Primary and secondary pyroelectric effects of ferroelectric 0-3 composites

K.-H. Chew,[a] F. G. Shin, B. Ploss, H. L. W. Chan, and C. L. Choy
Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

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Simple and tractable analytical expressions for determining the pyroelectricity in ferroelectric 0-3 composites have been developed. For the dilute suspension limit, expressions for the effective pyroelectric and other thermal electromechanical properties are derived within the framework of the Maxwell–Wagner approach. Then, an effective-medium theory is employed to examine the first and second pyroelectric coefficients in the concentrated suspension regime. The effective-medium approach as compared to the Maxwell–Wagner approach results in a better agreement with known experimental data up to higher volume fraction of inclusions. The pyroelectricity of 0-3 composites of ceramic inclusions embedded in the P(VDF–TrFE) copolymer matrix and of P(VDF–TrFE) inclusions embedded in a ceramic matrix are analyzed numerically under different polarization configurations. The theoretical predictions show that the secondary pyroelectric effects in composite systems with ceramic as the matrix are stronger than those with the copolymer as the matrix and can sometimes dominate the pyroelectricity for certain compositions. [DOI: 10.1063/1.1583154]

I. INTRODUCTION

Pyroelectric materials are extensively used for thermal infrared detectors[1] due to advantages such as good sensitivity, room temperature operation, and low cost.[2] In recent years, the research in the field of pyroelectricity has been concentrated on discovering materials with higher figures of merit. One way to attain this is to dilute the ferroelectric material in order to reduce the dielectric constant as observed in sol–gel processed $(Pb,Ca)TiO_3$.[3] Composite materials of ferroelectric ceramics particles embedded in polymer matrices with different connectivities[4] aroused great interest because of their mechanical flexibility, low cost, and excellent pyroelectricity.[5] Another advantage is that their dielectric, thermal, and pyroelectric properties can be changed by varying the volume fraction of ceramic particles or poling procedure.[6]

Many experimental works have been done on the pyroelectric properties of ferroelectric composites.[7] Theoretically, Bhalla *et al.* investigated the primary and secondary pyroelectric effects and derived expressions for the effective pyroelectric coefficients based on simple series and parallel connections.[5] Yamazaki *et al.* derived the pyroelectric coefficient of 0-3 composites with identical spherical ferroelectric particles.[8] Based on a modified Clausius–Mossotti relation,[9] Wang *et al.*[10] formulated the pyroelectric coefficient of ferroelectric composites by taking into account the depolarization coefficient. Nan[11] developed a formulation to describe the pyroelectricity of ferroelectric composite materials. The theoretical framework is developed in terms of a Green's function method and perturbation theory which is more rigorous but complicated. Recently, Levin and Luchaninov have derived expressions for the effective pyroelectric constants of composite materials with spherical inclusion[12] by means of effective field theory. While extensive theoretical studies[8–12] have been made on the pyroelectricity of 0-3 composites, the works are mainly concerned with the effective pyroelectric effect of ferroelectric composites and not explicitly on the secondary effect.

This work concerns deriving explicit analytical expressions for the primary and secondary pyroelectric effects of ferroelectric 0-3 composites. We employ two methods in succession in this study: the Maxwell–Wagner (MW) approach and then effective-medium (EM) theory; the former gives expressions for the case of a dilute suspension of inclusion particles while the latter gives results for a wider range of particle concentration. Section II contains the general expressions for the primary and secondary effects of ferroelectric 0-3 composites. The definition of pyroelectricity is given, followed by a detailed derivation of primary and secondary pyroelectric coefficients within the framework of the two methods mentioned earlier. In Sec. III, the pyroelectricity of composite systems consisting of ferroelectric ceramic and polymer phases is examined. Comparison with experimental results is performed to verify the two theoretical models. Some conclusions are given in Sec. IV.

II. THEORY

Pyroelectricity is the electrical response of a polar material as a result of a change in temperature. The pyroelectric effects at constant stress $\boldsymbol{\sigma}$ and electric field $\mathbf{E}$ are defined as[13] confining to scalar notations,

$$\left(\frac{\partial \mathbf{D}}{\partial T}\right)_{E,\sigma}=\left(\frac{\partial \mathbf{D}}{\partial T}\right)_{E,e}+\left(\frac{\partial \mathbf{D}}{\partial \mathbf{e}}\right)_{E,T}\left(\frac{\partial \mathbf{e}}{\partial T}\right)_{E,\sigma}, \tag{1}$$

where $\mathbf{D}$, $\mathbf{e}$, and T represent, respectively, the electric displacement, strain, and temperature of the material. The term $(\partial \mathbf{D}/\partial T)_{E,e}$ of Eq. (1) is called the primary pyroelectric response. The primary pyroelectric effect corresponds to the

[a]Electronic mail: khchew2@hotmail.com

