ELSEVIER

June 1999

Materials Letters 39 (1999) 287–291

MATERIALS LETTERS

www.elsevier.com/locate/matlet

Possible piezoelectric composites based on the flexoelectric effect

J. Fousek [a,1], L.E. Cross [a,*], D.B. Litvin [b]

[a] *Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA*
[b] *Department of Physics, The Pennsylvania State University, Berks Campus, Reading, PA 19610, USA*

Received 30 November 1998; accepted 2 December 1998

Abstract

Current piezoelectric composite materials contain two or more phases out of which at least one reveals piezoelectric properties in itself. We show that this is in fact not a necessary condition. The mechanism of the linear stress-polarization response averaged over a composite sample can be also based on flexoelectric properties of one or more constituents. Proper shaping of the composite constituents is required, such that the system as a whole acquires a symmetry allowing for nonzero piezoelectric coefficients even if none of the components is piezoelectric. Externally applied stress is transformed, due to proper geometry of the constituents with different elastic properties, into a strongly nonhomogeneous distribution of induced strain. Flexoelectric properties which are, by symmetry, allowed in all materials, transform the strain gradient into polarization. The proposed piezoelectric composite falls into the category of composites with product properties since it involves different assets of the phases (elastic, flexoelectric and dielectric) and the interaction between the phases, determining the inhomogeneous distribution of stress, is essential.

PACS: 77.84 − s; 77.90 + k

Keywords: Piezoelectric materials; Composites; Flexoelectric effect

1. Introduction

Composites are multiple-phase solids which combine materials of different chemical composition and macroscopic properties with the aim to produce samples with the desired average response. Figures of merit of the final composite can be tuned by choosing component phases with the right properties and coupling them in an optimum manner. Newnham et al. [1] offered a classification of composites based on three criteria. The most important aspects are the macroscopic properties of the constituents, e.g., their response to electric, magnetic and elastic fields. This determines the final assets of the composite. The second, connectivity, indicates the way in which each phase connects to itself. It is essential for the magnitude and symmetry of the composite's response. The third is scale, which determines the response of the composite when wavelengths of propagating waves become comparable with the characteristic dimensions of any of the constituents.

Many composites have been considered in connection with their piezoelectric properties [1,2]. To discuss or model the piezoelectric response of a composite, it was generally assumed that at least one

* Corresponding author. Tel.: +1-814-865-1181; Fax: +1-814-863-7846

[1] On leave from the Department of Physics, University of Technology, CZ-46117 Liberec, Czech Republic.

00167-577X/99/$ - see front matter
PII: S0167-577X(99)00020-8

of the components was piezoelectric. In this paper we reconsider this assumption.

2. Discussion

For a system to be piezoelectric, it has to fulfill certain symmetry criteria. If it has a crystalline structure, the material must, by symmetry, belong to one of 20 crystal classes. The remaining 12 classes do not show piezoelectric properties; these are the 11 centrosymmetric classes and the class 432 in which piezoelectricity is forbidden by the combined symmetry elements.

In Nye's widely used overview of the equilibrium properties of the 32 crystal classes [3], the properties of an isotropic medium are also included. The symmetry of an isotropic medium is primarily characterized by the presence of arbitrarily oriented symmetry axes of infinite order. Depending on whether its symmetry elements do or do not include arbitrarily oriented mirror planes, the isotropic medium represents one of the Curie symmetry groups (limiting groups), namely, ∞, ∞/m or $\infty\infty$, respectively. In

Table 1
Matrices of d_{ijk} in Curie groups which are piezoelectric

∞

$$\begin{vmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{vmatrix}$$

$\infty 2$

$$\begin{vmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{vmatrix}$$

∞m

$$\begin{vmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{vmatrix}$$

In all groups the ∞ axis is taken as x_3; the axes x_1, x_2 are perpendicular to x_3 and to each other, otherwise their orientation is arbitrary.

