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## Porous piezoelectric ceramics

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### 1. Introduction

Lead Zirconate Titanate (PZT) is the best performing, cost effective class of piezoelectric materials known to date (Kumamoto et al., 1991; Martin et al., 1993; Perez et al. 2005). Its success is strongly related to the flexibility in terms of composition (Zr/Ti ratio, use of different dopants) and microstructure. In particular, when PZT is doped with Nb and coupled with a controlled porous microstructure, it becomes a promising candidate for ultrasonic transducer applications.

To obtain high piezoelectric responses it is important to produce dense ceramics: in this respect, the porosity is generally considered a defect that causes the decreasing of the mechanical and piezoelectric properties. On the other hand, the introduction of tailored porosity can considerably improve the performances of ultrasonic devices, such as hydrophones (Geis et al., 2000) or medical diagnostic devices (Smith, 1989). Dense PZT-type piezoceramics show low hydrostatic figure of merit (FOM) and poor acoustic coupling to the media with which it is in contact and are therefore not suitable for these applications. On the contrary, in porous piezoelectric materials, a partial decoupling between transverse and longitudinal effects leads to an increase of the FOM while the transfer of acoustical energy to water or biological tissues is improved as a consequence of a lower acoustical impedance ( $Z$ ) (Li et al., 2003; Okazaki & Nagata, 1973). A low  $Z$  value, in fact, reduces the mismatch between the device and the media through which the signal is transmitted or received, leading to a more efficient acoustic wave transfer (Roncari et al., 2001).

Porous piezoceramic can be designed as a functionally graded material (FGM) (Mercadelli et al., 2010). This allows to match the need of an high response, typical of dense piezoceramic, to a good compatibility with the investigated media given by a porous material.

In this chapter the main processing routes necessary to obtain PZT-based materials with tailored porosity will be thoroughly analyzed and discussed. The electrical and acoustic properties of porous piezoelectric ceramics will be evaluated considering both porosity amount and pore morphology.

## 2. Porous Ceramics Processing

Materials containing tailored porosity exhibit special properties and features that usually cannot be achieved by their conventional dense counterparts. Therefore, porous materials find nowadays many applications in several technological processes.

Such applications include the filtration of molten metals, high-temperature thermal insulation, support for catalytic reactions, filtration of particulates, and filtration of hot corrosive gases in various industrial processes. The advantages of using porous ceramics in these applications are usually their high melting point, specific electronic properties, low thermal mass, low thermal conductivity, controlled permeability, high surface area, low density, high specific strength, and low dielectric constant.

Porous ceramics are classified (IUPAC) according to their pore size (macroporous ceramics, pore size  $> 50$  nm, microporous,  $d < 2$  nm and mesoporous ceramics,  $2 \text{ nm} < d < 50$  nm) and in terms of pore geometry (Araki & Halloran, 2005): foam, interconnected, pore spaces between particles, plates, and fibres, large or small pore networks.

The main processes to produce porous ceramics are well detailed in a review proposed by Studart et al., 2006. The most straightforward processing route for the preparation of porous ceramics is the partial sintering of cold-compacted powders. In this method many experiments have to be conducted in order to develop an appropriate sintering procedure to achieve the desirable porosity. The degree of porosity is in fact controlled by the degree of sintering, which, in turn, is controlled by temperature and/or soaking time. Many novel methods have been developed for the preparation of porous ceramics with controlled microstructure. The most widely used for macroporous ceramics could be classified into replica, sacrificial template and direct foaming methods (Fig. 1).

### 2.1 Replica Technique

The replica method is based on the impregnation of a cellular structure (sponge) with a ceramic suspension. The organic structure is then removed by controlled thermal treatments in order to produce a macroporous ceramic exhibiting the same morphology of the original porous material. Many synthetic and natural sponges can be used as templates for this method.

Porous ceramics obtained with the sponge replica method can generally reach total open porosity levels within the range 40%–95% and are characterized by a reticulated structure of highly interconnected pores with sizes between 200  $\mu\text{m}$  and 3 mm. The minimum cell size of replica-derived porous ceramics is however limited to approximately 200  $\mu\text{m}$ , for the difficulty of impregnating polymeric sponges with excessively narrow cells.

### 2.2 Sacrificial Template Method

The sacrificial template technique usually consists on the preparation of a biphasic composite comprising a continuous matrix of ceramic particles and a dispersed sacrificial phase. The latter is initially homogeneously distributed throughout the matrix and is ultimately extracted to generate pores within the microstructure. Predominantly open pores of various different morphologies can be produced with this method. The most crucial step in this technique is the removal of the sacrificial phase that can be done by pyrolysis, evaporation, or sublimation. These processes might involve the release of an excessive

amount of gases and must be carried out at sufficiently slow rates in order to avoid cracking of the cellular structure. The most widely used sacrificial templates can be summarized as follow:

- Synthetic organics: polyvinyl chloride (PVC), polystyrene (PS), polyethylenoxide (PEO) or Polyvinylbutiral (PVB), polymethylmethacrylate (PMMA) or polymethylmethacrylate-ethyleneglycole (PMMA-PEG) beads, methylhydroxyethyl cellulose (MHEC), phenolic resin, nylon, cellulose acetate, polymeric gels, naphtalene.
- Natural organics: gelatine, peas and seeds, cellulose/cotton, glucide, sucrose, dextrin, wax, alginate, starch.
- Liquids: water, camphene, emulsion-oils.
- Salts: NaCl, BaSO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>.
- Metals/ceramics: nickel, carbon (graphite, fiber, nanotubes), SiO<sub>2</sub> (particles, fibers), ZnO.

The natural or synthetic organic components are essentially removed by decomposition/combustion thermal treatments, while inorganic pore formers (salts, ceramic or metallic composites) are generally eliminated through chemical processes (aqueous or acidic leaching).

