

Processing of porous ceramics: Piezoelectric materials

Carmen Galassi*

CNR-ISTEC National Research Council, Institute of Science and Technology for Ceramics, Via Granarolo 64, I-48018 Faenza (RA), Italy

Available online 15 March 2006

Abstract

The paper reviews processing techniques used to produce porous ceramics with tri-dimensionally interconnected porosity, in a wide range of pore volumes and pore size and distribution. Attention is focused on the development of porous electroceramics and especially piezoelectric PZT materials. The porosity can be introduced through dry or wet techniques. In the dry techniques, a fugitive phase is added to the perovskitic powder by mechanical mixing. Wet techniques involve the manipulation of suspensions and a better control of the final morphology and microstructure of the samples can be achieved by the colloidal approach. The whole spectrum of techniques for generation of porosity is surveyed; it includes burnout of volatile particles or thermally unstable sponge structures, generation of porosity by foaming, slip casting, tape casting, direct consolidation, solid freeform fabrication, die pressing. Porosities of up to 70% are obtained in aerogels by sol–gel processing. The pore size distribution and microstructural differences resulting from various processing parameters influence the physical properties, particularly the acoustic/piezoelectric response of PZT materials.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Suspension; Porosity; Piezoelectric properties; PZT; Sensors

1. Introduction

The interest in porous ceramics has grown rapidly in the recent years with the demands from new fields of applications; processing routes to develop unique structures are now under extensive investigation. The use of porous ceramics in thermal insulation, substrates for catalysts and filtration systems has been assessed for many years and the materials are still expanding into other areas.¹ Porous membranes are used for filtration of high temperature, high pressure gas streams to remove pollutants, or recover gases like methane from mines or hydrogen in petroleum refineries, for separation of metallic inclusions from hot metals such as cast iron, steel, aluminium. These all require improvements of membrane resistance to high temperature environments, abrasion and chemical attack. Membranes^{2,3} find application in biotechnology, food processing, pharmaceutical, petrochemical, electronics; improvement of the thermo-mechanical properties while lowering production costs is necessary for further expansion of the applications. In the biomedical field⁴ porous ceramics (hydroxyapatite) find use in bone replacement and drug delivery systems⁵; because of its

excellent biocompatibility, it enables the production of architectures similar to those of real bones, and has the potential to repair the defects through a complete penetration of the osseous tissue.

Porous ceramics are classified according to their pore size (from the order of nanometer to several millimeters) and basic pore structure (open cell structure, closed cell structure, membranes, tangle fiber network ceramics, functionally gradient pore-size distribution, etc.). Membranes⁶ are classified on the basis of their pore size into filtration membranes (pore size greater than 104 nm), micro filtration membranes (pore sizes in the range 102–104 nm) and ultra filtration membranes (pore size in the range 2–100 nm)⁷ and hyper filtration, reverse osmosis or gas separation membranes (pore sizes 1 nm or less).⁸ In the open cell structure, the pores are interconnected, while they are isolated in a continuous ceramic matrix in the closed cell structure; the former, due to their permeability to gas or liquids (depending on the pore size) are suitable for applications involving fluid transport while the latter are used in those applications, like thermal insulation, where no fluid flow is required. Open cell structures are also called reticulated ceramics when the porosity degree is very high (70–95%) with rather large voids (10 μm to 5 mm) and are usually formed by replicating a polymer sponge or by the polymer foam method⁹; they have low strength and fracture toughness because, upon burning of

* Tel.: +39 0546 699711; fax: +39 0546 46381.
E-mail address: carmen@istec.cnr.it.

the organic matrix, very thin struts of ceramic remain that limit the mechanical properties.¹⁰ More complex structures are now developed, that combine closed and open porosity, alignment of continuous pores,^{11,12} anisotropic¹³ or functionally gradient porosity.¹⁴ Several new shaping methods convert natural templates, like coral skeletons or wood,¹⁵ into novel cellular ceramics with micro-, meso- and microstructure pseudomorphs of the initial porous tissue skeleton ranging from nanometers to millimeters. The control of pore size and morphology complexity can be achieved through the application of novel approaches to the powder processing, including direct casting methods and solid freeform fabrication.¹⁶ Electro ceramics with different porosity content and morphology are developed and the complexity of the interaction between the dominating factors like thermal and electrical conductivity, piezoelectricity, nonlinear phenomena of the grain boundaries, defects, impurities and domains means that the porosity property relationships are not completely understood.^{17,18} One of the applications of piezoelectric materials is in acoustic receiving systems. The dense PZT-type piezoceramic materials are not appropriate for hydrostatic sensing applications, due to their low hydrostatic figure of merit (FOM) (the product $d_h g_h^a$). Moreover, the stiff and dense PZT has also the disadvantage of poor acoustic coupling to water. Therefore, in the last few years, new piezoelectric porous materials with improved piezoelectric properties and good qualities for hydrophone applications, obtained by introducing soft material inhomogeneities into the perovskitic phase, have been investigated^{19,20,21} (in the case of tri-dimensionally interconnected pores they can be compared to composites with 3–3 connectivity). In porous piezoelectric materials, where the interconnected pores are filled with air, a partial decoupling between transverse and longitudinal effects avoids direct cancelation, therefore d_h increases. Moreover, due to the lower dielectric constant, g_h is further increased and consequently the hydrostatic FOM of porous piezoelectric materials can reach values a few orders of magnitude higher than in dense materials.