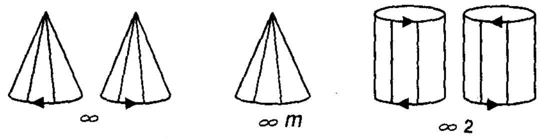

Fig. 1. Characteristic forms representing symmetry of the Curie groups which allow for piezoelectricity [4].

both these groups no nonzero piezoelectric coefficients are possible.

In addition to these two groups, however, we may consider systems representing the remaining Curie groups, namely ∞, ∞/m, $\infty 2$, ∞m and ∞/mm. Out of these, ∞/m and ∞/mm do not allow for the existence of nonzero components of a third-rank polar tensor d_{ijk} of symmetry $V\ [V^2]$, i.e., of the piezoelectric tensor. In the remaining groups nonzero components are possible, as shown in Table 1. It is useful to illustrate symmetry properties of these point groups by characteristic forms [4]; these are shown in Fig. 1. We realize that systems revealing the symmetries ∞ or $\infty 2$ can exist in two forms, left- and right-handed.

Thus, for instance, a composite with connectivity 0–3, in which the phase '0' is represented by cone-shaped particles whose ∞-axes are parallel to each other but which are randomly distributed in the phase '3', has the symmetry ∞m. Next we can imagine that the cones are subject to helical deformations so that spiral-shaped particles result. This lowers the symmetry to ∞. The system can exist in two forms, right- or left-handed. The third piezoelectric Curie group can be visualized starting again with a composite of connectivity 0–3 in which the phase '0' is represented by cylinders; its symmetry is nonpiezoelectric ∞/mm. If now all cylinders are subject to a helical deformation, the symmetry is reduced to $\infty 2$, which again can exist in two forms differing in handedness. Fig. 2 shows such composites schematically. These particular models are based on the 0–3 connectivity but similar considerations can be made for other connectivities as well.

It thus appears easily possible to manufacture composites whose symmetry properties allow for the existence of piezoelectric tensor although they consist of components which by themselves need not be made of piezoelectric materials.

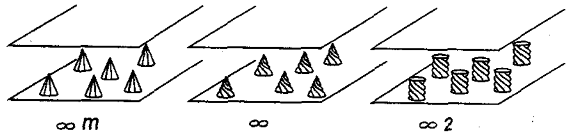

Fig. 2. Simple models of 0–3 composites allowing for piezoelectricity. There is an infinite number of shapes of the 0-constituent that could be tested for a maximum response of flexoelectric polarization.

A long time ago, Shubnikov et al. introduced the concept of *piezoelectric textures*; see Ref. [5] and the first chapter of Ref. [6]. This notion denotes systems composed of crystallites which show piezoelectric properties, some crystal axes of which are chaotically oriented in a given way, leading to specific averaging of properties characterizing the piezoelectric effect. In the subsequent parts of Ref. [6], two specific kinds of materials are discussed as examples. Plate-like samples containing crystallites of Rochelle salt separated by amorphous layers (chapter 2 by Konstantinova and Sil'vestrova) could indeed be considered a 0–3 composite. Polarized ceramic samples of barium titanate (chapter 3 by Zheludev), on the other hand, whose symmetry is ∞m, represent a piezoelectric texture by Shubnikov's definition but could only be included into the family of composites if the grain boundaries had an appreciable volume.

In both these cases basic components are piezoelectric by themselves (point symmetries 2 for Rochelle salt and $4mm$ for $BaTiO_3$). On the other hand, in the general symmetry approach this is not a specific requirement. As shown above, the possibility of a piezoelectric response in a 0–3 composite is assured, from the point of view of symmetry, already by shaping the particles of zero connectivity. We thus have to look for alternative mechanisms which would lead to formation of an average polarization proportional to an applied stress for a 0–3 composite made of nonpiezoelectric materials, with properly shaped particles.

