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Piezoceramic material with anisotropic graded porosity

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Abstract

Porous PZT ceramics were produced at increasing porosity content to a maximum of 40 vol.%. Anisotropic porosity was obtained by adding lamellar graphite as pore forming agent. The elasto-piezo-dielectric properties of the samples with uniform porosity were correlated to the increasingly higher degree of anisotropy introduced as the total pore volume increases. Higher anisotropy enhances the decoupling of the longitudinal to transverse effect. A piezoelectric bending actuator with functionally graded microstructure (FGM) was produced by stacking layer by layer, in the green state, the PZT powder at increasing graphite content, followed by die pressing and co-firing. The final pore distribution measured across the section and the performance of the porosity graded material arise from the combination of the properties of the homogeneous layers. This makes it possible to precisely tailor the performance of the porosity graded material.

Keywords: Pressing; Porosity; Piezoelectric properties; PZT; Actuators

1. Introduction

Porous piezoelectric ceramics show high piezoelectric figure of merit, $d_h g_h$, for application in low frequency hydrophones and sensors. High degree of tridimensionally interconnected porosity can be introduced in the ceramic body with different techniques.[1] The addition of organic particles in the dry state let to tailor the pore morphology and size in a wide range. The dependence of some properties like acoustic impedance or elastic modulus on the amount of porosity is well established, while the influence of the pore morphology on the piezoelectric constants is worthy of further investigations. As the decoupling of the longitudinal to transverse effect is one of the goals to improve the performance of the porous material, in this paper we studied the effect of a significantly anisotropic porosity on the piezoelectric properties.

Further, as there is a growing interest to develop functionally graded microstructures (FGM), the anisotropic porosity was introduced at increasing concentration through the thickness of the material and the properties of the FGM material were compared with those of the homogeneous samples, in view of the application of the material as an actuator. In fact, the bimorph configuration of the bending type actuators find a drawback in the intrinsic weakness of the junction between the two different poled materials that can delaminate. The stress at the junction could be drastically decreased with a graded microstructure.[2]

The bending effect[3,4] results from the gradient of mechanical and electrical properties arising when the gradient of porosity is introduced in the microstructure.

2. Experimental

2.1. Sample preparation

Powders of the composition $Pb(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$ were prepared following the mixed-oxide method. The starting oxides were wet ball milled in the stoichiometric amount with zirconia milling media for 24 h; the slurry was then freeze-dried, sieved to 200 μm and calcined at 850 °C for 4 h. Calcined powders were ball milled with zirconia balls in EtOH for 100 h, dried at 90 °C and sieved to 200 μm.

Fine grained graphite powders were mixed to the calcined powders at different graphite content (0, 5, 10, 20 and 40 vol.%); disk-shaped samples with 2 mm thickness and 25 mm diameter were produced from each batch of powder.

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Disks with graded porosity (25 mm diameter) were also manufactured by die pressing five layers at increasing graphite content. The total thickness of the samples was 2.5 mm (thick samples) and 1.2 mm (thin samples). In order to check the reproducibility of the process, 20 samples were manufactured. Thin beam-shaped actuators with 26 mm × 6 mm × 1.2 mm dimensions were produced as well.

The samples were sintered at 1150 °C for 2 h. In order to avoid the loss of PbO, all the sintering processes were carried out with the samples placed on ZrO_2 disks and covered with an Al_2O_3 crucible and sealed with pack ($PbZrO_3$ + 5 wt.% excess ZrO_2).

The yield of the pore forming agent (PFA) was calculated as follows:

$$\text{porosity yield} = \frac{(\rho_{\text{dense}} - \rho_{\text{porous}})/\rho_{\text{theoretical}}}{\text{PFA volume/batch volume}}$$

where ρ_{porous} is the density of the porous sample and ρ_{dense} is the density of the sample without PFA, sintered in the same conditions.

The density of the sintered samples was measured by the Archimedean method in water.

Homogeneous samples from every batch of powder and FGM samples were ground to remove surface layers, screen-printed with silver electrodes, fired at 700 °C and finally poled into silicon oil at 120 °C, under a dc field of 2 kV/mm for 40 min.

2.2. Characterization

SEM analysis (Leica-Cambridge by Oxford Instruments) was carried on in order to investigate the microstructure and the porosity gradient in the samples mechanically polished and coated with carbon.

