Separate Poling of Inclusions and Matrix in PT/P(VDF–TrFE) 0–3 Composites

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Abstract – A procedure for separate poling of the ceramic particles and the copolymer matrix of 0–3 composites has been developed. 2.5 μm thick films of 56/44 mol-% vinylidene fluoride–trifluoroethylene (P(VDF–TrFE)) copolymer embedded with 8 volume-% lead titanate (PT) ceramic particles were investigated. First, the ceramic particles in the composite are polarized under a DC–field at temperatures above the Curie temperature of the copolymer. In the second step the P(VDF–TrFE) matrix is poled at room temperature in an AC–field at a frequency of 1 Hz. The degree of poling of the composite is then investigated by the measurement of the second order permittivity and the pyroelectric coefficient over a temperature range covering the ferroelectric and paraelectric phase of the copolymer matrix. The results show that the polarization of the ceramic is unchanged by the subsequent AC poling of the copolymer matrix.

INTRODUCTION

Composites of ferroelectric ceramics and ferroelectric copolymers combine the high pyroelectric and piezoelectric coefficients of the ceramic with the excellent mechanical properties of the copolymer. The copolymer with embedded ceramic particles can be easily deposited from solution onto the surface of a silicon chip, thereby facilating the application in integrated devices. The use of composites allows the design of materials with dielectric properties taylored to specific applications by appropriate choices of the matrix and inclusion materials and their volume fractions. The procedure for the independent poling of inclusions and matrix, which is described in the following sections, introduces an additional degree of freedom for the design of composite properties. The pyroelectric coefficients of PT and P(VDF–TrFE) have the same sign while the piezoelectric coefficients have opposite signs. This particular behavior, together with the possibility of polarizing matrix and inclusions separately, opens a way for the fabrication of piezoelectric materials in which pyroelectricicty is internally compensated, or vice versa.

CHARACTERIZATION TECHNIQUES

To analyze the degree of poling of the composite without changing its polarization, the second order permittivity and the pyroelectric coefficient were investigated.

Second Order Dielectric Permittivity

The second order permittivity is a sensitive parameter for investigating the degree of poling [1, 2, 3]. The coefficients ε_n in the expansion of the dielectric displacement D as a power series of the electric field E

$$D = P_r + \varepsilon_0 \varepsilon_1 E + \varepsilon_0 \varepsilon_2 E^2 + \ldots \qquad (1)$$

are measured by the application of a sinusoidal electric field at a frequency of 1 kHz and with an amplitude small compared to the coercive field of the sample. The Fourier coefficients of the dielectric displacement were measured. An appropriately small exitation amplitude is selected such that the higher order even harmonics are small compared to the second order harmonic and the second order permittivity is evaluated (e.g. [2]). The second order permittivity vanishes for unpoled samples, i.e., the remanent polarization P_r is equal to zero, and it increases with increasing degree of poling. For P(VDF–TrFE) the quotient $\varepsilon_2/\varepsilon_1^3$ is proportional to the remanent polarization [3].

The linear and the nonlinear dielectric properties of the ceramic and the copolymer combine to give the composite dielectric properties. As the dielectric permittivity of PT is an order of magnitude higher than that of P(VDF–TrFE), the dependence of the second order permittivity ε_2 of the 0–3 composite on the second order permittivity of the ceramic inclusions ε_{c2} and of the copolymer matrix ε_{p2} is given by the following approximation:

$$\varepsilon_1 \approx (1 + fv)\,\varepsilon_{p1} \qquad (2)$$

$$\varepsilon_2 \approx (1 + g_p v)\,\varepsilon_{p2} + g_c v\,\frac{\varepsilon_{p1}^3}{\varepsilon_{c1}^3}\,\varepsilon_{c2} \qquad (3)$$

where ε_{c1} and ε_{p1} are the linear permittivities of the ceramic inclusions and the copolymer matrix, respectively, v is the ceramic volume fraction (assumed to be