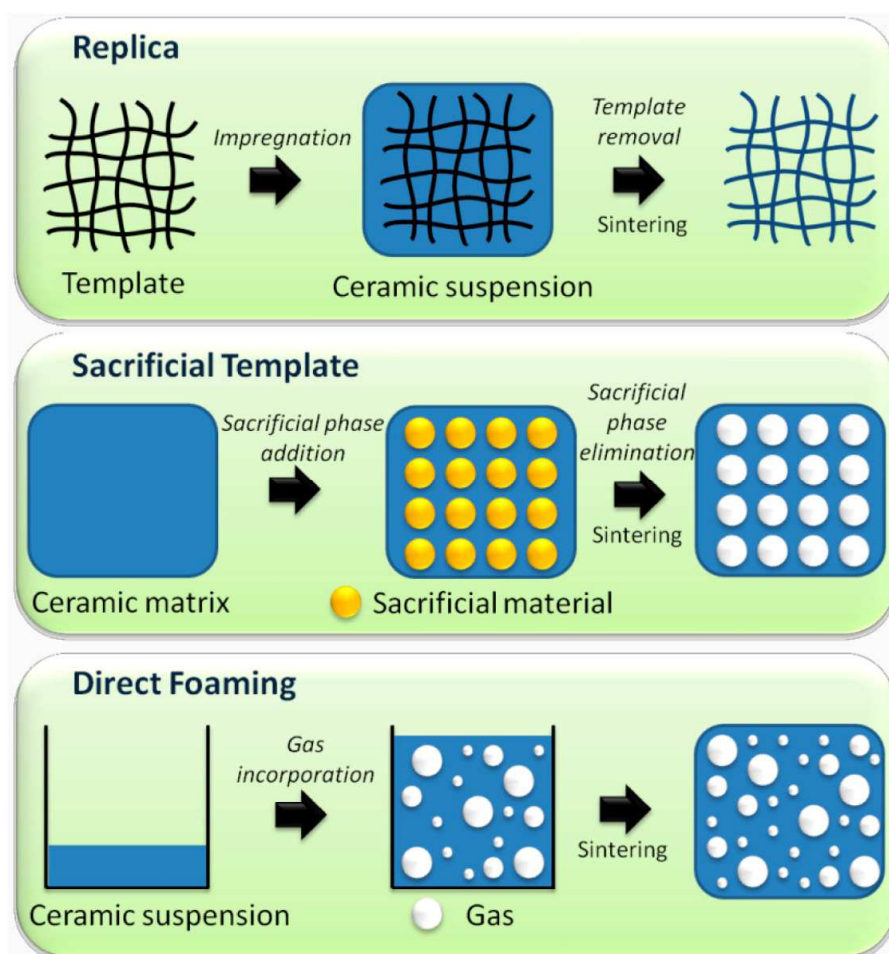
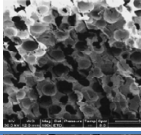
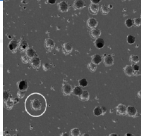
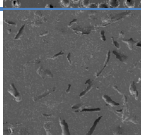
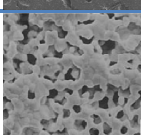
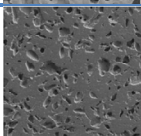
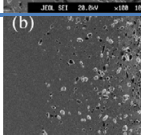
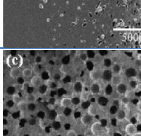
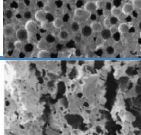
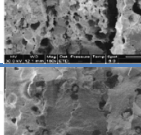
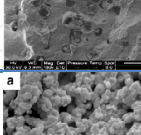
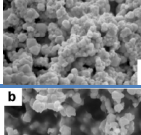
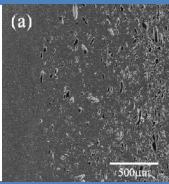
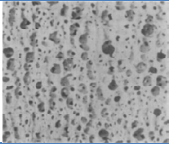
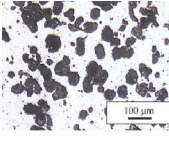
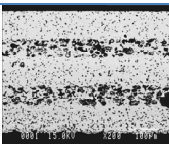
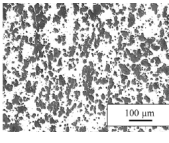
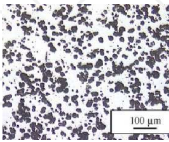
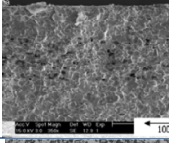
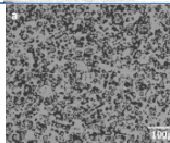


Fig. 1. Scheme of the main processing routes used for the production of porous ceramics

Pore former, Process used	Pore former shape and size ( $\mu\text{m}$ )	Ceramic pore size ( $\mu\text{m}$ )	Porosity (%)	Microstructure	Composition	
Synthetic organic	Spherical, 220	120-125 (3-3 connectivity)	20-50		PZT (Kumar et al., 2005; Praveenkumar et al., 2006))	
	Spherical, 15	10-15	4-18		PZT (Zeng et al., 2007) PMN-PZT (Zeng et al., 2006)	
	Irregular, 100-120	100-120	4-18		PZT (Zeng et al., 2007)	
	PMMA, die pressing	Spherical, 5-6	1-7	30-50		ZrO <sub>2</sub> , LaGaO <sub>3</sub> (Kaleva et al., 2006)
		120-170	> 100	55-35		PZT (Zeng et al., 2006)
		34-76	10-80	Gradient 10-40		PZT (Zhang et al., 2007)
		Spherical, 150-200	120-170	10-55		Y <sub>2</sub> O <sub>3</sub> (Gain et al., 2006)
	PEO, die pressing	Spherical, 150	100 (3-3 connectivity)	25-50		PZT (Kumar et al., 2005)
	PVC, die pressing	Spherical, 125	6 (0-3 connectivity)	40-50		PZT (Kumar et al., 2005)
	MHEC, die pressing	10-140	01-10	30-60		PZT (Roncari et al., 2001)
PVB, tape casting	-	01-1	45		PZT (Roncari et al., 2001)	
	-	0.8-1.6	60		PZT (Craciun et al., 1998)	