2. Processing

2.1. Dry methods

The simplest method to obtain porous ceramics is by partially sintering the cold compacted powders, when the thermal treatments involve only microstructure evolution and no chemical change of phase. In this way, a porous network is formed by the spaces between the necked powders; the stability of the pores is achieved by controlling the sizes of the particles. The degree of porosity is controlled by the degree of partial sintering, which, in turn, is controlled by sintering at different temperatures and/or different times, but the final body suffers from poor mechanical strength and low stability. Porous ZrO₂ ceramics²² were produced with pore volume as high as 50% by firing die pressed bodies in the temperature range 1100–1150 °C. Different com-

paction pressures and the agglomeration of the fine powder influences the flaws and voids that are reduced by using a higher compaction pressure, thus improving the mechanical properties. By sintering at 1000 °C to 1100 °C PZT samples, obtained²³ by uniaxial pressing into pellets the as-calcined powder, the sintered density was in the range 66.3–93.0%. Very small pores with a narrow size distribution were found for samples sintered at the lower temperature whilst a small number of large pores together with micro and meso porosity was found after sintering at 1100 °C.

Tri-dimensionally-interconnected porous ceramics are usually obtained by mixing appropriate amounts of a particulate organic substances with the ceramic powder followed by die pressing^{23–27}; the pore maker can be wax, polymer beads, starch or a fugitive phase material like graphite. The process involves burning off the organics. This preferentially occurs at the surface region during the early stages of pyrolysis and is greatly accelerated by the developing porosity,²⁸ as the cavities formed by the burning of the organics during sintering act as sites for pore generation, leading to an increase in the porosity. Pore fraction, size, morphology and distribution are controlled by the amount of the added volatile phase. Homogenization of the organics with the ceramic powders by dry mixing may be a critical step as the difference in the density is high and the ceramic powders may be agglomerated. Kim et al.²⁵ added various amounts of corn starch to (Ba, Sr) TiO₃ powder and obtained 21–44% pore volume; the PTCR effect for the ceramic was 1–2 orders of magnitude higher than that of samples without corn starch. Porous Al₂O₃ ceramics with high surface area were fabricated²⁹ by adding Al(OH)₃ to the Al₂O₃ starting powder followed by sintering at a temperature higher than 1100 °C. The decomposition of Al(OH)₃ produces 60% volume contraction and material with pore volume as high as 60% and a bimodal size distribution was obtained; the material still retaining superior mechanical properties. This is method specific for the production of alumina as the pore structure is derived from the decomposition of the precursor hydroxide and the phase transformation from θ - to α -Al₂O₃. Similarly, other specific porous structures can be designed when intermediate products undergo significant volume change.

2.2. Wet methods

2.2.1. Colloidal processing

Most of the cold consolidation procedures to fabricate porous ceramics are based on the colloidal processing approach that allows the development of designed, ordered mixtures of several components through the manipulation of interparticle forces. It involves the preparation of a suspension where the ceramic powder is dispersed in a liquid or a polymer precursor, a dispersant and other organic additives like binders, plasticizers, pore-forming or foaming agents, precursors of secondary phases, so as to enhance homogenization and stability during time, and tailor the rheological properties to the adopted shaping technique. Most of the novel approaches¹⁶ developed to optimise powder processing can be applied to the production of porous materials. They enable the design of microstructure in advanced ceramics, characterized by high reliability, sufficient strength, near net

^a The piezoelectric charge constant d_h is given by: $d_h = g_h / \epsilon_{33} \epsilon_0$. The piezoelectric charge constant d_{31} ($=d_{32}$) is given by: $d_{31} = (d_{33} - d_H) / 2$.

shape, simple processing concepts, high flexibility and low environmental impact. Depending on the pore volume and pore size range, the wet techniques include ceramic foams, impregnation of polymeric sponge with the powder slurry, casting of slurries with different types of pore-forming agents, direct coagulation methods, solid freeform fabrication and sol–gel processing.

2.2.2. Reticulated ceramics

Reticulated ceramics show high volume interconnected porosity with large pore size and can be produced either by the sponge impregnation method or by direct foaming, that can result either in open cell or closed cell structures.⁸ Pore volumes higher than 90% can be generated,³⁰ with a cell size of 150 μm by separately mixing the ceramic powder with two different foaming agents (a diphenylmethane di-isocyanate and a resin component). A silicon-free polyurethane system was chosen by Ebaretonbofa and Evans³¹ to fabricate hydroxyapatite (HA) with higher than 90% pore volume reticulated, open cell structure as large as 800 μm , with interconnecting passages of the order of 100 μm diameter, starting from coarse and fine HA powder. Porous HA is shaped through a “dual phase mixing” method³² where the porous body is generated simultaneously by the pore-forming template. Naphthalene was added as a pore former to yield a pore volume higher than 50%. Geometrical, chemical, physical and mechanical property data indicated that pore size distribution and interconnectivity could be adjusted as well as the windows between adjacent pores, which is a critical parameter for tissue-engineered scaffolds. The impregnation of a polymeric sponge is a consolidated method^{8,33} which is still under improvement as it produces low strength and fracture toughness as the ceramic structure based on very thin struts remains after the burn out of the organic sponge.¹⁰ The method involves the immersion of the polymer sponge in ceramic slurry followed by drainage and drying, so as to cover the sponge walls with a uniform layer of the ceramic powder. The pore size of the sponge determines the pore size of the final product. The foam must have open cells, a uniform degree of porosity, good flexibility, no combustion residue and a good ability to recover its original shape. Amongst the polymeric sponge materials, polyurethane is the most used.