The electrical characterization at low field (0.5 V) was performed on the disk-shaped samples (electroded perpendicularly to the direction of the applied pressure) following the standard IEEE 176-1987.[5] The elasto-piezo-dielectric constants were calculated from the values of resonance and antiresonance frequencies of the planar mode (maximum conductance (f_s) and maximum resistance (f_p)), minimum impedance and capacitance. The anisotropy of the dielectric permittivity was studied by cutting two bar-shaped samples (2 mm × 2 mm × 10 mm) from every rounded sample. The bars were than divided in two groups, one screen-printed with silver on the faces parallel to the direction of application of the pressure in the cold consolidation and the other screen-printed with silver on the faces perpendicular to the direction of the applied pressure.

3. Results and discussion

3.1. Microstructure

The samples were heated at 1150 °C for 2 h so that the density of the samples without graphite is 95% with a pore size of the order of micrometers (Fig. 1d). The properties of the material fully densified at 1200 °C are reported for comparison in Table 1. Graphite as pore forming agent (PFA) develops lamellar porosity oriented mostly perpendicular to the direction of the applied pressure during the cold consolidation step (Fig. 1a and b). The anisotropy degree depends on the agglomeration and particle size of the graphite powders; in fact, preliminary milling and de-agglomeration of the graphite powder is necessary to assure a homogeneous distribution in the PZT powder. Finer particles also introduce less micro-cracks in the body and let better mechanical properties (Fig. 1b). In fact, samples with coarse and agglomerated particles were subjected to delamination. The microstructure of the FGM sample (Fig. 1c) is the sum of the effects of the different graphite contents with the low sintering temperature. In addition, during the sintering process the five layers structure is cancelled developing a continuously grading porosity without growing cracks or delamination at the interfaces between the different layers.

In Fig. 2, the porosity of graphite is shown against the volume, the porosity volume being normalized to that of the samples sintered at 1150 °C without graphite. The yield increases from 74% to 87% as the graphite content increases. The porosity yield depends on the morphology and amount of PFA, the forming method and the thermal treatment used.[6] In particular, the observed yield increase evidences a decreased efficiency of the densification. It arises from the enhanced pore bridging caused by the increasing concentration of PFA. This is confirmed by the mercury intrusion analysis indicating that it is open porosity tridimensionally interconnected.

3.2. Electrical properties

The capacity of the unpoled samples with the same porosity was measured in the two directions and the relative difference of $\varepsilon_{33}^{\text{T}}$, $\Delta_a\varepsilon_{33}^{\text{T}}$, was then calculated following the formula:

$$\Delta_a\varepsilon_{33}^{\text{T}} = 1 - \frac{\varepsilon_{33\perp}^{\text{T}}}{\varepsilon_{33//}^{\text{T}}}$$

where $\varepsilon_{33\perp}^{\text{T}}$ is for samples with electrodes perpendicular to the direction of the applied pressure and $\varepsilon_{33//}^{\text{T}}$ is for samples with electrodes parallel to the direction of the applied pressure. In Fig. 3, the $\Delta_a\varepsilon_{33}^{\text{T}}$ is reported against the relative density of the samples. $\Delta_a\varepsilon_{33}^{\text{T}}$ increases with the porosity volume, as expected by the higher amount of pores and cracks aligned perpendicularly to the direction of the applied pressure, in samples with high porosity. In fact, $\varepsilon_{33\perp}^{\text{T}}$ decreases with the increase of the vol.% of anisotropic porosity in the samples.

This result is explained by the structure of the PZT body incorporating elongated voids that can be regarded as a layered structure with the pores aligned perpendicular to the pressing direction. Consequently, the capacity measured in the two directions results from the combination in series or in parallel of the layers when measured with the electrodes

Fig. 1. SEM BSE image micrographs of samples sintered at 1150 °C: (a) with 40 vol.% coarse graphite powder; (b) with 40 vol.% fine graphite powder; (c) FGM sample; (d) without pore forming agent.

Table 1
Physical and electrical properties of the samples at different porosity degree (sintered at 1150 °C)

Graphite (vol.%)	Density (g/cm^3)	Porosity (vol.%)	k_{31}	k_t	d_{31} ($\times10^{-12}$ m/V)	d_{33} ($\times10^{-12}$ m/V)	g_{31} ($\times10^{-3}$ V m/N)	g_{33} ($\times10^{-3}$ V m/N)	ε_{33}^{T}	s_{11} ($\times10^{-12}$ m^2/N)	Z_a ($\times10^6$ kg/(m^2 s))
0[a]	7.84	2.1	−0.40	0.53	−216	482	−12.4	27.7	1962	17.2	21.3
0	7.58	5.4	−0.36	0.51	−179	396	−12.3	27.1	1649	17.4	20.8
5	7.30	8.9	−0.31	0.51	−144	371	−11.9	30.6	1369	18.3	20.0
10	6.98	12.8	−0.26	0.42	−120	351	−11.7	34.4	1153	20.9	18.3
20	6.39	20.2	−0.13	0.47	−51	312	−7.9	48.3	730	26.0	15.7
40	4.95	38.2	−0.04	0.17	−15	202	−4.1	56.5	404	43.3	10.7

[a] Sintered at 1200 °C.