For several decades, the effect of inducing polarization by imposing spatially nonuniform strain was repeatedly discussed in the literature. Originally discovered experimentally in centrosymmetric (and therefore nonpiezoelectric) liquid crystals, it was termed the flexoelectric effect and described by the equation

$$P_l = \mu_{ijkl} \frac{\partial \varepsilon_{ij}}{\partial x_k} \tag{1}$$

from which it is obvious that the tensor μ has the general symmetry $[V^2]\ V^2$, i.e., $\mu_{ijkl} = \mu_{jikl}$ is the only requirement imposed by symmetry. A tensor of this symmetry has nonzero components in all crystal classes. The first attempt to observe the flexoelectric effect in a solid crystal of point symmetry $4/m$, namely $CaWO_4$ was made by Zheludev et al. [7]. As shown by Tagantsev [8], the static effect includes a bulk and a surface contribution. The bulk part is due to the fact that the crystal lattice which has been nonhomogeneously deformed in accordance with the laws of the theory of elasticity is not in equilibrium from the point of view of displacements in the unit cell. The displacements that are necessary to reach true equilibrium give rise to a dipole moment of the cell, i.e., to polarization. In addition, the deformation of the surface of a finite sample, whose electrical neutrality in the original state was achieved by compensating free charges, leads to a surface contribution which can be expected to be of the same order of magnitude as the bulk part of the effect. The simplest estimates [8] for a common insulator indicate that both contributions to the value of μ are of the order of the ratio of the electron charge to the lattice constant.

We now have in mind a 0–3 composite made of nonpiezoelectric constituents, in which the 0-elements are shaped and oriented in such a way that the overall symmetry is one of the Curie groups ∞, ∞m and $\infty 2$. As an example, consider a plate-like sample of composite of symmetry ∞m in which the orientation of the 0-constituents is such that the ∞ axis is perpendicular to the major plane. Since the tensor μ_{ijkl} has nonzero components even for continuous groups $\infty\infty$ and $\infty\infty m$ [4], one can imagine that both the 0-component and 3-components are made of isotropic materials. Their shaping is such that when a load $\sigma_{33\mathrm{appl}}$ is applied, the spatial distribution of stress will be nonhomogeneous, leading to gradients of strain in both constituents. To be concrete, we can imagine that a plate-like sample of thickness d is divided into a regular system of cubes of linear size d_0, each cube containing one particle of the component with zero connectivity and only this component is assumed to have nonzero flexoelectric properties. The dipole moment of each 0-particle within one cube will be given by

$$p_{3\text{flex}} = \int_{(d_0^3)} \mu_{3ijk} \frac{\partial \varepsilon_{ij}(\mathbf{r})}{\partial x_k} \mathrm{d}\mathbf{r} \tag{2}$$

where the strain gradient will be determined by a factor a_{ijk} which reflects the shape of the components 0 of the composite and depends on elastic compliances of both constituents:

$$\frac{\partial \varepsilon_{ij}(\mathbf{r})}{\partial x_k} = a_{ijk}(\mathbf{r})\,\sigma_{33\text{appl}}. \tag{3}$$

The induced charge density on the electrode of the plate will be

$$Q = \frac{p_{3\text{flex}}}{d_0^3} \tag{4}$$

so that the effective polarization of the sample $P_3 = Q$ will be given by

$$P_3 = d_{33\text{flex}}\,\sigma_{33\text{appl}}, \tag{5}$$

where

$$d_{33\text{flex}} = \frac{1}{d_0^3} \int_{(d_0^3)} a_{ijk}(\mathbf{r})\,\mu_{3ij3} \mathrm{d}\mathbf{r}. \tag{6}$$

A piezoelectric composite based on flexoelectricity will be useful if a reasonably high value of $d_{33\text{flex}}$ could be reached, e.g., 100 pC/N. It follows from the preceding formulae that the latter can be influenced by a proper tuning of several independent factors: selecting materials with high values of those components of μ_{ijkl} which are involved in a particular geometry of the constituents, choosing a high density of the constituents 0, but also by achieving large factors a_{ijk} which depend on the shape of the 0-components and on the elastic tensors of both 0 and 3 constituents.

