Second Order Dielectric Permittivity of PT/P(VDF–TrFE) 0–3 Composites

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For a fundamental understanding of a composite material comprising two ferroelectrics and also with respect to applications, it is important to know the degree of poling in the two constituent phases. The second order dielectric permittivity of 0–3 composites of lead titanate (PT) and vinylidene fluoride–trifluoroethylene (PVDF–TrFE), with various volume fractions of the ceramic phase, is reported. Composites with only the ceramic phase polarized, i.e. poled at temperature above the Curie temperature of the copolymer and below the Curie temperature of the ceramics, and composites with both the ceramic and the copolymer phases polarized have been studied. The experimental results have been analyzed with a model of ferroelectric cuboides embedded in a ferroelectric matrix. The contributions of the ceramic and copolymer phases to the second order permittivity have been separated, thereby giving the degree of poling in each of the two phases.

I. INTRODUCTION

Composites of ferroelectric ceramics like lead zirconate titanate (PZT) or modified lead titanate (PT) with the ferroelectric copolymer P(VDF–TrFE) have attracted considerable research interest in recent years. The composites combine the high pyro– and piezoelectric coefficients of the ceramic with the good mechanical properties of the polymer. The poling of this two phase system composed of two ferroelectric materials is a complex process. Its investigation is both of fundamental interest and important to achieve a high polarization for applications. The nonlinear dielectric permittivity of second order is a measure for the polarization of a ferroelectric. In the following, it is shown how the polarization of each component of a composite can be determined by analysing the measured second order dielectric nonlinearity on the basis of a capacitor model.

II. THEORY

1. Second Order Permittivity as a Measure of the Remanent Polarization

The nonlinear permittivities ε_n are the coefficients in the series expansion of the dielectric displacement D in powers of the electric field E

$$D = P_s + \varepsilon_0\varepsilon_1 E + \varepsilon_0\varepsilon_2 E^2 + \varepsilon_0\varepsilon_3 E^3 + \dots . \quad (1)$$

For ferroelectric materials which can be described by a Landau free energy expansion

$$F = F_0 + \frac{1}{2}\alpha D^2 + \frac{1}{4}\gamma D^4 + \frac{1}{6}\delta D^6 \quad (2)$$

the second order permittivity is given by the relation [1]

$$\varepsilon_0\varepsilon_2 = -P_r(\varepsilon_0\varepsilon_1)^3\left(3\gamma + 10\,\delta P_s^2\right), \quad (3)$$

where P_s and P_r are the spontaneous and the remanent polarization, respectively.

For the P(VDF–TrFE) copolymers things are more complicated because they are semicrystalline, and in addition the linear permittivity ε_1 depends on the degree of poling. For these materials, however, the quotient $\varepsilon_0\varepsilon_2/(\varepsilon_0\varepsilon_1)^3$ is proportional to the remanent polarization, as we found experimentally.

2. Second Order Permittivity of a Composite of Two Ferroelectric Materials

We use a simple capacitor model depicted in Fig. 1 to describe the first and second order permittivities of a composite of ferroelectric particles (e.g. ceramic material) embedded in a ferroelectric matrix (e.g. polymer material). The results for the linear and second order permittivity of the entire system are

$$\varepsilon_1 = \frac{\Phi}{h}\frac{\varepsilon_{p1}\varepsilon_{c1}}{h\varepsilon_{p1} + (1-h)\,\varepsilon_{c1}} + (1 - \frac{\Phi}{h})\varepsilon_{p1}, \quad (4)$$

$$\varepsilon_2 = \frac{\Phi}{h}\frac{(1-h)\,\varepsilon_{c1}^3\varepsilon_{p2} + h\,\varepsilon_{p1}^3\varepsilon_{c2}}{(h\,\varepsilon_{p1} + (1-h)\,\varepsilon_{c1})^3} + (1 - \frac{\Phi}{h})\varepsilon_{p2}, \quad (5)$$

where ε_{p1}, ε_{p2} are the first and second order permittivities of the polymer matrix, ε_{c1}, ε_{c2} are the permittivities of the ceramic, Φ is the ceramic volume fraction and $h = d_c/d$ is a geometric factor. If the ceramic particles are approximated by cuboids of width a_0 and thickness d_0 (parallel to the applied field), h can be calculated as a function of Φ and the ratio $q = a_0/d_0$. For cubic particles, $q = 1$ and $h = \Phi^{1/3}$.