The frequent changes in the flow direction of the slurry and sudden contractions and enlargements require adequate viscous and elastic properties of the dispersion in order to replicate the original structure of the foam.^{34,35} The thickness of the struts can be improved³⁶ by recoating the reticulated perform, to achieve good handling strength. Repeated recoating with thinner slurry of the same composition allows the strut diameter to be increased. Alumina with a bimodal pore distribution was produced³⁷ by combining the sponge method with the pore-forming method. Porous cordierite type of foam was prepared by foaming the slurry (mechanical mixing), followed by gel casting, drying and sintering.³⁸ Porosity of 80% and a mean pore diameter in the range 100–200 μm were obtained.

2.2.3. Direct casting methods

Direct casting methods use some of the inherent properties of concentrated suspensions to transform a fluid sus-

pension into a stiff gel.¹⁶ When porous materials are fabricated, the general concept is to retain homogeneity of the slurry with respect to the ceramic powder and the organic additives (which include pore-forming agents) when porosity must be uniformly distributed. They are based on the formation of either physical or chemical bonds between the particles or some species in the dispersion. The advantage is a reasonable low viscosity of the suspension that facilitates easy mold-filling to process complex shapes, while a constant volume green body results from the induced thickening. Porous ceramics have been obtained by “starch consolidation”, a temperature-induced forming³⁹ based on the gelling ability of starches in water. Starch grains are insoluble in water at room temperature. The hydroxyl groups exposed by the glucose units of the polysaccharides provide a strong hydrophilic character. By raising the temperature to 50–80 °C, the intermolecular bonds are weakened and a rapid and irreversible swelling occurs by water uptake. The aqueous slurry of the ceramic powder, with added starch granules is fluid enough to fill any complex mould at room temperature. Upon heating, water is removed by swelling and it consolidates into a solid body.

Al_2O_3 ,^{39,40} hydroxyapatite,⁴¹ PZT⁴² porous materials were produced with the above technique. Pore volumes 20–70% were obtained and large spherical pores created by the original starch granules and small pores interconnecting the larger pores characterize the pore size distribution. Alumina foams were obtained by using gelatin as a gelling agent of the water-based suspension of the powder; this is proposed as an alternative method⁴³ to the more conventional in situ polymerization of water-soluble monomers. The association of an alginic acid salt with a time-delaying supplier of polyvalent ions is also suggested⁴⁴ for the preparation of concentrated suspensions with low initial viscosity suitable for direct casting. Pore orientation can be obtained by freeze drying⁴⁵ of the water-based slurry, yielding a complex structure of macro and micro pores. When the lower part of the suspension is frozen and the upper part is kept at room temperature, ice grows macroscopically in the vertical direction thereby generating open porosity (36–50%) aligned with the growth direction upon the sublimation of water. Unidirectional, aligned continuous pores were obtained¹¹ by using mercerized cotton thread as the fugitive fiber; a pore diameter of 165 μm and 34% open porosity in the alumina body was obtained and the material still retained flexure strength as high as 155 MPa. A pore structure similar to a honeycomb results from the gelling of alginate by cross-linking with multivalent metal ions⁴⁶; gelling starts from the upper surface of the suspension, dispersed with Na alginate and maintained at controlled pH, and the primary gel layer works as a selective membrane for the passage of metal ions. The slurry gradually transforms into a gel with the formation of capillaries in the direction of diffusion of the metal ions. Samples 3–6 mm long, 5–10 mm diameter, with up to 90% porosity and capillary diameters of 10–30 μm were fabricated. Gas generation in an aqueous electrophoretic deposition (EPD) process is proposed as a mean of developing unidirectional aligned pores of diameter $\sim 100 \mu\text{m}$ ⁴⁷: an alumina aqueous slurry, electrostatically stabilized by adjusting pH, is deposited at the carbon

cathode of the EPD equipment by applying direct current. The size and distribution of the pores depend on the pH of the suspension; deposition rate increases with current. During the EPD process, H₂ and O₂ gases are generated by the H₂O hydrolysis that controls the pore morphology. Thin walled alumina tubes were made by combining gel casting and freeform fabrication.⁴⁸ An alumina slurry containing methylolurea and urea undergoes gelation by acid-catalyzed condensation polymerization; gelation is immediate in the presence of relatively concentrated acid solutions; a filter paper tube filled with HNO₃ solution was dipped in the slurry at varying time intervals; the tube was formed by gelation of the slurry on the surface of the paper tube. By heating, the filter and binder are burned off and the alumina tube is sintered; wall thickness 0.7–2 mm with 40% interconnected open porosity was obtained with an average pore size of 300 nm.

2.2.4. Tape casting

Porous thin plates have been obtained by adding pyrolyzable pore-forming agents to a tape-casting colloidal suspension. The tape casting process involves the preparation of the suspension of ceramic powder and pore-forming agents in an organic solvent (or water) with further addition of a binder and a plasticizer. The de-aired suspension is then cast on a tape; a dried thickness of 0.15–0.7 mm can be obtained. The samples punched from the tape can be laminated together to produce multilayer structures. Before final sintering, the organic compounds are removed through controlled heating in air. Starch, graphite and polyethylene with different average particle sizes were used as pore-forming agents⁴⁹ in an organic dispersant-based formulation. The green tape properties were optimized by systematically varying the total amount of organic additives in terms of weight or volume ratio. The sintering characteristics of the ZrO₂ based tapes are influenced by the amount, size shape and distribution of the pore-forming agents as well as the degree of open and closed porosity. By applying the concept of pore-forming particle percolation, and a conceptual model of the green tape microstructure, the influence of pore-forming agents and tape formulation on the pore morphology and pore volume was explained. Nickel-yttria-stabilized zirconia composites were tape cast from an aqueous slurry containing graphite and NiO as pore-forming agents⁵⁰ for the production of anode-supported fuel cells. Pores are formed by selectively leaching nickel (derived from the reduction of the oxide in H₂) with nitric acid; Ni is completely removed and the pore volume increase depends on the amount of NiO introduced; the structure remains intact until the removal of 50% of the mass by reduction and acid leaching. Fine-tuning of the pore structure can be achieved by changing the particle size of the starting oxides and pore formers (graphite, polyethylene, polymethyl methacrylate)⁵¹; as high as 80% pore volume with a wide pore size distribution, up to 100 μm, was achieved. Tape cast PZT samples were produced using a binder and plasticizer in the formulation as pore-forming agents,⁵² resulting in a uniform micro porosity, as a consequence of the homogeneous distribution of the organic additives in the liquid phase.

