Full length article

Modelling and fabrication of porous sandwich layer barium titanate with improved piezoelectric energy harvesting figures of merit

J.I. Roscow [a, *], R.W.C. Lewis [b], J. Taylor [c], C.R. Bowen [a]

[a] Materials and Structures Centre, Department of Mechanical Engineering, University of Bath, Bath, BA2 7AY, UK
[b] Renishaw Plc., Wotton Road, Charfield, Wotton-under-Edge, GL12 8SP, UK
[c] Department of Electronic and Electrical Engineering, University of Bath, Bath, BA2 7AY, UK

ABSTRACT

This paper demonstrates that porous 'sandwich' structures can provide an effective route for the design and optimisation of piezoelectric materials for energy harvesting applications, which is becoming an increasingly important technology for self-powered wireless networks and sensors. A numerical model is presented that accounts for the complex poling distribution throughout a layered ferroelectric and helps to develop a detailed understanding of the relationship between the geometry of the porous structure and the poling characteristics of porous ferroelectric materials, with good agreement with experimental data. Novel layered barium titanate ceramics were fabricated whereby dense outer layers surround a highly porous sandwich layer, and for specific layer geometries an unusual condition was achieved where the longitudinal piezoelectric strain coefficients (d_{33}) increased as the thickness of the porous layer and total porosity level of the layered structure increased. The permittivity (ε_{33}^T) decreased with increasing thickness and increasing porosity level of the porous layer due to the presence of a low permittivity air phase. These two factors in combination led to an increase in the longitudinal energy harvesting figure of merit, $d_{33}^2/\varepsilon_{33}^T$, for the layered structure, with a maximum of 3.74 pm^2/N when the relative thickness of the porous layer was 0.52 and the porosity within this layer was ~60 vol%. This harvesting performance of these novel structures is much larger than both dense barium titanate (1.40 pm^2/N) and barium titanate with randomly distributed porosity at the same 60% volume fraction (2.75 pm^2/N).

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1. Introduction

There is significant interest in the use of ferroelectric materials for energy harvesting applications due to their inherent ability to convert energy from mechanical vibrations and thermal fluctuations, via the piezoelectric and pyroelectric effects, respectively, to electrical energy. A variety of figures of merit (FOMs) have been devised to assist with the selection of piezoelectric materials for energy harvesting applications. When a piezoelectric is subjected to mechanical vibrations at low frequencies (≪100 kHz) and away from the electromechanical resonance (i.e. off-resonance) the relevant FOM is:

$$FOM_{ij} = d_{ij}^2 \big/ \varepsilon_{33}^T \qquad (1)$$

where d_{ij} is the relevant piezoelectric strain coefficient associated with the direction of stress relative to the poling direction (such as d_{33} or d_{31}), ε_{33}^T is the permittivity at constant stress, T, and subscripts i and j follow conventional piezoelectric matrix notation [1]. The FOM_{ij} is derived from capacitor energy storage equations ($E = \frac{1}{2}CV^2$, where E is stored electrical energy, C is capacitance and V is potential difference across a capacitor) and effectively describes the change in stored electrical energy within a piezo-active material when a stress is applied. Another important factor for effective piezoelectric energy conversion is the electromechanical coupling coefficient, k_{ij}^2, which takes into account the mechanical properties of the material and describes the efficiency of conversion from mechanical to electrical energy:

* Corresponding author.
  E-mail address: j.i.roscow@bath.ac.uk (J.I. Roscow).

$$k_{ij}^2 = d_{ij}^2 \Big/ \left(\varepsilon_{33}^T \cdot S_{ij}^E \right) \qquad (2)$$

where S_{ij}^E is the mechanical compliance at constant electric field. From Eqns. (1) and (2) it can be seen that optimum materials for energy harvesting mechanical loads should have high piezoelectric strain coefficients, low permittivity and low compliance.

One approach to reduce significantly the effective permittivity of piezoelectric composites is to introduce a low permittivity phase, such as air or a polymer ($\varepsilon_{33}^T \sim 1 - 10$), into the high permittivity ferroelectric ceramic; e.g. lead zirconate titanate (PZT $\varepsilon_{33}^T \sim 1000 - 3500$, depending on composition) and barium titanate (BaTiO$_3$, $\varepsilon_{33}^T \sim 1500$) [2]. This has been achieved by introducing randomly distributed porosity throughout the ferroelectric microstructure [2] and has led to an increase in the longitudinal mode energy harvesting figure of merit, FOM_{33} [3], where $d_{ij} = d_{33}$ in Eqns. (1) and (2). The FOM_{33} increases as porosity is introduced into the material since there is a large reduction in permittivity and a relatively small decrease in d_{33}. By understanding the reasons behind the reduction in d_{33} and permittivity in porous ferroelectrics it is possible to design porous structures that yield further increases in the relevant FOMs, and will be discussed throughout this paper.