	Pore former, Process used	Pore former shape and size ( $\mu\text{m}$ )	Ceramic pore size ( $\mu\text{m}$ )	Porosity (%)	Microstructure	Composition
Synthetic organic	Stearic acid, die pressing	Irregular	10-100 (3-3 connectivity)	Gradient 10-40		PZT (Zhang et al., 2007)
	-	-	10-30 (long axis connectivity)	Gradient 2.4-21.4	-	PZT (Li et al., 2003)
	Dextrin, die pressing	Irregular, ~ 15	-	4-12	-	PZT (Zeng et al., 2007)
Natural organics	Glucide, die pressing	~ 20	10-1000	60-90		PZT (Montanaro et al., 1998)
	Potato starch, starch consolidation	45-50	>50	25-50		Al <sub>2</sub> O <sub>3</sub> (Gregorová & Pabst, 2007; Gregorová et al. 2006)
	-	-	30-40	30-50	-	PZT (Galassi et al., 2005)
	Potato starch, die pressing	10-20	-	-	-	ZrO <sub>2</sub> , LaGaO <sub>3</sub> (Kaleva, 2006)
	Potato starch, tape casting	-	~ 30-40	25		PZT (Palmqvist et al., 2007)
	Wheat starch, starch consolidation	~ 20	~ 20	25-50		Al <sub>2</sub> O <sub>3</sub> (Gregorová & Pabst, 2007; Gregorová et al. 2006)
	Tapioca starch	12-14	-	-	-	(Gregorová et al. 2006)
	Corn starch, starch consolidation	12-14	~ 14	25-50		Al <sub>2</sub> O <sub>3</sub> (Gregorová & Pabst, 2007; Gregorová et al. 2006)
	Corn starch, tape casting	~ 15	~ 5	5-10		PZT (Shaw et al., 2007)
	Corn starch, die pressing	12	10-40 (3-3 connectivity)	35		PZT (Galassi et al., 2005; Roncari et al., 1999)

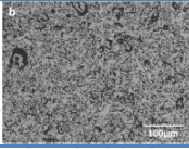
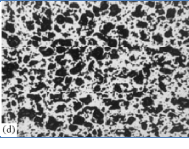
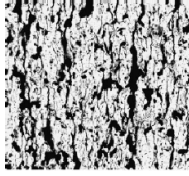
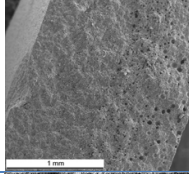
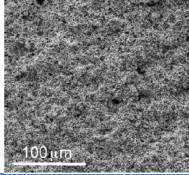
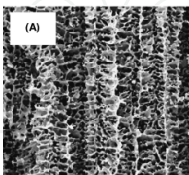
	Pore former, Process used	Pore former shape and size ( $\mu\text{m}$ )	Ceramic pore size ( $\mu\text{m}$ )	Porosity (%)	Microstructure	Composition
Natural organics	Rice starch	4-5	-	-		(Gregorová et al., 2006)
	Rice starch, die pressing	6	10-20 (3-3 connectivity)	35		PZT (Galassi et al., 2005)
	Ammonium citrate monohydrate, die pressing	10-50	-	-		ZrO <sub>2</sub> , LaGaO <sub>3</sub> (Kaleva et al., 2006)
	Ammonium oxalate monohydrate, die pressing	-	5-30 (3-3 connectivity)	24-40		PZT (Eremkin et al., 2004)
	K <sub>2</sub> CO <sub>3</sub> (solid state synthesis with PbSO <sub>4</sub> and TiO <sub>2</sub> ), and leaching	-	5-30 (3-3 connectivity)	-		PbTiO <sub>3</sub> (Toberer & Seshadri, 2006; Toberer et al., 2004)
Inorganics	Graphite, die pressing	Elongated, 200	5-30 (3-3 connectivity)	Gradient 10-40		PZT (Piazza et al., 2005), YSZ (Corbin & Apte, 1999)
	Carbone	Spherical, 5-50	1.4-3.5	Gradient 10-40		Ni-YSZ (Holtappels et al., 2006)
		Spherical, 1-30	≤ 1	48		Ni-YSZ (Sanson et al., 2008)
Liquids	Canfene, sublimazione	-	(3-3 connectivity)	90		PZT (Lee et al., 2007; Lee et al., 2008)

Table 1. Pore formers and processes used to produce porous ceramics: state of the art.

### 2.3 Direct Foaming Method

The pores produced with this approach result from the direct incorporation of air bubbles into a ceramic suspension, therefore there is no need for extensive pyrolysis steps before sintering of the green body. The stabilization and setting of the wet foams is the decisive step in direct foaming methods. The total porosity of directly foamed ceramics is

proportional to the amount of gas incorporated into the suspension or liquid medium during the foaming process and can reach values ranging between 45 and 95%. The pore size, on the other hand, is determined by the stability of the wet foam before setting. Wet foams are thermodynamically unstable: these destabilization processes significantly increase the size of incorporated bubbles, resulting in large pores in the final cellular microstructure. The use of surface modified particles to stabilize the wet foam has decreased the lower limit of pore size achievable via direct foaming to 10  $\mu\text{m}$ , with the upper one being around 1.2 mm.

