_{\sim}$  at frequency  $f$  from a lock-in amplifier is superimposed on the dc voltage  $U$  from a programmable voltage source to form the reference signal input to a PID regulator. The PID regulator compares this signal to the true temperature signal measured by a thermocouple and controls a Peltier element to generate the modulated temperature  $T_m(t) = T + T_{\sim} \sin 2\pi ft$ . The sample under investigation is in contact with the Peltier element. The pyroelectric current signal and the ac temperature signal are measured with a lock-in amplifier.

An ac method was used to measure the pyroelectric coefficient as shown in Figure 2. At a certain temperature  $T$  the sample temperature was sinusoidally modulated  $T_m(t) = T + T_{\sim} \sin 2\pi ft$  at a frequency  $f = 5$  mHz and an amplitude  $T_{\sim} = 1$  K using a Peltier element controlled by a proportional integral differential (PID) regulator [11-13]. The pyroelectric current signal was amplified with an electrometer and the component of the current  $90^\circ$  out of phase with respect to the temperature  $T_m(t)$  (i.e. in phase with the temporal derivative  $dT_m(t)/dt$ ) was measured with a lock-in amplifier. After adjusting to a measurement temperature  $T$  the sample was kept at  $T$  for 15 min for the signal to become stable before the pyroelectric measurement was performed.

The piezoelectric  $d_{33}$  coefficient of the composite material was measured at room temperature using a piezo tester. A sinusoidal mechanical stress at a frequency of 60 Hz was applied to the sample while the current signal was recorded.

To measure the dielectric permittivity at the same frequency ( $f = 5$  mHz) used for pyroelectric coefficient measurements, a sinusoidal

electric field of amplitude  $E_{\sim} = 1$  V/ $\mu$ m was applied to the sample. The electric current through the sample was amplified with an electrometer and the real and imaginary parts of the signal were measured with a lock-in amplifier.

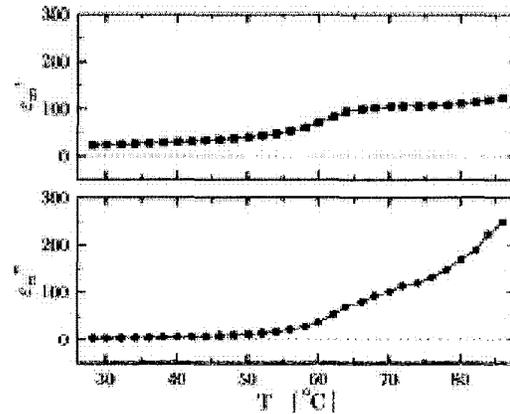


Figure 3. Real and imaginary part of the dielectric permittivity of PVDF-TRFE 56/44 mol-% as a function of temperature measured at 5 mHz. The lines are drawn to guide the eyes.

### 4 RESULTS

The complex dielectric permittivity  $\epsilon_m$  of unpoled PVDF-TRFE measured at a frequency  $f = 5$  mHz is shown in Figure 3. At such a low frequency the real part  $\epsilon'_m$  does not show a maximum around the Curie temperature  $T_C \approx 65^\circ\text{C}$  (a feature normally observed at frequencies  $>10$  Hz); the ferroelectric phase transition is only seen as a step in  $\epsilon'_m$  at  $T_C$ . The strong rise in the imaginary part  $\epsilon''_m$  above  $T \approx 60^\circ\text{C}$  is assumed to be related to the slow relaxation processes in the amorphous phase and also to dc conduction. The complex dielectric permittivity  $\epsilon$  of the unpoled composite sample is shown in Figure 4.

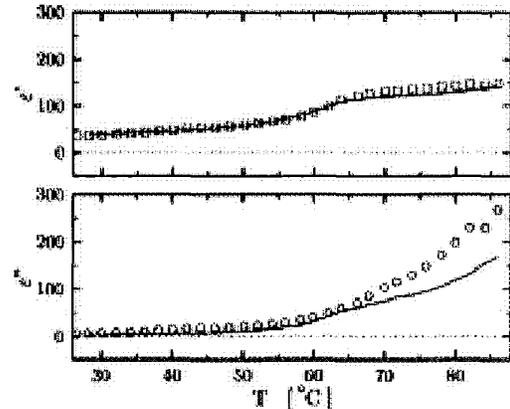


Figure 4. Real and imaginary part of the dielectric permittivity of PT/PVDF-TRFE with 27%vol PT as a function of temperature measured at 5 mHz. The data are compared with the prediction (lines) according to Equation (6) with  $\epsilon_m$  taken from Figure 3 and  $\epsilon_i = 140$ .