2.2.5. Solid freeform fabrication

Solid freeform fabrication (SFF) or rapid prototyping allows the fabrication of three-dimensional objects on a fixtureless platform directly from a computer aided design (CAD)¹⁶; ceramic prototypes or a small series of complex shapes can be produced without a mold. The process includes the virtual slicing of the three-dimensional CAD data of the ceramic component into thin sheets; the piece is then fabricated slice-by-slice by computer-controlled devices. Most techniques use polymeric binder systems to bond ceramic particles to form the green body, by immobilization of free-flowing powder, or by solidification of suspended particles. The green body is then subjected to burn out of the organics, followed by sintering. Three-dimensional printing develops parts by a layered printing process; in direct ink-jet printing droplets of ceramic ink are printed onto previous layers. Robocasting is based on the casting of highly loaded slurries through a fixed nozzle onto a porous or heated plate, which is moved tri-dimensionally. Some techniques are based on chemical gels like stereo-lithography that involves polymerization of liquid monomers through exposure to ultraviolet laser radiation or solidification of a liquid photopolymer by a computer aided laser beam. Fused deposition of ceramics is based on the deposition of extruded filaments of the powder mixed with binder feedstock that solidify on cooling from the melt. Fused deposition has been utilized to develop three-dimensional honeycomb ceramic structures with controlled porosity.⁵³ The technique is used to fabricate polymeric moulds, which are then infiltrated with ceramic slurry, dried and subjected to binder removal and sintering to form the final structure.

2.2.6. Sol-gel techniques

Sol-gel techniques are adopted to produce microscale thin membranes with nanoscale pore diameter and narrow pore size distribution.⁵⁴ Microporous coatings and large specific area powders can be produced. There are two types of sol-gel processing, colloidal suspensions and polymeric gel methods, both starting from metal salts or alkoxides as precursors. The precursors are hydrolyzed while simultaneously a condensation or polymerization reaction occurs. After processing, the gel is dried in controlled conditions and sintered. The fabrication of crack-free ceramic compacts is difficult because very large shrinkage occurs during densification. The technique is well developed for the production of porous silica,⁵⁵ thin ceramic film and fibers and is applied to the fabrication of ferroelectric aerogels⁵⁶. PZT gel has been prepared by starting from Zr- and Ti-propoxides and lead acetate trihydrate; monolithic algogels are prepared that, after supercritical drying and heat treatment up to 700 °C, are converted in crystalline aerogels with 70% porosity. Porous structures can be designed by mimicking natural materials, among which native lignocellulosic structures draw a considerable interest; the highly anisotropy cellular structure of wood is employed as a hierarchical template to generate cellular ceramics. As a wide variety of pore structures is exhibited by wood either monomodal or multimodal ceramic replicas can be obtained. The process of conversion can start either from native plant tissue or from preprocessed structures and oxide or non-oxide materials can be obtained¹⁵; the native tissue can

be infiltrated with organometallic or metalorganic precursors and heat treated to oxidize the free carbon phase; preliminary high temperature pyrolytic decomposition into a porous carbon replica followed by reaction with gas to form carbide phases⁵⁷ or infiltration with non reacting sols or salts can finally lead to oxide materials.

3. Porous electroceramics

In several applications of electroceramics, different degrees of porosity are required⁵⁸; the properties of PTC thermistors, humidity sensors, magnetic media are strongly influenced by tailoring pore volume and size distribution. Humidity sensitivity improves one order of magnitude by introducing 30 vol% open porosity, 1.2 vol% porosity improves the resistivity ratio by 20 times in PTC thermistors, etc. The physical properties of the materials depend on porosity, with interrelated importance of percolation effects, pore characteristics and the mixture of types of porosity.¹⁸ General trends are found between mechanical properties or thermal and electrical conductivity by plotting the absolute property versus the volume fraction porosity. A nearly linear region is followed by a region where the property decreases with increasing porosity, and finally the property decreases rapidly to zero at a specific volume fraction porosity, P_c , which is the percolation limit for the solid phase defining the particular porosity. The elastic modulus of ceramic materials strongly depends on porosity⁵⁹ and theoretical models proposed to correlate ultrasound velocity and pore structure often do not take in consideration the influence of pore shape, or even pore size distribution; the predictive capability of such models need further improvement.⁶⁰

Porosity affects the electrical fatigue occurring under high a.c. field; the rate of fatigue increases by orders of magnitude as pore volume increases from 2 to 8%.⁶¹ A study of the effect of porosity on the depoling behaviour of a PZT 95/5 composition⁶² with porosity 2–18% evidenced (a) a monotonic decrease of

the bulk modulus with increasing porosity, and (b) the hydrostatic pressure-induced ferroelectric to antiferroelectric phase transformation is more diffuse and occurs at lower hydrostatic pressure with increasing porosity.

