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Characterisation of High Porous PZT Piezoelectric Ceramics by Different Techniques

B. Praveen Kumar*, Bhupender Rawal, and K.M. Rajan

DRDO-Armament Research and Development Establishment, Pune - 411 021, India
**E-mail: praveenkumar@arde.drdo.in*

ABSTRACT

Ultimate properties of a porous ceramic is highly process dependent. In this study, prevalent porous ceramics fabrication methods (Freeze casting, Foam reticulation and Burnable Plastic Sphere (BURPS) method) have been compared by fabricating the porous lead zirconate titanate (PZT) based piezoelectric ceramics. Field emission scanning electron microscopy (FESEM) studies were performed to analyse the pore size and distribution of the ceramics. Hydrostatic co-efficients increased tremendously on incorporation of porosity which led to Hydrostatic Figure of Merit of 7480 in Foam reticulation samples (porosity 86 per cent). The three dimensionally interconnected networks in the freeze casted samples led to lowest acoustic impedance (6 MRayls) despite not having the lowest density.

Keywords: BURPS; Freeze casting; Foam reticulation; Porous; Piezoceramics

1. INTRODUCTION

Recently, worldwide the trend in materials research are shifting from high dense and structurally perfect to low dense and porous materials. Porous ceramics and composites have been widely studied by Newnham[1], *et al.* and these are getting technologically important because of low density, better sensitivity and impedance matching. Porous PZT ceramics are vital for medical and underwater imaging, hydrophones, non-destructive testing, energy harvesting and ferroelectric pulse power applications[2-4]. In spite of known fabrication routes and distinctive properties, the porous PZT ceramics have not been commercialised extensively because of its selective applications.

Porous PZT ceramics has been developed by various techniques like foam reticulation (FR), Burnable plastic spheres (BURPS), freeze casting (FC), gel-casting, rapid prototyping and replamine process[5-10]. Every technique has its own advantages and dis-advantages. In freeze casting[11], highly oriented microstructure can be obtained but it is mainly reliant on solvent and freezing direction. Whereas in foam reticulation method, higher porosity and improved pore connectivity are the merits, and weak active ceramic walls are demerits. The BURPS technique[12] is suitable and easy to accommodate for commercialisation, whereas the amount of porosity obtained will be low. Rapid prototyping is a recent process where accurate dimensionality can be controlled with improved structure but the process is costly. The electro-mechanical properties are mainly reliant on pore size, pore morphology, pore distribution, pore connectivity and processing method. Depending on the fabrication process, ceramics have either open or closed pores or a blend of both open and closed pores, and also interconnected or isolated pores. Hence the fabrication route should be chosen sensibly to obtain controlled porosity and dense ceramic walls without any larger cracks.

In porous PZT ceramics, the essential properties are porosity, hydrostatic charge and voltage coefficient, figure of merit, acoustic impedance and dielectric constant. These parameters determine the actuating capability, sensitivity and suitability of ceramics for required electronics applications. Variation in impedance matching of the piezo and water medium decides the reflection and transmission of acoustic energy at the boundary. The nearer the value of difference in impedance, lesser the acoustic energy reflected at the boundary. As we increase porosity, larger reduction in the transverse piezocoefficient ($-d_{31}$) relative to the longitudinal piezocoefficient (d_{33}) and reduction in dielectric constant will be obtained. Hence hydrostatic coefficients increases and subsequently more charges are produced per unit hydrostatic force. The porous ceramics fabricated by different routes are characterised in terms of density, dielectric constant, porosity, and hydrostatic properties.

In this work, a brief summary and comparison of different processing methods as well as porous microstructures, and their correlation with dielectric and piezoelectric properties are presented. This work will be supportive for beginners to choose the appropriate fabrication technique for required structural and electrical properties.