The pyroelectric coefficient  $p_m$  of a PVDF-TRFE copolymer sample which was poled at room temperature under condition (1) is shown in Figure 5.  $p_m$  first increases, reaches a maximum at  $\sim 52^\circ\text{C}$  and then drops to zero above  $T_C$ .

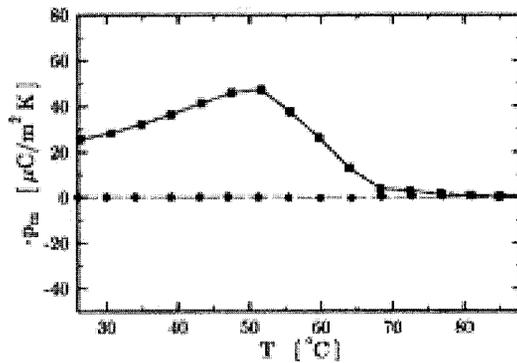


Figure 5. Pyroelectric coefficient of PVDF-TRFE as a function of temperature  $T$  measured in a heating (■) and cooling (●) cycle. The lines are drawn to guide the eyes.

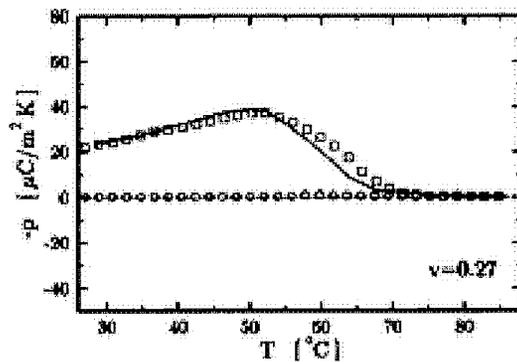


Figure 6. Pyroelectric coefficient of PT/PVDF-TRFE with only the copolymer matrix polarized measured in a heating (□) and cooling cycle (○). The data are compared with the predictions (lines) according to Equation (8).

Figure 6 shows the pyroelectric coefficient of PT/PVDF-TRFE as a function of temperature first measured in a heating run and then in a cooling run. The sample has been poled at room temperature under condition (1). After heating above the Curie temperature of the copolymer matrix, the pyroelectric coefficient vanishes and stays zero during cooling. This shows that the application of an ac voltage to the composite at room temperature polarizes only the copolymer matrix and has no effect on the inclusions.

Next, we study a sample poled at 100°C under condition (2). The result of a heating and cooling cycle in Figure 7 shows the pyroelectric activity in the ceramic inclusions. Since the copolymer matrix is unpolarized, coincident data are obtained from the heating and cooling run.

Finally we applied the two poling procedures in succession. The copolymer matrix of the sample mentioned above, in which the ceramic inclusions had been polarized using procedure (2), was then polarized by procedure (1). In applying the latter procedure, there is the option of polarizing the matrix parallel or antiparallel to the polarization direction of the ceramic established by the former procedure. This can be accomplished because the final polarization direction of the polymer matrix is determined only by the electric field direction in the last half cycle of the ac voltage used in procedure (1). We have first polarized the ceramic and polymer phases in parallel. Then the pyroelectric

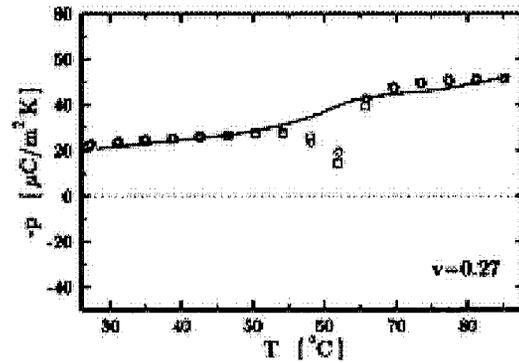


Figure 7. Pyroelectric coefficient of PT/PVDF-TRFE with only the ceramic inclusions polarized measured in a heating (□) and cooling cycle (○). The data are compared with the prediction (line) according to Equation (7).