The above processing techniques have been only partially applied to the development of electroceramics, and their potential has not been fully explored yet.

3.1. Porous piezoelectric materials

The very high values of certain piezoelectric and elastic coefficients with respect to dense materials make porous piezoelectric ceramics good candidates for piezoelectric ultrasonic transducers. In fact, in the vicinity of the percolation threshold, porous ceramics behave like self-controlling percolating systems, with physical properties scaling with power laws. Therefore, some piezoelectric coefficients could be increased significantly in highly porous systems.

In a previous work, it was found⁶³ that the dielectric permittivity of porous materials obeys the same power law as the conductivity of a percolation resistor network, and that the percolation threshold occurs at a critical volume fraction of approximately 0.17. Nevertheless, in many useful systems, it is necessary to make a compromise between increasing selected properties and maintaining good mechanical strength; therefore, it may be necessary to choose a somewhat lower porosity regime. It was also noted that far from percolation, when properties are plotted as a function of porosity, there is dispersion in the properties of the ceramics, which should originate from microstructural differences.⁵² Different processing routes (Fig. 1) were followed to improve the figure of merit of material for underwater acoustics applications, as well as the reproducibility of the process. Selected results are presented in Table 1. A wide range of pore volume and pore size and distribution was studied, from a few percent in partially sintered die pressed perovskitic powders to more than 50% when large amounts of PFA were

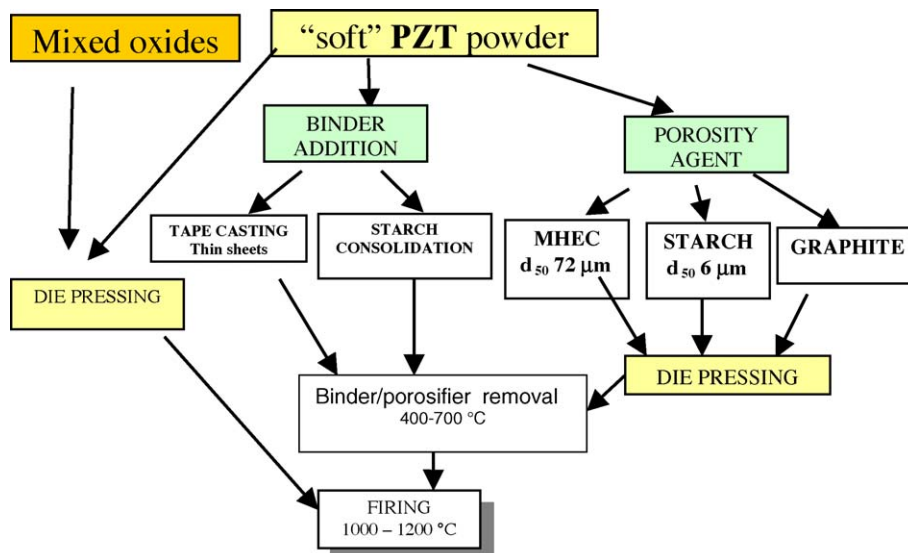


Fig. 1. Processing routes followed to produce a wide range of pore volumes, and pore size distributions.

Table 1

Processing parameters, total pore volume and selected properties of porous PZT ceramics (composition $\text{Pb}_{0.988}[(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.976}\text{Nb}_{0.024}]\text{O}_3$)

Method	Pore former	PZT/binder	$T_{\text{ sint }} (^{\circ}\text{C})$	Pore volume (%)	$\varepsilon_{33}/\varepsilon_0$	FOM $10^{-15} \text{ m}^2/\text{N}$	Acoustic impedance ($10^6 \text{ kg}/\text{m}^2 \text{ s}$)	Reproducibility
Die pressing	–		1000	36	500	112	13	Good
Tape casting	Binder	50/50	1100	44	190	320	7.4	Good
Starch consolidation	Starch	63/37	1160	45	864	1800	8.1	Good
Pore former + die pressing	MHEC	60/40	1100	52	62	500	4.7	Poor
Pore former + die pressing	Starch	50/50	1180	32	478	1264		Poor
Dense PZT	–		1200	0.9	1551	11	21.6	Very good

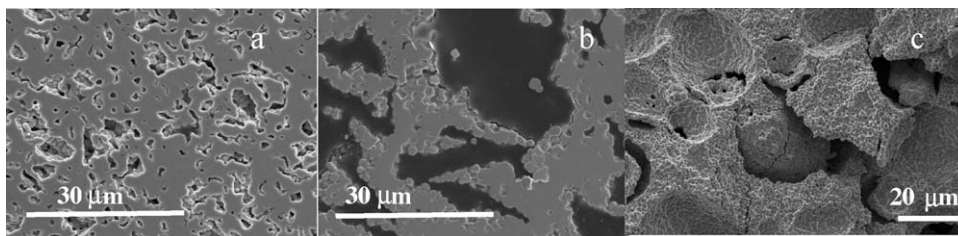
MHEC: methyl-hydroxyethyl-cellulose; FOM: factor of merit ($d_h \times g_h$).

Fig. 2. Different pore morphology for different pore-forming routes: (a) direct synthesis, (b) graphite addition and (c) starch consolidation.

added. Pore structure is more homogeneous in die pressed or tape cast samples, while pore-forming agents leave large pores connected by small windows with cracks in the pore walls. The wet process, based on the careful dispersion of the powder in water or organic solvents, is more reproducible. Samples produced by either the dry or wet technique show high figure of merit. The acoustic impedance depends linearly on the total pore volume, regardless the shaping technique, while it is more difficult to correlate electromechanical parameters with pore size distribution and shape⁶⁴ (Fig. 2). The dispersion of physical properties in porous samples could be attributed to differences introduced by the preparation methods. A theoretical approach to predict the electromechanical properties of porous piezoelectric ceramics⁶⁵ achieved acceptable agreement with experimental data in a rather narrow range of pore volumes (0–20 vol%).