2. EXPERIMENTAL

PZT5A developed indigenously (d_{33}= 505 pC/N, ε_r = 2357) was used as an active phase[13]. In the Foam reticulation (FR) method polystyrene foam is dipped in the slurry having 50 per cent solid loading. The slurry was prepared by milling calcined PZT5A powder in water with 3 per cent Poly vinyl

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alcohol and 0.5 per cent dispersant for 24 h. The process has been shown in Fig. 1(a). Excess of the slurry is removed by compressed air and samples are left in open for natural drying. Subsequently, it is slowly heated at 600 °C for 10 h to burnout the foam and subsequently sintered in lead rich environment under inverted alumina crucible at 1250 °C for 30 min. In the Freeze drying method chemicals used were: Camphene (Make: Sigma Aldrich) as the pore generating medium, Triton (Make-RFCL) as dispersant, Polyvinyl alcohol as binder and grease as de-moulding agent. Slurry was prepared by mixing Camphene and calcined PZT5A powder in 50/50 ratio by weight and ball milled for 3 h at 60 °C with 3 per cent TRITON and 1 per cent Poly Vinyl Alcohol (PVA) by weight. Triton prevented the agglomeration of powder while Poly Vinyl Alcohol role is to provide the strength to green -porous PZT discs. Fig. 1(b) shows the schematic of freeze casting process. Pre-cooled Plastic moulds are filled with the slurry. Before pouring, inner surfaces of these moulds were coated with de-moulding agent so as to facilitate taking out of solidified green samples. Slurry is left at room temperature for solidification and then frozen at -5 °C for 1h for strengthening. Green discs are taken out of moulds and kept over the alumina discs laid with PZT separating powder and left in open condition for 60 h to let entire camphene sublime and, thus, giving the green disc. Under the BURPS method, as shown in Fig. 1(c), Polymethyl Methacrylate (PMMA), used as pore former, was mixed with PZT5A in 50/50 ratio by weight and processed as discussed in our previous study[3]. Similar to FR samples, freeze casted (FC) and BURPS green discs were also sintered at 1250 °C for 30 min. Porous sintered discs are lapped, silver electroded by screen printing on both the sides and cured at 650 °C for 10 min. Densities of the sintered discs were evaluated by measuring the dimensions and weight. Phase composition was determined by X-Ray Diffraction studies (BRUKER D8 Advance). Piezo coefficients were analysed using piezo d_{33} meter (Piezotest PM300). The porous samples were poled applying DC field of 3 kV/mm at 100 °C in silicon oil bath. LCR meter (Novocontrol, Gmbh) was employed to ascertain dielectric properties at 1 kHz. SEM analysis was performed using Field Emission Scanning Electron Microscope (Carl Zeiss Sigma).

