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Effect of porosity on dielectric properties and microstructure of porous PZT ceramics

B. Praveen Kumar, H.H. Kumar, D.K. Kharat *

PZT Centre, Armament Research & Development Establishment, Pune 411021, India

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Abstract

Porous piezoelectric materials are of great interest because of their high hydrostatic figure of merit and low sound velocity, which results in to low acoustic impedance and efficient coupling with medium. Porous lead zirconate titanate (PZT) ceramics with varying porosity was developed using polymethyl methacrylate by burnable plastic spheres (BURPS) process. The porous PZT ceramics were characterized for dielectric constant (ε), dielectric loss factor ($\tan\delta$), hydrostatic charge (d_h) and voltage (g_h) coefficients and microstructure. The effect of the porous microstructure on the dielectric constant and loss factor at frequencies of 10–10^5 Hz are discussed in this paper.

Keywords: Ceramics; PZT; Sensors; Ferroelectrics

1. Introduction

In the recent years, porous PZT ceramics are being used as a sensor material for medical, pyroelectric and underwater applications [1,2]. These materials can be formed in 0–3, 1–3 and 3–3 connectivities in which, the first number represents the connectivity of the active PZT phase, and second is the connectivity of the passive polymer or air phase [3,4]. In 3–3 porous piezoceramics, both ceramic phase and porosity are interconnected in all the three directions. These materials offer advantages over dense PZT ceramics, particularly for low frequency hydrophone applications (10–100 kHz) [5].

The porous PZT ceramic materials can be developed using various processing techniques such as the lost wax replication of a coral skeleton, replamine foam and mixing of burnable plastic spheres (BURPS) processes, etc. [6]. Each process results in the formation of its own microstructure, properties and morphology with varied amount of porosities [7–9]. However, the BURPS process offers advantages such as the ability to control porosity and pore size along with ease to manufacture at larger scale [10].

In the present work, polymethyl methacrylate (PMMA) was used as a pore-forming agent for BURPS process. PMMA was mixed with PZT powder and allowed to burn out while sintering so as to leave pores in the materials. The porous PZT ceramics with varied amount of PMMA was investigated for structural and dielectric properties such as density, microstructures, dielectric constant and loss factor.

2. Experimental work

In this work, PZT-5A developed at our centre [11] was used as a base material. An appropriate quantity of this powder was weighed and mixed using a ball mill for 24 h using zirconia balls as a grinding media and water as a solvent. After milling, the mixture was calcined at 800 °C for 2 h. The calcined PZT powder was then mixed with 10, 20, 30, 40 and 50 vol% of PMMA for 1 h using agate pestal mortar. The specimens were designated as PZT/10PMMA, PZT/20PMMA, PZT/30PMMA, PZT/40PMMA and PZT/50PMMA, respectively. Approximately 7 wt% of poly vinyl alcohol, water and fish oil were added to the mixture as a binding agent. The powder was then uniaxially pressed at 150 MPa to produce 22 mm × 3.5 mm disk specimens. The specimens were subsequently fired at 500–600 °C for 10 h to remove PMMA. The porous specimens were then stacked in an alumina crucible and sintered at 1280 °C and soaked for 1 h. The densities of the sintered specimens were measured from its mass and dimensions. The sintered specimens were then poled by corona poling

* Corresponding author. Tel.: +91 20 25886361; fax: +91 20 25893102.
E-mail address: dkkharat@rediffmail.com (D.K. Kharat).

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technique [12]. Copper foils were applied on the specimen to measure the dielectric properties. To study the microstructure, scanning electron micrographs of the sintered specimens were recorded by using the scanning electron microscope, Quanta 200 (FEI, Netherlands). The dielectric constant (ε) and dielectric loss factor ($\tan\delta$) at 10–10^5 Hz frequencies were measured by using a dielectric impedance analyzer, Concept 50 ALPHA-ATB (Novocontrol, Germany). The hydrostatic charge (d_h) and voltage coefficients (g_h) were measured using dual range piezometer system, PM 35 (Take control, UK).

3. Results and discussion

In a transducer design, the density of a piezoelectric material plays important role to achieve efficient energy transfer for improved impedance matching. Fig. 1 shows the density of the specimens in relation to the amount of PMMA. This graph indicates that the density (ρ) of specimen decreases with increasing PMMA content which subsequently decreases the acoustic impedance (z) of the material since the acoustic impedance is a product of density and the sound velocity (c) in the material, i.e. $z=\rho c$. Similarly increase in porosity decreases the sound velocity in the material. Further as the density of material decreases, the porosity increases, which subsequently affects the dielectric properties and hydrostatic coefficients in line with Eq. (1):

$$\text{Porosity}\,(P) = \left(\frac{1-\rho}{\rho_o}\right) \times 100\,(\%) \qquad (1)$$

where ρ_o is the theoretical density of PZT (7.82 g/cm^3) and ρ is the density of porous PZT. In this case, PMMA develops the porosity in the material when specimens were heated at 500–600 °C. As the amount of PMMA increases, the porosity in the material also increases and subsequently reduces the density of the material.