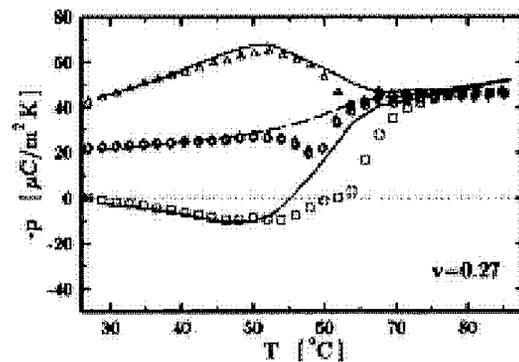


Figure 8. Pyroelectric coefficient of PT/PVDF-TRFE with both phases polarized measured as a function of temperature: (a) ceramic and copolymer polarized in the same direction ( $\Delta$ : heating,  $\diamond$ : cooling), (b) ceramic and copolymer polarized in opposite directions ( $\square$ : heating,  $\circ$ : cooling). After heating above  $T_C$  the copolymer matrix is depolarized as shown by the identical  $p$  in the cooling runs ( $\diamond$  and  $\circ$ ). The sign of  $p$  refers to the polarization direction of the ceramic inclusions. The data are compared with the predictions (lines) according to Equation (5).

coefficient was measured in a heating and cooling cycle. The result is shown in Figure 8. By heating the sample above the Curie temperature of the copolymer, the matrix has been depolarized again. The cooling run shows the pyroelectric activity in the ceramic inclusions (compare Figure 7). After this cycle the copolymer matrix of the sample again has been polarized by procedure (1), but now in a direction antiparallel to that of the ceramic inclusions. The pyroelectric coefficient again measured in a heating and cooling cycle is also included in Figure 8.

We have thus prepared composite material with the ceramic and polymer phases polarized in parallel or antiparallel directions. The results in Figure 8 show that the polarization of the inclusions is not changed by poling procedure (1), as shown by the overlapping cooling curves.

For the anti-parallel poled composite the contributions of the inclusions and matrix to the effective pyroelectric coefficient cancel out at room temperature. Due to the opposite signs of their piezoelectric coefficients, the piezoelectric activities of the inclusions and matrix reinforce each other to give a piezoelectric  $d_{33}$  coefficient of +20 pC/N. Thus we have produced a composite which is piezoelectric but not

pyroelectric. On the other hand, poling the inclusions and matrix in parallel directions gives a material with a pyroelectric coefficient  $-p = 42 \mu\text{C}/\text{m}^2\text{K}$  but with vanishingly small piezoelectric activity ( $d_{33} \approx 1 \text{ pC}/\text{N}$ ) around room temperature.

## 5 COMPARISON WITH THEORY

While  $\varepsilon(T)$  and  $\varepsilon_m(T)$  of the composite sample and the copolymer can be measured, there is no direct experimental access to  $\varepsilon_i$ . The permittivity of the ceramic particles  $\varepsilon_i$  is likely to differ from that of the bulk material. We assume that  $\varepsilon'_i$  is not dependent on temperature in the investigated interval between 20 and 90°C, and that  $\varepsilon''_i$  is negligible. With the measured  $\varepsilon_m(T)$  (see Figure 3) as input into the Bruggeman formula (Equation (6)) and using  $\varepsilon'_i$  as a parameter to fit the calculated complex  $\varepsilon(T)$  to the experimental data in Figure 4, one obtains  $\varepsilon'_i = 140$ . The result of the fit is shown in Figure 4. Good agreement between theory and experiment is obtained for  $\varepsilon'$  over the entire temperature range. For  $\varepsilon''$  the calculated and observed values agree well at low temperatures but differ significantly above 70°C. A significant rise in  $\varepsilon''_i$  with temperature would contribute to  $\varepsilon''$ . To account for the total additional high temperature increase of  $\varepsilon''$  at 80°C,  $\varepsilon''_i$  would have to be  $\sim 500$ . However, such a high  $\varepsilon''_i$  would also decrease the pyroelectric coefficient, in contrast to the experimental observation. Therefore, we assume that at high temperatures the copolymer matrix of the composite may show higher dielectric loss than the copolymer film. This may be related to a higher dc conductivity or to an enhanced relaxation.