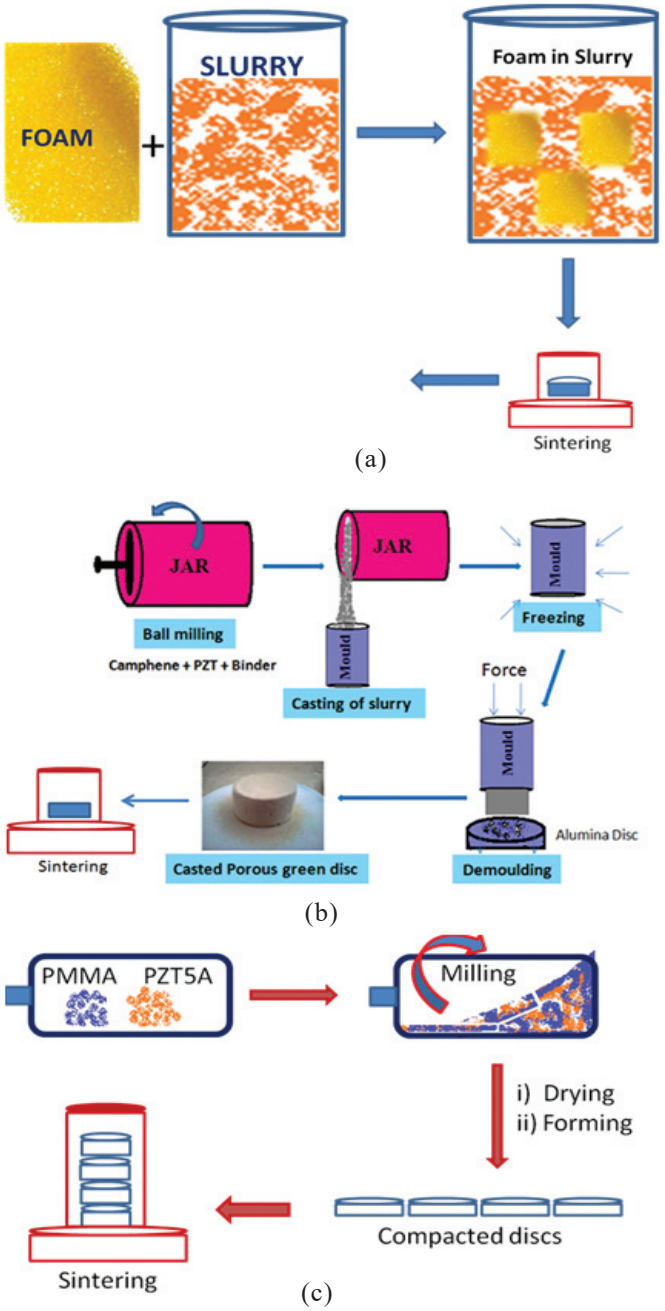

Figure 1. Schematic of different methods (a) Foam reticulation, (b) Freeze casting, and (c) BURPS process.

3. RESULTS AND DISCUSSION

The X-ray diffractograph of Bulk and porous samples are as shown in Fig. 2 which demonstrates pure perovskite phase without any presence of secondary phases. Crystal structure of the sintered ceramic was found to be a morphotropic phase boundary having tetragonal and rhombohedral phase, matching the JCPDS file no.PDF-01-070-4060 and PDF 01-070-6379, respectively, for tetragonal and rhombohedral structures and, thus, has been labeled accordingly. The particle size of PZT powder used for processing is measured by laser diffraction method and found to be around 1µm.

Density of the sintered porous components was calculated using the formula:

$$P = \left(\frac{\rho_o - \rho}{\rho_o}\right) \times 100 \quad (1)$$

where P is the % porosity, ρ_o is the theoretical density of PZT (7.9 g/cm^3) and ρ is the density of porous PZT.

The field emission scanning electron micrograph of the bulk sample and corresponding EDX result are studied as Fig. 3(a) and 3(b), respectively. The FESEM reveals the bimodal microstructure having grains of the size ranging between 0.9 µm to 2 µm. The microstructure reveals dense morphology having cuboidal grains. The energy dispersive x-ray analysis of PZT sample is shown as Table 1.

The Scanning electron micrographs of fractured surface of porous discs sintered at 1250 °C for 30 min are as shown in Fig. 4(a) – 4(f). In Foam reticulated and sintered samples, disordered pores and thin shell were observed. The pores are bigger (~ 400 µm), deep and propagate in the form of cracks on

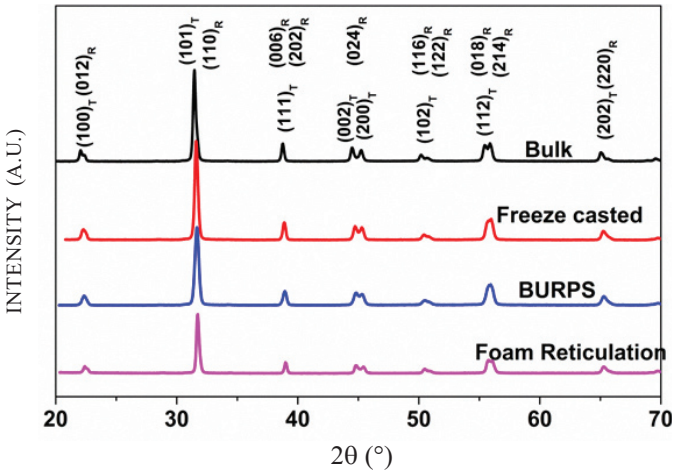

Figure 2. X-ray diffraction profile of bulk and porous samples.