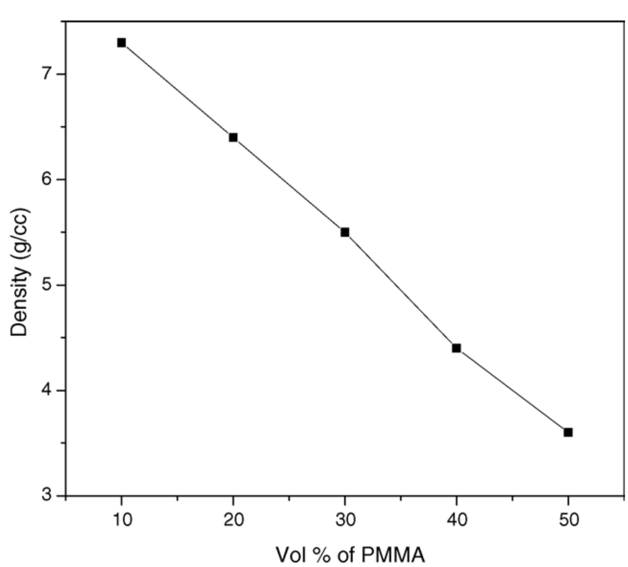

Fig. 1. Variation of density with PMMA.

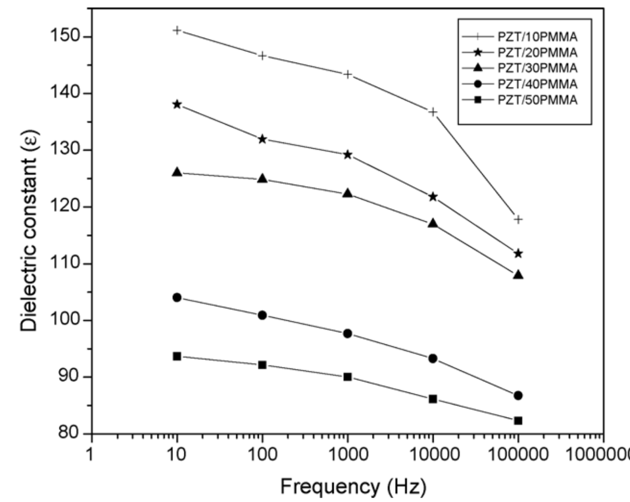

Fig. 2. Variation of dielectric constant with frequency.

Figs. 2 and 3 show the dielectric constants and dielectric losses of the porous PZT ceramics measured at different frequencies, respectively. As the frequency increases, the dielectric constant decreases where as dielectric losses increases marginally for all the specimens. This is mainly due to the presence of (i) lanthanum dopant in the base PZT material and (ii) porous defects created due to addition of PMMA in the base PZT material. Additionally, it is also predicted that dipole relaxation connected with impurities and domain wall motion of the ionic particles contributes to the frequency dependence vis-à-vis dielectric properties of the material [13,14]. The results in Figs. 2 and 3 reveal that for a particular frequency, the dielectric constant decreases and dielectric loss increases with increase in the amount of PMMA. This is mainly due to the high porosity in the porous PZT ceramics, which contributes for low dielectric constant and high dielectric loss [15]. The lower dielectric

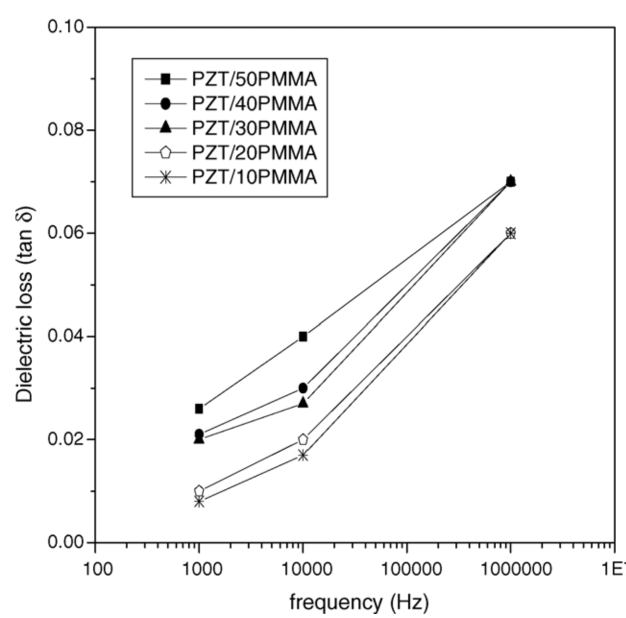

Fig. 3. Variation of dielectric loss with frequency.