### 3. Porous ceramics via the sacrificial template methods: state of the art

The three techniques above mentioned allow a wide range of pore size and porosity amount. The foaming method is generally used to produce a high level of interconnected porosity, while the replica technique, (depending on the template) leads to high porosity amount and tailored pore size ranging between 10  $\mu\text{m}$  and 1.2 mm. The sacrificial template method not only allows a strict control of the amount, mean size and morphology of the porosity produced but, tailoring the nature and size of the pore former agent, guarantees a wider range of porosity level and dimension. Moreover this method is the only one able to produce small pores (< 10  $\mu\text{m}$ ).

For these reasons the sacrificial template method must be considered for those applications that require micrometric pore size. A panoramic of the pore forming agents and of the processes involved in the fabrication of porous piezoelectric materials is reported in Table 1.

### 4. Porous piezoelectric ceramics: characteristics and applications

As already mentioned, the porosity is usually unwanted for its detrimental effect on the piezoelectric and mechanical properties. However the introduction of a controlled porosity into a piezoelectric ceramic could strongly improve its acoustic performances and therefore its ultrasonic response.

#### 4.1 Porous ceramics as composites

Composites are materials that are receiving a growing attention by the scientific as well as the industrial world. They can in fact show specific properties (electronic, magnetic, mechanical, etc.) that cannot be otherwise achieved by the single phase materials. This approach has been applied for the first time to the piezoelectric materials at the end of the 1970s combining them with polymeric and/or metallic phases to obtain actuators or transducers (Akdogan et al., 2005).

In the production and design of a piezocomposite the right choice of the spatial distribution between the two phases determines the effective improvement of the piezoelectric properties (Levassort et al., 2007). For this reason, the concept of connectivity has been defined to describe the way in which the individual phases are self-connected (that is, continuous) (Skinner et al., 1978). There are 10 connectivity patterns for a two-phase (diphasic) system, in which each phase can be continuous in zero, one, two, or three dimensions. The internationally accepted nomenclature to describe such composites is (0-0), (0-1), (0-2), (0-3), (1-1), (1-2), (1-3), (2-2), (2-3) and (3-3). The first digit refers to the number of dimensions of connectivity for the piezoelectrically active phase, and the second digit is



used for the electromechanically inactive phase. A porous ceramic can be as well considered a composite where the main phase is the active ceramic and the second phase is the porosity. The development of such piezoelectric composites aims to combine the specific properties of each single phase to maximize either the electromechanical and ultrasonic response of a particular device. A single material, or a unique phase, cannot in fact satisfy the need of maximize the piezoelectric response and at the same time minimize the material density to acoustically match the transducer with the water or the media to which it is in contact. In these cases, when two opposite requirements have to coexist, the production of a composite is the only way to produce an efficient device (Akdogan et al., 2005).

#### 4.2 Properties

Nowadays, many types of piezoelectric composites are used as active materials for transducers. These composites are fabricated by incorporating different second phases, e.g. dielectric ceramics (Jin et al., 2003), metals (Li et al., 2001), polymers (Klicker et al., 1981) or pores (Li et al., 2003), to modulate the electrical properties. The porosity has several advantages as non-piezoelectric second phase. Firstly, porous piezoelectric ceramics are composed of ceramics only, thus there is no possibility of detrimental chemical reactions between the piezoelectric ceramic and the second phase during production. Secondly, their piezoelectric properties are easily tailored by changing the porosity level and the pore morphology. Finally, they are cheaper to produce and lighter than other possible piezoelectric composites (Jin et al., 2003; Li et al., 2001).

Since porous piezoelectric ceramics have lower acoustic impedances than dense ceramics, they could be used to improve the mismatch of acoustic impedances at the interfaces of medical ultrasonic imaging devices or underwater sonar detectors (Kumar et al., 2006). Therefore, the electrical and acoustic properties of porous piezoelectric ceramics need to be thoroughly evaluated in the light of either porosity level and pore morphology. Three are the characteristics that a porous piezoceramic has to satisfy to be used for ultrasonic applications:

1. high hydrostatic figure of merit;
2. acoustic impedance similar to the one of the investigated media;
3. low mechanical quality factor.

##### Hydrostatic figure of merit

The efficiency of a piezoceramic for ultrasonic applications and for hydrophone devices in particular is measured by the hydrostatic figure of merit  $d_{hg_h}$ . In hydrostatic condition, the transducer behaviour is proportional to this figure of merit through the equation:

$$d_{hg_h} = (d_{33} - 2 |d_{31}|) \cdot (g_{33} + 2 |g_{31}|) \quad (1)$$

where for PZT ceramics  $d_{33} \approx 2 |d_{31}|$  and  $g_{33} \approx 2 |g_{31}|$ . From this equation, the figure of merit for dense PZT tends to zero. On the other hand in the porous piezoceramics a partial decoupling of the piezoelectric response between the longitudinal and transversal direction occurs. As a consequence, the more the porosity increases the more the  $|d_{31}|$  value decreases in respect to the  $d_{33}$  one. In this way, the electrical response is maximized along the most useful direction (i.e. in the thickness, 33) and, at the same time, minimized in the other ones.

The figure of merit is in this way improved by more than three orders of magnitude, decreasing the effect in the 31 direction while keeping constant the one in 33.

#### Acoustic impedance

The acoustic impedance ( $Z_a$ ) of a material is a measure of the propagation of the acoustic wave throughout the interfaces of different media. The wave transfer is maximized when the two media have the same acoustic impedance. The higher is the difference of impedance between the two media, the higher would be the acoustic wave's fraction reflected at the interface. In the case of a transducer, its efficiency is linked to the acoustic matching between the piezoceramic (high  $Z_a \sim 30-33 [10^6 \text{ Kg} / \text{m}^2\text{s}]$ ) and the investigated media (water, biological tissues) to which is in contact (low  $Z_a \sim 1-1.5 [10^6 \text{ Kg} / \text{m}^2\text{s}]$ ) (Bowen et al., 2004). This large impedance difference leads to poor acoustic matching and low axial resolution. This problem is generally overcome reducing the ceramic density. It has been shown (Levassort et al., 2007) that the introduction of 40% vol of isotropic porosity into a piezoceramic leads to a reduction of 60% the acoustic impedance thus dramatically increasing the device efficiency.