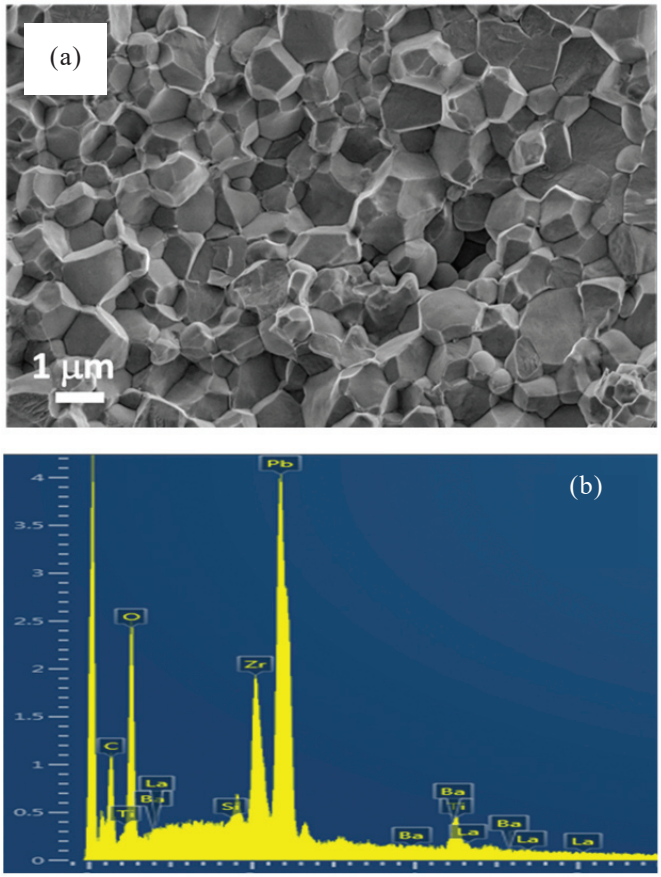

Figure 3. (a) FESEM and (b) EDAX of bulk sample.

Table 1. Chemical composition as revealed in EDAX analysis

Element	Wt. %
Pb	52.9
O	14.5
Zr	13.1
Ba	4.2
La	2.7
Ti	3.7

the surface of ceramic. The removal of pore forming agent, and subsequent reticulation leads to larger cracks. The sintered FC sample exhibited higher porosity and entire matrix is zigzag where PZT and pores both forms a continuous structure with 3-3 inter-connectivity. The pores' average size is around 20 µm with some bigger pores of ~ 50 µm length. The pores-ceramic shell interface is well-built and sturdy, unlike the FR samples where the interface looks to be fragile. However, despite such high porosity, the samples were sturdy and easy to handle for further processing. The BURPS sample displayed the presence of well-shaped concave cavities of ~50-90 µm size, formed due to burnout of PMMA spheres. Among the concave cavities (pores) irregular pores are also interspersed, similar to FR sample, but without any larger cracks.

Figure 5 illustrates the variation of dielectric constant, acoustic impedance and porosity of samples prepared by different processing routes. A tremendous diminish in dielectric constant was observed in all the cases which can be attributed to reduce in PZT content, as the density decreases. The FR samples displayed highest porosity of more than 86 per cent and as a result of such high porosity the samples were delicate in contrast to BURPS and FC which was evident in the microstructures. Analysis of the data reveals direct relationship between density and acoustic impedance. As the density decreased the acoustic impedance also decreased. However, there is a marginal increase in acoustic impedance of FR sample, in comparison to FC sample, despite decrease in density. This can be attributed to the more organised and 3-D network structure of active phase in the FC sample, as observed in microstructure.