1.1. Poling of ferroelectrics

Ferroelectric ceramics, such as PZT and BaTiO$_3$, exhibit no bulk piezo- or pyro-electric properties when manufactured by traditional methods such as compaction of powders and heat-treatment at high temperature, known as sintering. This is due to the random distribution of domains as the polycrystalline material cools, post-sintering, below the Curie temperature and it relaxes to its lowest energy state, resulting in zero net polarisation [4]. To align the ferroelectric domains so as to yield the net polarisation required for ferroelectric ceramics to exhibit piezoelectric behaviour the material has to be 'poled', whereby a large static electric field is applied across the material, usually at elevated temperatures close to the Curie point where the domains are more mobile. A ferroelectric material will become poled in the direction of the applied field when the local electric field, E_f, (i.e. within a grain or domain) is greater than the coercive field, E_c, i.e. when $E_f > E_c$. In a dense single phase ferroelectric, E_f is homogenous, leading to a fully poled structure if the applied field is sufficiently large and greater than E_c. However, when a second phase with a different permittivity is introduced into the microstructure of the material the electric field will tend to concentrate in the low permittivity phase, in particular the pores of a porous ferroelectric material.

To illustrate this effect, the complex electric field distribution in a porous ferroelectric material is demonstrated in Fig. 1, which shows a two-dimensional finite element (FE) model of a single pore (relative permittivity, $\varepsilon_r = 1$) in barium titanate ($\varepsilon_r = 1500$) with a static electric field applied. This simulates the electric field distribution within a porous ferroelectric material during the poling process. A high electric field concentration (red contour in Fig. 1) is observed within the low permittivity pore while the field in the ceramic phase varies with location. Regions of low electric field (blue contour in Fig. 1) are observed in the immediate vicinity of the pore parallel to the direction of the applied field, which in a ferroelectric material may lead to incomplete poling in these regions. This phenomenon can be described by an adaptation of Gauss' law where the electric field, E_f, is related to the relative permittivity by the relationship [5]:
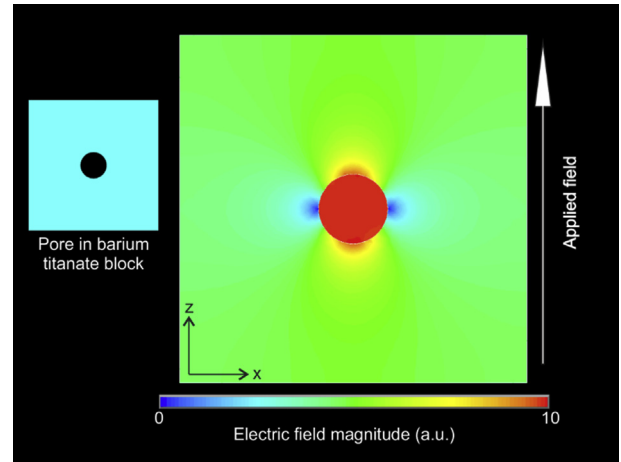

Fig. 1. Contour plot of local electric field magnitude (arbitrary units) due to an applied field across a two dimensional finite element model whereby a circular pore of low permittivity is contained within a high permittivity barium titanate matrix. Blue regions represent areas of low field in the BaTiO$_3$ phase that may result incomplete poling in a porous ferroelectric material. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$E_f = q \Big/ (A \cdot \varepsilon_r \cdot \varepsilon_0) \qquad (3)$$

where q is charge, A is area and ε_0 is the permittivity of free space. In a two phase material where $\varepsilon_1 \neq \varepsilon_2$ (subscripts denote phase), the electric field will not have the continuous and linear path that is present in a dense ferroelectric material during the poling procedure. As a consequence of the field concentrating in the low permittivity air phase, porous ferroelectrics are difficult to pole, which reduces the effective piezoelectric response, and d_{ij}, of the material. Previous work has shown a gradual decrease in d_{33} as the porosity levels increase to 50-60 vol%. Beyond 60 vol% porosity there is a rapid decrease in d_{33} with increasing porosity [3,6]. The decrease in d_{33} at high porosities is due to incomplete poling of the ferroelectric phase and cannot be counteracted by simply increasing the poling field, as high electric fields will eventually lead to electrical breakdown in either the air or in the ferroelectric ceramic.

A further consideration for designing porous ferroelectric ceramics is the increase in the elastic compliance, S_{33}^E, associated with the introduction of porosity, which is approximately proportional to the amount of porosity present for randomly distributed porosity [7]; the influence of spherical porosity on compliance of ceramics has been described in detail elsewhere [8,9]. Therefore, despite the potential benefit of introducing porosity into ferroelectric ceramics for energy harvesting applications due to the significant reduction in permittivity, careful consideration of the porous structure is necessary to achieve improvements in harvesting FOMs and electromechanical coupling factors (see Eqns. (1) and (2)).

One potential approach to improving both the mechanical and piezoelectric properties of porous piezoelectric composites is to consider porous piezoelectric 'sandwich layer' structures, where the porous layer is formed between two outer dense piezoelectric layers. A porous sandwich layer structure can be described in this case by two variables. Firstly, the relative thickness of the porous layer, which is defined as follows:

$$t_p^{rel} = thickness\ of\ porous\ layer / total\ thickness = \frac{t_{porous}}{t_{porous} + 2t_{dense}} \qquad (4)$$