#### Mechanical quality factor ( $Q_m$ )

The increasing of mechanical losses (and the consequent reduction of the mechanical quality factor) is another effect induced by the presence of porosity into a piezoceramic. This property is useful to increase the transducers bandwidth, i.e. to reduce the electrical signal losses in operating conditions.

### **4.3 Piezoelectric ceramics as ultrasonic transducers**

Piezoceramics devices are widely used as ultrasonic transducers because they can generate powerful ultrasonic waves useful for cleaning, drilling and welding, as well as to stimulate chemical processes. Moreover, they act either as transmitters and receivers of ultrasonic waves in medical diagnostic equipments and non-destructive material testing apparatus for locating defects within a structure. Ultrasonic waves are mechanical vibrations that propagate in a material as a consequence of a series of very small continuous displacements of atoms and chain segments around their equilibrium positions. Displacements are induced at neighbouring zones by the forces within a chain segment and between adjacent chain segments, propagating in this way a stress-strain wave. Several kinds of ultrasonic waves may propagate in solid materials: longitudinal waves, shear waves, Rayleigh waves (or surface acoustic waves), Lamb waves (or plate waves). The most common method of ultrasonic wave generation and detection uses longitudinal waves in which the piezoceramic transducers are required to move like pistons at very high frequencies (from 20 kHz to hundreds of MHz) (Lionetto et al., 2004).

Recently the research interest in this field is focused on the development of suitable transducers for the medical diagnosis.

#### 4.4 Transducers for ultrasonic medical diagnostics

A classical ultrasonic transducer (Fig. 2) is composed by:

- an active piezoelectric element (that works as either transmitter and receiver);
- a backing layer (that absorbs the acoustic emission in the back side of the actuator)
- a matching layer (that matches the acoustic impedance of the piezoelectric material with the one of the investigated surface).

With this architecture, the energy emission is maximized and therefore the axial resolution (that is the capability to distinguish two points along the axis of an ultrasonic beam) increased thus improving the image resolution (Levassort et al., 2004).

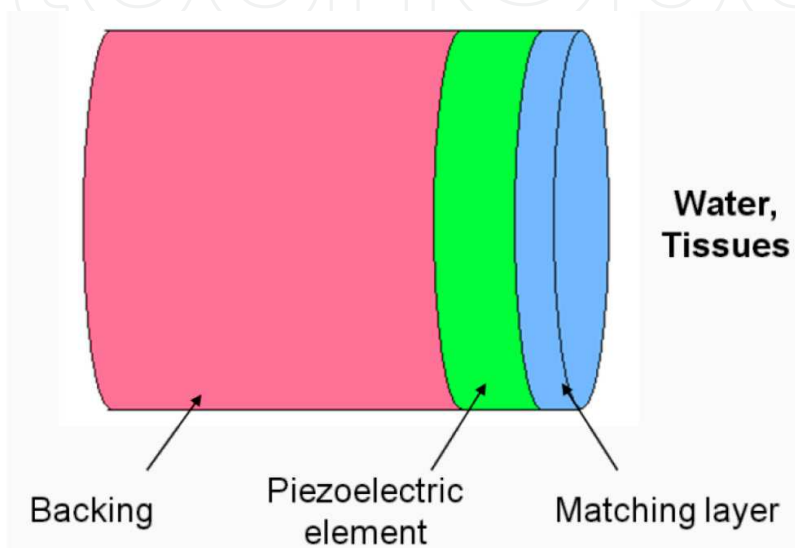


Fig. 2. Scheme of a classical ultrasonic transducer.

##### Active piezoelectric element

The active piezoelectric element is typically a piezoelectric disk, 1-2 cm thick, with two electroded parallel faces. The application of an alternating current between the two electrodes generates a synchronous thickness variation of the transducer (inverse piezoelectric effect); on the other hand a mechanical perturbation (ultrasonic pulse) induces an electrical signal as a consequence of the direct piezoelectric effect.

The piezoelectric element thickness is a crucial parameter that defines the resonance frequency of the device. High-frequency ultrasonic devices are, for example, needed for the medical diagnosis in organs such as skin, eye and blood vessels, where high resolution is requested at low depth of field (Levassort et al., 2004). The depth of penetration of the ultrasounds is in fact inversely proportional to the frequency. High-frequency ultrasounds are therefore only used to study relatively "superficial" structures.

In the case of a transducer with a fixed thickness  $d$ , the resonance condition occurs at a wave length  $\lambda$  equal to:

$$\lambda = 2d \quad (2)$$

The corresponding frequency is linked to the ultrasound speed ( $c$ ) into the transducer material through the equation:

$$f = \frac{c}{\lambda} \quad (3)$$

It is clear that the frequency and the piezoceramic thickness are inversely proportional. Therefore it is necessary to reduce the thickness of the piezoelectric element to work at high resonance frequencies.

#### Backing layer

The backing layer has two functions: on one hand it works as mechanical support for the active element, on the other hand it has to attenuate the acoustic energy lost from the back face of the transducer. In this way no energy is radiated back to the active layer hindering therefore the production of parasitic echoes (Levassort et al., 2004). To optimize the transmission of the ultrasounds to the back surface of the transducer, the backing and active layer materials must have similar impedance values. For this reason epoxy resins filled with tungsten particles are generally used as materials for backing layers.

#### Matching layer

On the front of the transducer (i.e. between the piezoceramic and the propagation medium) a matching layer is generally used. This layer must mediate the impedance values of the ceramic with those of the biologic tissues thus maximizing the acoustic energy amount transmitted by the transducer and improving consequently its efficiency.