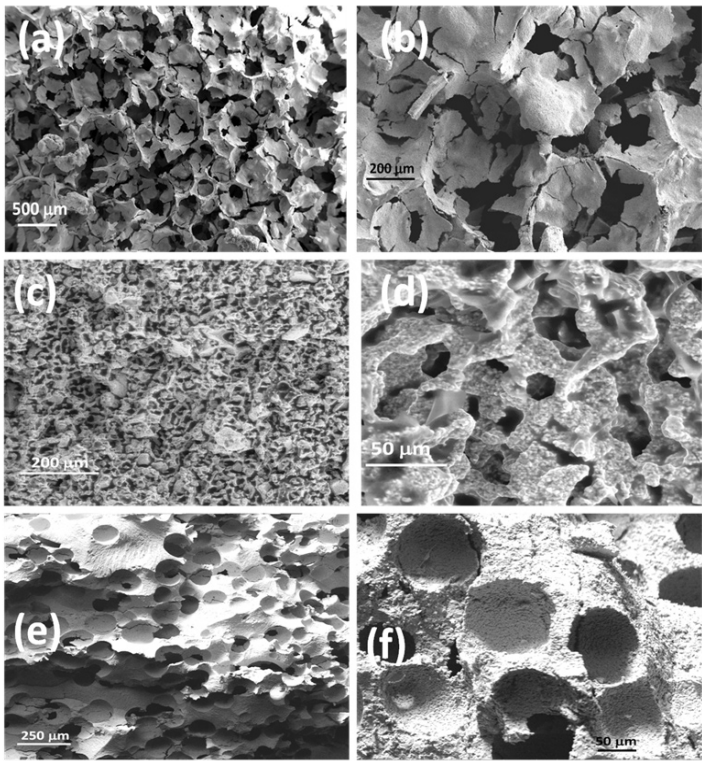

Figure 4. SEM of (a) and (b) Foam reticulated porous PZT samples, (c) and (d) Freeze casted PZT samples and (e) and (f) Burps porous PZT samples.

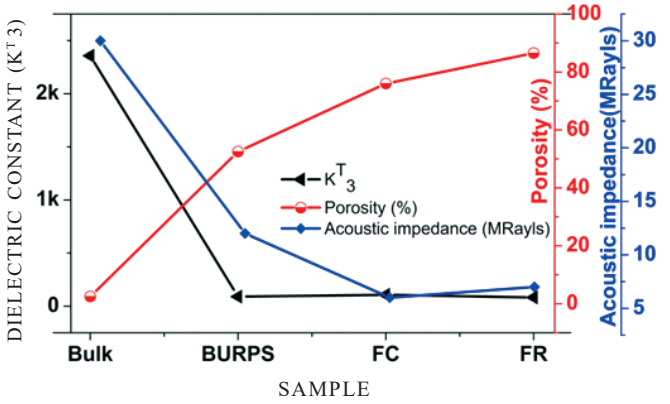

Figure 5. Dielectric constant, porosity and acoustic impedance for Bulk, FR, FC and BURPs Porous PZT samples.

Figure 6 displays the hydrostatic piezo co-efficients and hydrostatic figure of merit (FOM) of dense and porous PZT discs. Theoretically, the hydrostatic charge co-efficient, d_h (pC/N) is related to the piezo-charge co-efficient (d_{33} and d_{31}) as follows:

$$d_h = d_{33} + 2d_{31} \quad (2)$$

As the proportionate decrease of d_{31} is very high, as compared to d_{33}, on introduction of porosity in the samples, the d_h value increases in porous samples, as shown in the previous studies[3,7]. Because of high porosity the hydrostatic voltage coefficient, g_h (Vm/N) also shows remarkable increase which can be linked directly to decrease in dielectric constant since d_h, ε, ε_o and g_h are related by the equation

$$g_h = \frac{d_h}{\varepsilon_o \varepsilon_r} \quad (3)$$

where ε_o and ε_r are the permittivity of free space and dielectric constant of material, respectively.