Recently, a material with graded porosity content was used to produce a beam-shaped component²⁷; the porosity gradient was formed in situ by sintering a series of layers of PZT powder having stepwise variation in the stearic acid content. Anisotropic porosity was introduced by adding graphite as pore-forming agent⁶⁶; this resulted in strong decoupling of properties in the planar and transverse direction, reflecting the dominating orientation of porosity perpendicular to the pressing direction. The piezoelectric properties in the thickness direction (d_{33} , g_{33} and k_t) decreased less than the properties in the planar direction (d_{31} , g_{31}).

4. Conclusion

Recent literature on the processing of porous ceramics has been reviewed, concentrating on the techniques that produce tri-dimensionally, interconnected structures. Novel approaches to design pore morphology through the control of pore size dis-

tribution and shape are highlighted. The colloidal approach is widely applied; it contributes to the improvement in the reproducibility of the process and the ceramic products.

Acknowledgements

The POLENER Network and the COST Action 525 are gratefully acknowledged.

References

- Shepard, L. M., Corrosion resistant ceramics for severe environments. *Am. Ceram. Soc. Bull.*, 1991, **7**, 1146–1158.
- Beltsios, K. G., Steriotis, T. A., Stefanopoulos, K. L. and Kanellopoulos, N. K., *Handbook of Porous Solids. Membrane Technology, Vol 4*, ed. F. Schuth, K. S. W. Sing and J. Weitkamp. Wiley-VCH, Weinheim, 2002, pp. 2281–2433.
- Vercouteren, S., Keizer, K., Vansant, E. F., Luyten, J. and Leysen, R., Porous ceramic membranes: preparation, transport properties and applications. *J. Porous Mater.*, 1998, **5**, 241–258.
- Frieß, W. and Warner, J., *Handbook of Porous Solids Biomedical Applications, Vol 5*, ed. F. Schuth, K. S. W. Sing and J. Weitkamp. Wiley-VCH, Weinheim, 2002, pp. 2923–2970.
- Suchnek, W. and Yoshimura, M., Processing and properties of hydroxyapatite-based materials for use as hard tissue replacement implants. *J. Mater. Res.*, 1998, **13**, 94–117.
- McLeary, E. E. and Jansen, J. C., Basic views on the preparation of porous ceramic membrane layers—A comparison between amorphous and crystalline layers, leading to a new method for the preparation of microporous continuous layers. *Topics Catal.*, 2004, **1–2**, 85–92.
- van de Water, L. G. A. and Maschmeyer, T., Mesoporous membranes—a brief overview of recent developments. *Topics Catal.*, 2004, **1–2**, 67–77.
- Hirschfeld, D. A., Li, T. K. and Liu, D. M., Processing of porous oxide ceramics. *Key Eng. Mater.*, 1996, **115**, 65–80.
- Saggio-Woyansky, J., Scott, C. E. and Minnear, W. P., Processing of porous ceramics. *Am. Ceram. Soc. Bull.*, 1992, **11**, 1674–1682.
- Guicciardi, S., Galassi, C., Landi, E., Tampieri, A., Satou, K. and Pezzotti, G., Rheological characteristics of slurry controlling the microstructure