The optimal impedance value for a matching layer is defined as:

$$Z_m = \sqrt{Z_t \cdot Z_{st}} \quad (4)$$

where  $Z_m$ ,  $Z_t$  and  $Z_{st}$  are the acoustic impedance values of respectively the matching layer, the transducer and the biological tissue. The matching layer thickness must be  $\lambda/4$  to produce destructive interference with the waves reflected back. For example, in the case of a single porous matching layer, suitable for a PZT transducer working at a frequency of 50 MHz, with a speed of sonar wave propagation of  $v = 1882$  m/s and acoustic impedance of  $Z_m = 9.64$  [ $10^6$  Kg /  $m^2s$ ], its thickness  $t$  would be:

$$t = \frac{v}{f} = \frac{1882 \text{ ms}^{-1}}{50 \times 10^6 \text{ s}^{-1}} = 38 \mu\text{m} \quad (5)$$

Whereas the optimal impedance value for the matching layer would be:

$$Z_m = \sqrt{Z_t \cdot Z_{st}} = \sqrt{25 \cdot 1} = 5 \text{ [} 10^6 \text{ Kg/m}^2\text{s]} \quad (6)$$

Therefore the matching layer must be optimized in terms of either the material, to match the acoustic impedance, and the thickness to maximize the device performances. The porous piezoceramics could be successfully used as matching layer, allowing an optimal chemical-physical compatibility with the active piezoelectric element (dense ceramic) and offering at the same time the possibility to tailor the microstructural properties to improve the efficiency.

## 5. Porosity Graded Piezoelectric Ceramics (PGPC)

The ultrasonic properties of the piezoelectric materials could be improved producing a transducer (the active layer) with a functionally-graded structure (Fig. 3). The porosity-graded structure could match a dense active layer with high piezoelectric constant able to efficiently transmit/receive the acoustic/electrical signal with a porous layer with a lower piezoelectric response but with an acoustic impedance appropriate for the porous matching layer and the investigated media.

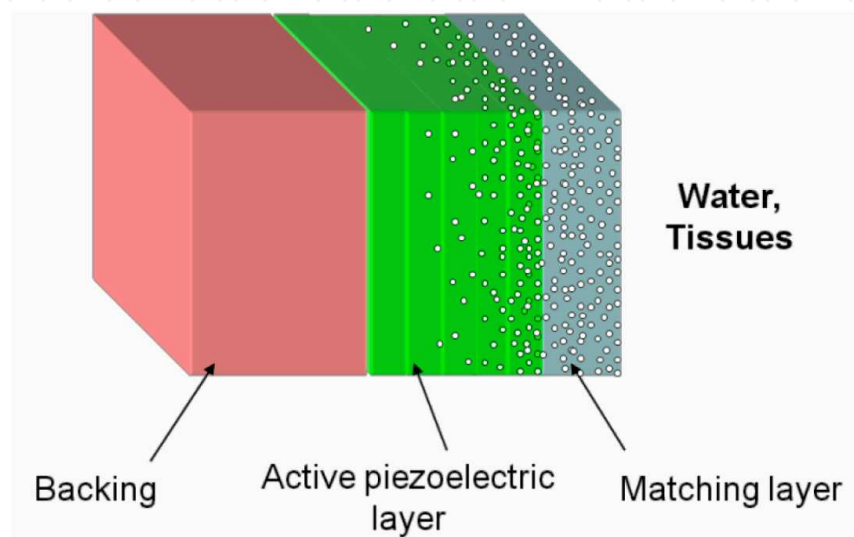


Fig. 3. Scheme of a transducer with a porosity-graded active layer and a porous matching layer.

The transducer performances could be improved even further by adding more matching layers (Fig. 4): in fact a gradient of the acoustic impedance values could minimize the differences between the ceramic and the media, maximizing, as a consequence, the acoustic energy transmitted to the biological tissues. The ideal would be the production of a continuous porosity-gradient material able to assure a uniform properties-variation from the transducer to the tissues.

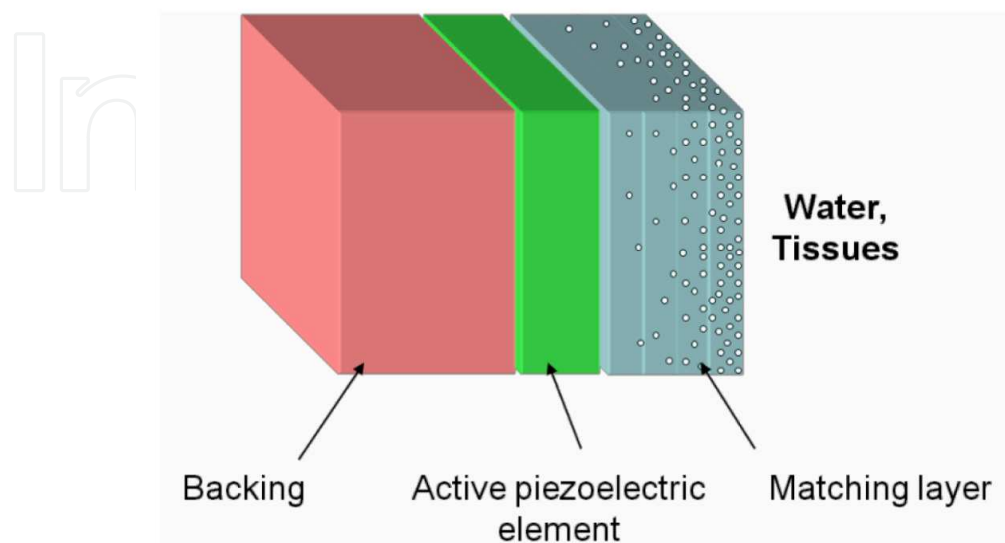


Fig. 4. Scheme of a transducer with a porosity-graded matching layer.