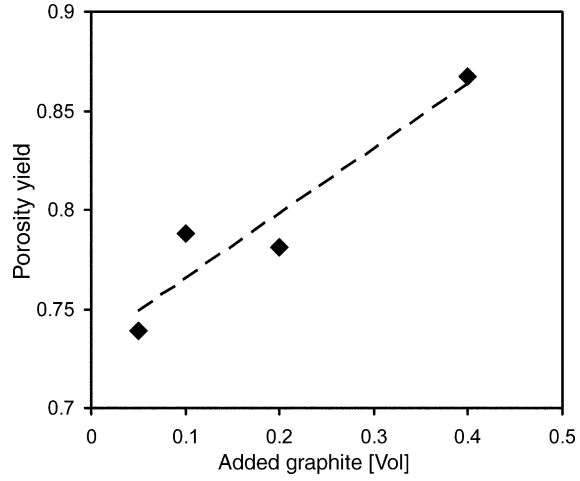

Fig. 2. Yield of graphite powders as pore forming agent.

perpendicular or parallel to the pressing direction, respectively. In fact, the permittivity of the dense ceramic layer is a factor of 1000 higher than that of the pore, which can be approximated to the permittivity of air. The series combination (i.e. the product of the capacities) of such different capacitors (dense layers alternated to voids) makes the components with lower capacity (pores) prevailing in the total value of the ε_{33}^{T}. On the other end, the parallel combination (i.e. the sum of the capacities) enhances the role of the dense layer. The actual capacity of the composite samples will be thus determined mostly by the higher amount of ceramic layers perpendicular to the electrodes.[7] Therefore, $\Delta_a\varepsilon_{33}^{T}$ of unpoled samples is a valid parameter to evaluate the mean anisotropy of the pores, if there is not a significant effect of cracks on the value of capacity.

The values of the piezoelectric constants, reported in Table 1, show that the piezoelectric properties decay at increasing porosity content, excluding the g_{33}, but with different trends. In fact, the increase of the value of g_{33} means that the value of ε_{33}^{T} decreases faster than that of d_{33}. Moreover, the piezoelectric properties in the thickness direction (d_{33}, g_{33} and k_t) decrease less than the properties in the planar direction (d_{31}, g_{31}). The samples with different porosities show this decoupling effect that increases the factor of merit of the material for application as acoustic transducer.

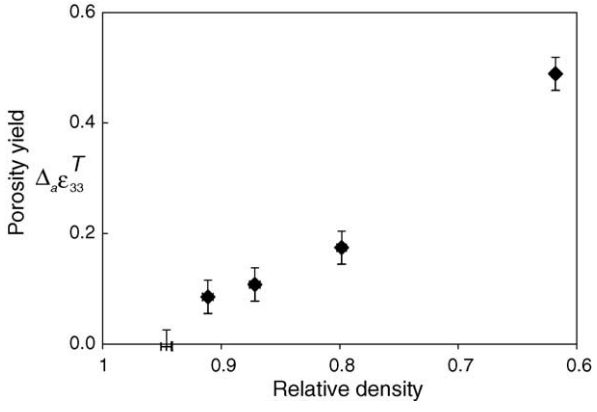

Fig. 3. Relative difference of the dielectric permittivity, measured in the ⊥ and // directions to the applied pressure.

In application as bending actuator, one of the parameters of concern is the g_{31} of every layer. In fact, in a unimorph[4] configuration, the layers with higher g_{31} drive the actuator while the layers with lower g_{31} are the clamping elements.

4. Conclusions

The porous samples produced with homogeneous or graded porosity show a strong difference of the properties in the planar and transverse direction due to the strong anisotropy of the microstructure. The structure produced by introducing lamellar voids through the addition of graphite as PFA can be regarded as a layered structure where the capacities are combined in series or parallel in perpendicular directions. The porosity graded material show a continuously varying morphology without delamination at the interfaces between the layers, with properties tailored following the properties of the homogeneous layers.

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