- and the compressive strength behavior of biomimetic hydroxyapatite. *J. Mater. Res.*, 2001, **1**, 163–170.
11. Zhang, G.-J., Yang, J.-F. and Ohji, T., Fabrication of porous ceramics with unidirectionally aligned continuous pores. *J. Am. Ceram. Soc.*, 2001, **6**, 1395–1397.
 12. Araki, K. and Halloran, J. W., Porous ceramic bodies with interconnected pore channels by a novel freeze casting technique. *J. Am. Ceram. Soc.*, 2005, **5**, 1108–1114.
 13. Yang, J. F., Zhang, G. J., Kondo, N., Ohji, T. and Kanzaki, S., Synthesis of porous Si₃N₄ ceramics with rod-shaped pore structure. *J. Am. Ceram. Soc.*, 2005, **4**, 1030–1032.
 14. Darcovich, K. and Cloutier, C. R., Processing of functionally gradient ceramic membrane substrates for enhanced porosity. *J. Am. Ceram. Soc.*, 1999, **8**, 2073–2152.
 15. Greil, P., Biomorphous ceramics from lignocellulosics. *J. Eur. Ceram. Soc.*, 2001, **2**, 105–118.
 16. Sigmund, W. M., Bell, N. S. and Bergstrom, L., Novel powder-processing methods for advanced ceramics. *J. Am. Ceram. Soc.*, 2000, **7**, 1557–1574.
 17. Sun, H. T., Cantalini, C. and Pelino, M., Porosification effect on electro-ceramic properties. *Key Eng. Mater.*, 1996, **115**, 167–180.
 18. Rice, R. W., The porosity dependence of physical properties of materials: a summary review. *Key Eng. Mater.*, 1996, **115**, 1–20.
 19. Young, J. W., Optimization of acoustic receiver noise performance. *J. Acoust. Soc. Am.*, 1977, **61**, 1471.
 20. Newnham, R. E., Skinner, D. P. and Cross, L. E., Connectivity and piezoelectric–pyroelectric composites. *Mater. Res. Bull.*, 1978, **13**, 525–536.
 21. Marselli, S., Pavia, V., Galassi, C., Roncari, E., Craciun, F. and Guidarelli, G., Porous piezoelectric ceramic hydrophone. *J. Acoust. Soc. Am.*, 1999, **2**, 733–738.
 22. Deng, Z.-Y., Yang, J.-F., Beppu, Y., Ando, M. and Ohji, T., Effect of agglomeration on mechanical properties of porous zirconia fabricated by partial sintering. *J. Am. Ceram. Soc.*, 2002, **8**, 1961–1965.
 23. Roncari, E., Galassi, C., Craciun, F., Capiiani, C. and Piancastelli, A., A microstructural study of porous piezoelectric ceramics obtained by different methods. *J. Eur. Ceram. Soc.*, 2001, **21**, 409–417.
 24. Rittenmyer, K., Shrout, T., Schulze, W. A. and newnham, R. E., Piezoelectric 3–3 composites. *Ferroelectrics*, 1982, **41**, 189–195.
 25. Kim, J.-G., Sim, J.-H. and Cho, W.-S., Preparation of porous (Ba, Sr)TiO₃ by adding corn-starch. *J. Phys. Chem. Solids*, 2002, **11**, 2079–2084.
 26. Roncari, E., Galassi, C., Craciun, F., Guidarelli, G., Marselli, S. and Pavia, V., Ferroelectric ceramics with included porosity for hydrophone applications. In *Proceedings of the Eleventh IEEE International Symposium on Applications of ferroelectrics*, ed. E. Colla, D. Damjanovic and N. Setter, 1999, pp. 373–376.
 27. Li, J.-F., Takagi, K., Ono, M., Pan, W., Watanabe, R., Almajid, A. *et al.*, Fabrication and evaluation of porous piezoelectric ceramics and porosity-graded piezoelectric actuators. *J. Am. Ceram. Soc.*, 2003, **7**, 1094–1098.
 28. Shaw, H. M. and Edirisinghe, M. J., Porosity development during removal of organic vehicle from ceramic injection mouldings. *J. Eur. Ceram. Soc.*, 1994, **13**, 135–142.
 29. Deng, Z.-Y., Fukasawa, T., Ando, M., Zhang, G.-J. and Ohji, T., High-surface-area alumina ceramics fabricated by the decomposition of Al(OH)₃. *J. Am. Ceram. Soc.*, 2001, **3**, 485–491.
 30. Peng, H. X., Fan, Z. J., Evans, R. G. and Busfield, J. J. C., Microstructure of ceramic foams. *J. Eur. Ceram. Soc.*, 2000, **7**, 807–813.
 31. Ebaretonbofa, E. and Evans, J. R. G., High porosity hydroxyapatite scaffolds for bone substitute. *J. Porous Mater.*, 2002, **9**, 257–263.
 32. Li, S. H., de Wijn, J. R., Layrolle, P. and de Groot, K., Novel method to manufacture porous hydroxyapatite by dual-phase mixing. *J. Am. Ceram. Soc.*, 2003, **1**, 65–72.
 33. Lange, F. F. and Miller, K. T., Open cell low density ceramics fabricated from reticulated polymer substrates. *Adv. Ceram. Mater.*, 1987, **4**, 827–831.
 34. Roncari, E., Galassi, C. and Bassarello, C., Mullite suspensions for reticulate ceramic preparation. *J. Am. Ceram. Soc.*, 2000, **12**, 2993–2998.
 35. Galassi, C., Landi, E., Tampieri, A. and Celotti, G., Rheological characterization of hydroxyapatite dispersions for sponge impregnation. In *Ceramic Transactions, Ceramic Processing Science VI, Vol 112*, ed. S. Hirano, G. L. Messing and N. Claussen. *J. Am. Ceram. Soc.*, 2001, pp. 215–220.
 36. Zhu, X., Jiang, D., Tan, S. and Zhang, Z., Improvement in the strut thickness of reticulated porous ceramics. *J. Am. Ceram. Soc.*, 2001, **7**, 1654–1656.
 37. Sheng, H. Y., Bao, L. J., Chen, L. J. and Jun, Y., Fabrication of bimodal porous alumina ceramics. *Mater. Res. Bull.*, 2003, **2**, 373–379.
 38. Park, J. K., Lee, J. S. and Lee, S. I., Preparation of porous cordierite using gel casting method and its feasibility as a filter. *J. Porous Mater.*, 2002, **9**, 203–210.
 39. Lyckfeldt, O. and Ferreira, J. M., Processing of porous ceramics by “starch consolidation”. *J. Eur. Ceram. Soc.*, 1998, **18**, 131–140.
 40. Olhero, S. M., Tari, G., Coimbra, M. A. *et al.*, Synergy of polysaccharide mixtures in gel casting of alumina. *J. Eur. Ceram. Soc.*, 2000, **4**, 423–429.
 41. Rodriguez-Lorenzo, L. M., Vallet-Regi, M. and Ferreira, J. M. F., Fabrication of porous hydroxyapatite bodies by a new direct consolidation method: starch consolidation. *J. Biomed. Mater. Res.*, 2002, **2**, 232–240.
 42. Galassi, C., Roncari, E., Capiiani, C., Fabbri, G., Piancastelli, A., Peselli, M. *et al.*, Processing of porous PZT materials for underwater acoustics. *Ferroelectrics*, 2002, **268**, 47–52.
 43. Ortega, F. S., Valenzuela, F. A. O., Scaracchio, C. H. and Pandolfelli, V. C., Alternative gelling agents for the gel casting of ceramic foams. *J. Eur. Ceram. Soc.*, 2003, **23**, 75–80.
 44. Studart, A. R., Pandolfelli, V. C., Tervoort, E. and Gauckler, L. J., Gelling of alumina suspensions using alginate salt and hydroxyaluminum diacetate. *J. Am. Ceram. Soc.*, 2000, **11**, 2711–2718.
 45. Fukasawa, T., Ando, M., Ohji, T. and Kanzaki, S., Synthesis of porous ceramics with complex pore structure by freeze-dry processing. *J. Am. Ceram. Soc.*, 2001, **1**, 230–232.
 46. Dittrich, R., Tomandl, G. and Mangler, M., Preparation of Al₂O₃, TiO₂, and hydroxyapatite ceramics with pores similar to a honeycomb structure. *Adv. Eng. Mater.*, 2002, **7**, 487–490.
 47. Nakahira, A., Nishimura, F., Kato, S., Iwata, M. and Takeda, S., Green fabrication of porous ceramics using an aqueous electrophoretic deposition process. *J. Am. Ceram. Soc.*, 2003, **7**, 1230–1232.
 48. Prabhakaran, K. R., Babu, N., Kumar, S. R. and Warriar, K. G., Freeform gel casting of porous tubular alumina substrate. *J. Am. Ceram. Soc.*, 2002, **12**, 3126–3128.
 49. Corbin, S. F., Lee, J. and Qiao, X., Influence of green formulation and pyrolyzable particulates on the porous microstructure and sintering characteristics of tape cast ceramics. *J. Am. Ceram. Soc.*, 2001, **1**, 41–47.
 50. Kim, H., da Rosa, C., Boaro, M., Vohs, J. M. and Gorte, R. J., Fabrication of highly porous yttria-stabilized zirconia by acid leaching nickel from a nickel-yttria-stabilized zirconia cermet. *J. Am. Ceram. Soc.*, 2002, **6**, 1473–1476.
 51. Boaro, M., Vohs, J. M. and Gorte, R. J., Synthesis of highly porous yttria-stabilized zirconia by tape-casting methods. *J. Am. Ceram. Soc.*, 2003, **3**, 395–400.
 52. Craciun, F., Galassi, C., Roncari, E., Filippi, A. and Guidarelli, G., Electro-elastic properties of porous piezoelectric ceramics obtained by tape casting. *Ferroelectrics*, 1998, **205**, 49–67.
 53. Bose, S., Sugira, S. and Bandyopadhyay, A., Processing of controlled porosity ceramic structures via fused deposition. *Scripta Materialia*, 1999, **9**, 1009–1014.
 54. Burggraaf, A. J. and Keizer, K., Synthesis of inorganic membranes. In *Inorganic Membranes: Synthesis, Characteristics and Applications*, ed. R. R. Bhavde. Van Nostrand Reinhold, New York, 1991.
 55. Klein, L.C., Woodman, R.H., Porous silica by the sol–gel process. *Key Eng. Mater. Porous Ceramic Materials, Vol 115*, ed. D.-M. Liu, 1996, pp. 109–124.
 56. Lobmann, P., Gaubitt, W., Geis, S. and Fricke, J., Development of ferroelectric aerogels. *J. Sol–Gel Sci. Technol.*, 1999, **16**, 173–182.
 57. Sun, B., Fan, T. and hang, D., Porous TiC ceramics derived from wood template. *J. Porous Mater.*, 2002, **9**, 275–277.
 58. Sun, H. T., Cantalini, C. and Pelino, M., Porosification effect on electro-ceramic properties. *Key Eng. Mater.*, 1996, **115**, 167–180.