### 5.1 Processes for the production of (PGPC): state of the art

The production of functionally graded materials has to face and overcome the technological difficulties related to the fabrication of layers with different microstructural characteristics (different shrinkage, various organics content to be eliminated, etc.). Few works are reported till now regarding this kind of architectures.

Porous graded piezoelectric materials more than 1 mm thick and with porosity ranging from 10 to 40 % have been already produced by die-pressing layers of powders with different pore former amounts (see Table 1). With this technique it is however difficult to produce graded materials with thickness less than 1 mm. As mentioned above, for the design of an ultrasonic medical device it is very important to cover a wide range of thicknesses to assure resonance frequency from 20 kHz to hundreds of MHz (Opielinski & Gudra, 2002). Working at high frequency ( $f > 20$  MHz) means to have a suitable resolution at low depth of field, requirement needed for the ultrasound probes for the skin, eye and blood vessels diagnostic. In this case it is particularly important to have a transducer with thicknesses below 1 mm.

In the next paragraph we will consider the tape casting process to obtain porous piezoelectric thick layers with these characteristics. Tape casting is in fact the most used technique for the production of ceramic thin layers. These can be then stacked to obtain graded materials less than 1 mm thick. With this process a functionally-graded material can be obtained by sintering layer-stacked green tapes with stepwise varied compositions.

This process has been already used to produce porous piezoelectric multilayers with a sandwich-like structure (dense/porous/dense layers and vice versa) for piezoelectric applications (Palmqvist et al., 2007; Shaw et al., 2007).

## 6. Tape cast porosity-graded piezoelectric ceramics

We have recently reported the optimization needed to produce a flat, 400  $\mu\text{m}$  thick, functionally-graded porous Nb-doped PZT material ( $\text{Pb}_{0.988}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.976}\text{Nb}_{0.024}\text{O}_3$ , PZTN) by tape casting (Mercadelli et al., 2010). Casting, lamination, debinding and sintering are necessary steps to obtain multilayer structures with this technique. Any variation of each of these steps strongly affects the final product. Therefore each of them (slurry formulation, lamination and thermal treatments) has to be thoroughly investigated.

Combining the sacrificial template method with tape casting, an engineered porosity could be produced. The choice of the right pore former deeply influences the size and morphology of the pores and, as a consequence, the final electrical properties of the piezoelectric product. A preliminary study was conducted to identify the most suitable pore former to obtain micrometric and isotropic porosity. A literature analysis indicated rice starch (RS) and carbon black (CB) as the more appropriate pore formers to obtain fine porosity. Sintered tapes with 30%vol of CB and RS lead to about the same amount of total porosity (35%). However the tapes fracture sections in figure 5 clearly show that CB produces uniform micrometric pores while RS leads to 5-6  $\mu\text{m}$  size pores. The CB was therefore chosen as pore former for the fabrication of porous piezoelectric layers and multilayers.

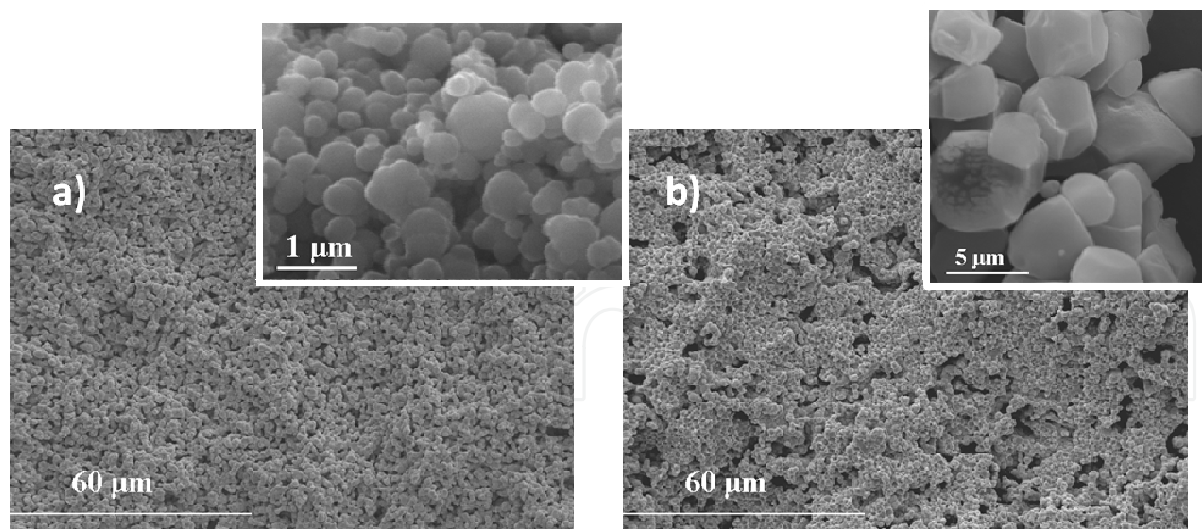


Fig. 5. SEM micrographs of the fracture section: sintered tape with CB (a) and RS (b). The insertions show the pore former morphology of a) CB and b) RS.

The porosity gradient was formed in situ by sintering layer-stacked green tapes with stepwise varied contents of pore former.

Graded porous piezoceramics were fabricated by gradually increasing CB content, adjusting the binder burnout procedure and tailoring the multilayer thickness. In this way cracks and delaminations were avoided, leading to a well developed and controlled microstructure with porosity ranging from 10 to 30 vol% (Fig. 6).

The preliminary tests done on PZTN-FGM multilayer showed a mean acoustic impedance of  $15 \cdot 10^6 \text{ Kg}/(\text{m}^2\text{s})$  and piezoelectric properties of  $S_{11}^E = 26 \cdot 10^{-12} \text{ m}/\text{N}$ ,  $k_p=0.38$ ,  $d_{31} = -106 \cdot 10^{-12} \text{ m}/\text{V}$ . Those data confirmed the potentiality of this material for ultrasonic devices and tape casting as suitable technique to produce porosity-graded piezoelectric ceramics.