Newnham [2] classified properties of composite materials into three groups: sum properties (the composite property coefficient depends on the corresponding coefficients of its constituent phases), combination properties (the composite property coefficient depends on two or more corresponding coefficients of its constituent phases) and product properties. In the latter case the composite property coefficient involves different properties of the constituent phases with interactions between them. It appears that piezoelectric composites based on flexoelectricity fall into this last category and the effect might be referred to as a 'shape-controlled product property'; indeed the combined effect involves different properties of the constituent phases (elastic, flexoelectric and dielectric) and the interaction between the phases is essential; here it is the nonhomogeneous distribution of stress which depends primarily on the shapes of constituents and on their elastic tensors. The following sequence of phenomena describes the combined effect: homogeneous applied stress → inhomogeneous stress in the 0-constituents → polarization in the 0-constituents due to flexoelectric effect → nonhomogeneous distribution of polarization in the sample depending also on spatial distribution of permittivity → nonhomogeneous surface bound charge → averaged surface bound charge density defining effective polarization. Considering a stress σ_{zz} applied perpendicularly to a plate-like composite sample, we have the sequence

$$\sigma_{zz,\text{appl}} \to \operatorname{grad} \sigma_{ij,\text{sample}}(\mathbf{r}) \to P(\mathbf{r}) \to q(x,y)_{\text{surf}}$$
$$\to \bar{q}_{\text{surf}} \propto P_{z,\text{surf}} \propto \sigma_{zz,\text{appl}}.$$

At this stage very few data on the tensor μ_{ijkl} in solids seem to be available. A fairly strong flexoelectric response was reported for crystals of Cd_2WO_4 [7]. Marvan and Havránek [9] studied the flexoelectric effect in elastomers of isotropic symmetry. Samples in the form of truncated pyramids were deformed by axial pressure along the axis 3. Then for constant volume of the sample the only active coefficient is μ_{3333} which was estimated to be of the order 10^{-11} to 10^{-10} C/m. Experiments with 0–3 composites in which the 0-constituent or both components of the composite would be a polymer might be worthwhile.

We may also note that such composite samples might be interesting to investigate in which one of the constituents is piezoelectric; due to flexoelectricity, its induced dipole moment could be considerably enhanced by proper shaping to optimize the nonhomogeneous distribution of strain.

Acknowledgements

J. Fousek: This work was supported in part through grants VS 96006 and 202/96/0722 of the Ministry of Education and of the Grant Agency of the Czech Republic, respectively. D.B. Litvin: This work was supported in part by the National Science Foundation through grant No. DMR-9722799.

References

[1] R.E. Newnham, D.P. Skinner, L.E. Cross, Mater. Res. Bull. 13 (1978) 525.
[2] R.E. Newnham, Jpn. J. Appl. Phys. 25 (1986) 9, Suppl. 25-1.
[3] J.F. Nye, Physical Properties of Crystals, Clarendon Press, Oxford, 1993.
[4] Yu.I. Sirotin, M.P. Shaskolskaya, Fundamentals of Crystal Physics, Mir Publishers, Moscow, 1982.
[5] A.V. Shubnikov, Piezoelectric Textures (in Russian), Publishing House of the Academy of Sciences of USSR, Moscow–Leningrad, 1946.
[6] A.V. Shubnikov, I.S. Zheludev, V.P. Konstantinova, I.M. Sil'vestrova, Investigation of Piezoelectric Textures (in Russian), Publishing House of the Academy of Sciences of USSR, Moscow–Leningrad, 1955.
[7] I.S. Zheludev, Yu.S. Likhacheva, N.A. Lileeva, Sov. Phys. Crystallogr. 14 (1969) 425.
[8] A.K. Tagantsev, Sov. Phys. JETP 61 (1985) 1246.
[9] M. Marvan, A. Havránek, Progr. Colloid Polym. Sci. 78 (1988) 33.