The d_h and g_h of dense disc were 16 pC/N and 5.56×10^{-3} Vm/N, respectively, while for FR sample these were ~74 pC/N and 101×10^{-3} Vm/N in the same order, which shows an increase of 75 times in Hydrostatic Figure of Merit, FOM (Pa^{-1}) in porous samples. FOM is related to d_h and g_h by equation:

$$FOM = d_h \times g_h \quad (4)$$

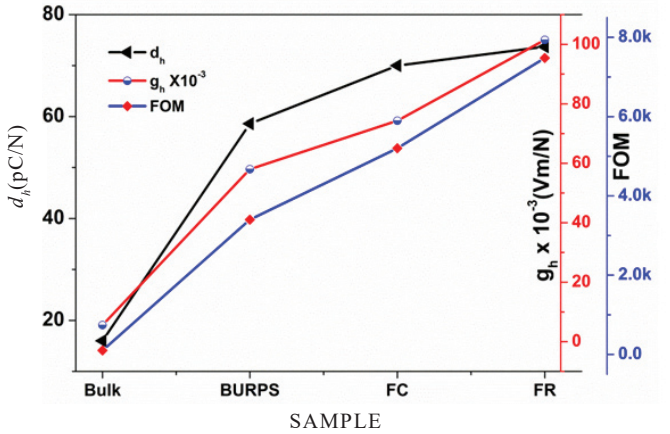

Figure 6. Hydrostatic charge and voltage coefficents and Figure of Merit for Bulk, FR, FC and BURPs Porous PZT samples.

Due to such a high value of g_h, which is a measure of sensitivity of transducer, and low acoustic impedance, porous PZT is considered as a suitable candidate for applications in underwater receiving transducer applications.

4. CONCLUSIONS

The PZT 5A porous discs having very low density (1.02 - 2.0 g/cc) were fabricated successfully using different methods viz. BURPS, freeze casting and Foam reticulation method. The arrangement of pores, pore size and pore connectivity has a great effect on acoustic impedance and hydrostatic properties of PZT. Despite high level of porosity the samples were sturdy enough for easy handling. Porous samples are potential candidate for hydrophone applications because of high d_h, g_h values and hence high FOM. The acoustic impedance as low as 6 MRayls was achieved which is very close to that of water.

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CONTRIBUTORS

Dr Praveen Kumar B. recieved his BE from NIT Trichy and PhD from IIT Madras, in the field of sensor materials and devices. Currently working as Scientist in Centre for Functional Materials, Young Scientist Centre, DRDO-Armament Research and Development Establishment, Pune. His current research interests are processing and characterisation of advance functional materials, porous ceramics, pulse power generators and sensor devices. He has published 24 research paper in journals and 15 paper in conference proceedings.
In the present paper, he has carried out BURPS and foam reticulation process studies and its characterisation.

Shri Bhupender Rawal did his MSc from H.N.B Garhwal University, Srinagar, Uttarakhand, in 2004. He is currently working as Scientist 'D' at DRDO-Armament Research and Development Establishment, Pune. His area of interest is synthesis and characterisation of Piezomaterials, lead free piezoceramics and alternate forming techniques.
In the present paper, he has carried out freeze casting studies and its characterisation.

Dr K.M. Rajan having received his BTech from NIT Calicut and MTech from IIT Bombay. He has obtained his PhD in the area of flow forming from IIT Bombay. Currently working as Distinguished Scientist and Director, DRDO-Armament Research and Development Establishment, Pune. He has rich experience in the design and development of various armament systems, particularly artillery rockets. He has international recognition for his work in the area of flow forming of rocket motors and is a well known rocket propulsion expert, with publication of more than, 70 research paper in journals and conferences.
In the present work, he has guided the team and reviewed the manuscript.