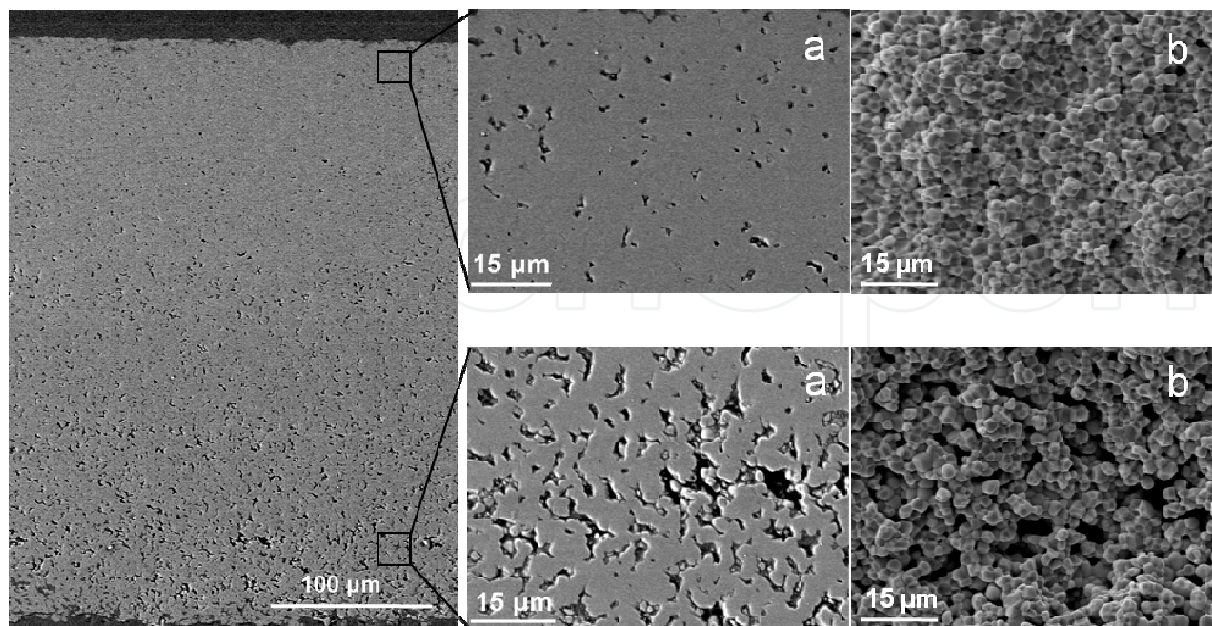


Fig. 6. SEM micrographs of the 6 layers porous graded PZTN material: a) polished surface, b) fracture surface (Mercadelli et al., 2010).

## 7. Conclusions and feature trends

Porous piezoceramics find nowadays many applications as ultrasonic transducers. The introduction of a controlled porosity into a piezoelectric ceramic could in fact strongly improve the acoustic performances for this kind of applications.

In this chapter the more recent literature on the processing of porous ceramics has been reviewed. The decisive influence of the processing method on the material's microstructure and properties was pointed out as well as the role of the application needed for the choice of the more suitable processing route for the production of porous ceramics. The sacrificial templating methods provide a straightforward way for the fabrication of macroporous ceramics with porosities and average pore sizes ranging from 20% to 90% and 1–700  $\mu\text{m}$  respectively. The possibility to easily tailor the morphology and amount of porosity makes this method effective for the production of porous piezoceramics. The combination of this technique with the tape-casting process allows the production of sub-millimetre porous and porous-graded piezoelectric structure.

Reducing the piezoceramic thickness is a key point to reach higher resonance frequency and, as a consequence, high resolutions medical transducers application. In this respect, the drive toward device miniaturization has created a strong interest in PZT thick-film technology and as a consequence into the screen printing process. With thicknesses in the range 5–80  $\mu\text{m}$ , screen-printed PZT thick films fill an important technological gap between thin-film and bulk ceramics offering the advantage of miniature scale and direct integration into hybrid electronic packages. This technique therefore could be very promising for the production of porosity-graded structure for high-frequency (from 20 to 50 MHz) ultrasonic transducers.

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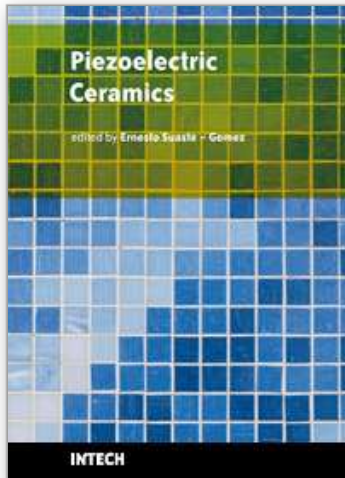


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## **Piezoelectric Ceramics**

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This book reviews a big window of opportunity for piezoelectric ceramics, such as new materials, material combinations, structures, damages and porosity effects. In addition, applications of sensors, actuators, transducers for ultrasonic imaging, positioning systems, energy harvesting, biomedical and microelectronic devices are described. The book consists of fourteen chapters. The genetic algorithm is used for identification of RLC parameters in the equivalent electrical circuit of piezoelectric transducers. Concept and development perspectives for piezoelectric energy harvesting are described. The characterization of principal properties and advantages of a novel device called ceramic-controlled piezoelectric with a Pt wire implant is included. Bio-compatibility studies between piezoelectric ceramic material and biological cell suspension are exposed. Thus, piezoelectric ceramics have been a very favorable solution as a consequence of its high energy density and the variety of fabrication techniques to obtain bulk or thin films devices. Finally, the readers will perceive a trend analysis and examine recent developments in different fields of applications of piezoelectric ceramics.

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