59. Wanner, A., Elastic modulus measurements of extremely porous ceramic materials by ultrasonic phase spectroscopy. *Mater. Sci. Eng.*, 1998, **A248**, 35–43.
60. Aduda, B. O. and Boccaccini, A. R., Velocity of elastic waves in porous ceramic materials: influence of pore structure. *Br. Ceram. Trans.*, 2003, **3**, 103–108.
61. Jiang, Q. J. and Cross, L. E., Effects of porosity on electric fatigue behaviour in PLZT and PZT ferroelectric ceramics. *J. Mater. Sci.*, 1993, **28**, 4536–4543.
62. Tuttle, B. A., Yang, P., Gieske, J. H., Voigt, J. A., Scofield, T. W., Zeuch, D. H. *et al.*, Pressure-induced phase transformation of controlled-porosity $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ ceramics. *J. Am. Ceram. Soc.*, 2001, **6**, 1260–1264.
63. Craciun, F., Galassi, C. and Roncari, E., Experimental evidence for similar critical behaviour of elastic modulus and electrical conductivity in porous ceramic materials. *Europhys. Lett.*, 1998, **1**, 55–60.
64. Galassi, C., Snijkers, F., Cooymans, J., Piazza, D., Capiani, C. and Luyten J., Influence of the pore size and morphology on the piezoelectric properties of PZT material. In *Proceedings of the Conference PCM 2005* ISBN 90-5857-006-1 Legal Deposit no. D/2005/8642/1 Brugge, 20–21 October 2005.
65. Dunn, M. L. and Taya, M., Electrochemical properties of porous piezoelectric ceramics. *J. Am. Ceram. Soc.*, 1993, **7**, 1697–1706.
66. Piazza, D., Capiani, C. and Galassi, C., Piezoceramic material with anisotropic graded porosity. *J. Eur. Ceram. Soc.*, 2005, **25**, 3075–3078.