For a composite with only the ceramic inclusions polarized, Equation (5) reduces to

$$p(T) = \frac{\varepsilon(T) - \varepsilon_m(T)}{\varepsilon_i - \varepsilon_m(T)} p_i \quad (7)$$

$\varepsilon(T)$  of the composite sample and  $\varepsilon_m(T)$  of the copolymer sample have been measured, and  $\varepsilon_i$  has been determined by fitting to the measured  $\varepsilon(T)$ . The only unknown parameter in Equation (7) is determined as  $p_i = 160 \mu\text{C}/\text{cm}^2$  by a fit to the measured  $p(T)$  between 25°C and 55°C. It already has been discussed that  $\varepsilon''_m$  of the matrix in the composite sample and the copolymer reference sample differ at higher temperatures, so that the measured  $\varepsilon_m$  is not the most appropriate input to Equation (7) in this regime. Instead, a realistic data set is obtained by calculating  $\varepsilon_m(T)$  of the composite from the measured  $\varepsilon(T)$  and the earlier determined  $\varepsilon_i$  ( $\varepsilon'_i = 140$ ,  $\varepsilon''_i = 0$ ) in terms of Equation (6). We are using this calculated  $\varepsilon_m(T)$  for temperatures  $>55^\circ\text{C}$ , and the measured  $\varepsilon_m(T)$  for lower temperatures (where measured and calculated data actually coincide).

Figure 7 shows the experimental data together with the theoretical fit. The measured pyroelectric coefficient is described well by Equation (7) at low and high temperatures. The observed dip in  $-p$  of the composite at the Curie temperature  $T_C \approx 65^\circ\text{C}$  of the matrix is due to an incomplete compensation of the ceramic polarization by the charge trapped at the interface of inclusions and matrix. This effect is not included in Equations (5) and (7). It reflects essentially a contribution to the pyroelectric activity from the temperature dependence of the dielectric permittivity of the copolymer matrix under the influence of an internal field. This phenomenon will be discussed in detail in a subsequent paper.

After the dielectric and pyroelectric coefficients of the copolymer matrix and ceramic inclusions have been determined, all the parameters in Equation (5) are known. In the following, the pyroelectric coefficients of the composite samples in three other polarization states (only the copolymer matrix polarized, two phases polarized in parallel or in antiparallel directions) are compared with the predictions of Equation (5).

When only the matrix is polarized, Equation (5) reduces to

$$p(T) = \frac{\varepsilon_i - \varepsilon(T)}{\varepsilon_i - \varepsilon_m(T)} p_m(T) \quad (8)$$

Figure 6 shows a comparison of the measured pyroelectric coefficient with the prediction according to Equation (8). It is clear that there is good agreement between theory and experiment.

The observed and calculated (in terms of Equation (5)) pyroelectric coefficients for the composites with both phases poled in parallel or antiparallel directions are depicted in Figure 8. With the exception of the temperature range around the ferroelectric phase transition of the PVDF-TRFE matrix, the theoretical predictions agree well with the experimental data.

## 6 CONCLUSION

THE application of two different poling procedures allows the separate poling of the inclusions and matrix of PT/PVDF-TRFE composites. The polarization state of the individual constituents can be determined by comparing the effective pyroelectric coefficient before and after thermal depolarization of the copolymer matrix. Using 27%vol of PT a pyroelectric compensated piezoelectric material or a piezoelectric compensated pyroelectric material can be fabricated by antiparallel or parallel poling of the inclusions and matrix, respectively.

The pyroelectric coefficients of the composites in four different polarization states are well described by a theoretical model.

## ACKNOWLEDGMENT

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