DIELECTRIC NONLINEARITIES OF P(VDF-TRFE)

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Abstract

The nonlinear dielectric permittivities of copolymers of polyvinylidenfluoride (PVDF) with trifluoroethylene (TrFE) have been measured as a function of temperature. The phase transition from the ferroelectric to the paraelectric phase is characterised by the sign of the third order permittivity in the paraelectric phase. The observed third order permittivity is positive for a copolymer of 70/30 mol-% VDF-TrFE, but negative for 56/44 mol-% VDF-TrFE. This shows a change of the nature of the phase transition with the composition. Poling of the material causes a strong increase of the permittivities of even order in the ferroelectric phase, while the linear dielectric constant and the odd order permittivities slightly decrease. In the paraelectric phase, the investigated 56/44 mol-% VDF-TrFE specimens show a non vanishing second order permittivity. This deviation of the inversion symmetry is described by an internal bias field. While the absolute value of the bias field varies for different samples, it is found to be independent of temperature and a previous poling.

1. Introduction

Polyvinylidenfluoride (PVDF) and its copolymers with trifluoroethylene (P(VDF-TrFE)) consist of polar crystallites embedded in an amorphous matrix. Crystallites and amorphous phase both determine the dielectric properties. The measurement of dielectric nonlinearities is useful to obtain information on the ferroelectric properties of these complex materials [1]. Investigations of dielectric nonlinearities have been performed with respect to three particular topics: the transition from the ferroelectric to the paraelectric phase, the poling of the material and bias fields in the paraelectric phase.

2. Theory

A phenomenological description of ferroelectric materials is given by the Landau theory [2]. The ferroelectric contribution to the free energy F is written as a polynom of the dielectric displacement D:

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

The Landau parameters α, γ and δ are temperature dependent in general. A direct determination of the Landau parameters is possible by a measurement of the dielectric nonlinearities i.e., of the coefficients ϵ_n in the power series representation of the dielectric

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