# Internal fields in
# PT/PVDF–TrFE 0–3 Composites

Beatrix Ploss, Bernd Ploss, F.G. Shin, H.L.W. Chan, and C.L. Choy
Department of Applied Physics and Materials Research Center,
The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

*Abstract* – Composites of ferroelectrics have a promising potential for applications, as it is possible to obtain new properties by combining two different ferroelectric materials. The spontaneous polarization of lead titanate (PT) is about an order of magnitude higher than that of vinylidenefluoride-trifluoroethylene copolymer (PVDF-TrFE). Therefore, in order to polarize the PT inclusions in a PT/PVDF-TrFE 0-3 composite, the depolarizing field must be compensated to a large extent by a counter field due to charge accumulated at the interface between the matrix and inclusions. An internal field will arise within the composite when the accumulated charge is insufficient to generate a fully compensating counter field. To demonstrate the existence of such an internal field we have studied the pyroelectric activity of composites with 27 volume % of PT in 56/44 mol % PVDF-TrFE. In the temperature range around the ferroelectric phase transition of the copolymer, induced pyroelectric activity is observed. The internal field can be estimated from an analysis of the pyroelectric activity of the composite.

## INTRODUCTION

The interaction of charge and polarization plays an important part in inhomogeneous ferroelectrics. In semicrystalline polyvinylidene fluoride (PVDF) and its copolymers with trifluoroethylene (PVDF–TrFE) charges are essential to stabilize the polarization of the crystalline phase [1, 2]. The interfacial charges compensate the polarzation of the crystalline phase locally, but overcharging of the interfaces has also been reported [3]. To polarize the ceramic inclusions in 0–3 composites of e.g. lead titanate (PT) in PVDF–TrFE charges must be injected into the material and migrate through the copolymer to the interfaces with the PT particles [4], a fact which can also be used to polarize the matrix and inclusions separately [5].

When the compensation of polarization by charge is not precise, i.e. when the interfaces between polar and nonpolar regions or between regions with different remanent polarizations are undercharged or overcharged, electric fields will persist in the material. A better understanding of the polar state of composite ferroelectrics is important for the further optimization of these materials and their processing. Here, we report a study of internal fields in 0-3 composites by pyroelectric investigations.

## THEORY

A model for the pyroelectric coefficient of a composite of spherical pyroelectric inclusions embedded in a pyroelectric matrix with 0–3 connectivity is given in [6]. In the following we consider an unpoled, i.e., nonpyroelectric matrix.

We assume that the surfaces of the spherical inclusions with a homogeneous polarization in $z$-direction $\vec{P}_{ri} = (0, 0, P_{ri})$ are covered by charges with a surface charge density $\sigma(\Theta) = -\sigma_0 \cos \Theta$ (see Fig. 1). When the polarization is fully compensated by charge, i.e. $P_{ri} = \sigma_0$, the electric field in the matrix and inclusions is zero, and the pyroelectric coefficient of the composite is [6]:

$$p = \frac{\varepsilon - \varepsilon_m}{\varepsilon_i - \varepsilon_m} \, p_i \tag{1}$$

$p_i$ is the pyroelectric coefficient of the inclusions, $\varepsilon_m$ and $\varepsilon_i$ are the dielectric permittivities of the matrix and inclusions, respectively, and $\varepsilon$ is the effective dielectric permittivity of the composite.

If the polarization is not precisely compensated by charges an electric field persists in the material. When the permittivity of matrix or inclusions varies with temperature $T$ an induced pyroelectric activity contributes also to $p$ and Eq. (1) is extended to:

$$p = \frac{\varepsilon - \varepsilon_m}{\varepsilon_i - \varepsilon_m} \, p_i + f \, \Delta P_r \tag{2}$$

with

$$f = \frac{d}{dT} \left( \frac{\varepsilon - \varepsilon_m}{\varepsilon_i - \varepsilon_m} \right). \tag{3}$$

$\Delta P_r = P_{ri} - \sigma_0$ is the uncompensated part of the polarization, whereby $\Delta P_r > 0$ indicates undercharging and $\Delta P_r < 0$ overcharging. $\Delta P_r = P_{ri}$ would indicate the absence of any compensating charge.