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Effects of foam composition on the microstructure and piezoelectric properties of macroporous PZT ceramics from ultrastable particle-stabilized foams

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Abstract

Porous lead zirconate titanate (PZT) ceramics could be produced by combining the particle-stabilized foams and the gelcasting technique. In this study, the foaming capacity of particle-stabilized wet foams was tailored by changing the concentration of valeric acid and pH values of suspension. Accordingly, porous PZT ceramics with different porosity, microstructure, dielectric and piezoelectric properties were prepared with the respective wet foam. Increase in the porosity led to a reduction in the relative permittivity (ε_r), a moderate decline in the longitudinal piezoelectric strain coefficient (d_{33}) and a rapid decline in the transverse piezoelectric strain coefficient (d_{31}), which endowed porous PZT ceramics with a high value of hydrostatic strain coefficient (d_h) and hydrostatic figure of merit (HFOM). As a result, the prepared samples possessed a maximal HFOM value of $19{,}520 \times 10^{-15}$ Pa^{-1} with the porosity of 76.3%. The acoustic impedance (Z) of specimens had the lowest value of 1.35 Mrayl, which could match well with those of water or biological tissue; accordingly, the material would be beneficial in underwater sonar detectors or medical ultrasonic imaging.

Keywords: A. Particle-stabilized foams; C. Dielectric properties; C. Piezoelectric properties; D. PZT

1. Introduction

Lead zirconate titanate (PZT) has been extensively used for a host of sensor and actuator applications for its excellent piezoelectric properties [1–3]. However, for low frequency hydrophone application (10–100 kHz), underwater transducers, and biomedical imaging etc., porous PZT composites are preferred for low density, improved acoustic matching with water, high hydrostatic coefficients, and high hydrostatic figure of merit (HFOM). Generally, porous PZT composites could be classified into PZT/polymer and PZT/air (porous PZT ceramic). Compared with the PZT/polymer composites, porous PZT ceramics possess numerous advantages, such as brief manufacturing procedure, broad usage temperature, and roughly linear relationship between the piezoelectric properties and porosity [4]. In recent years, porous PZT ceramics have been developed using various processing techniques such as the lost wax replication of a coral skeleton [5], carbon fabrics [6], mixing of burnable plastic spheres (BURPS) processes [7], gelcasting [8], etc. Each process leads to the formation of its own microstructure and properties with varied porosities.

Due to the simplicity, versatility and low cost, the direct foaming technique is always of great interest to produce porous ceramics [9]. In this method, air bubbles are incorporated into a ceramic suspension by mechanical frothing to produce wet foams. Then the foams are dried and sintered to obtain high-strength porous ceramics. However, wet foams are thermodynamically unstable systems which undergo continuous Ostwald ripening and coalescence processes in order to decrease the foam overall free energy, so the wet foams are usually stabilized by long-chain surfactants or by colloidal particles. Recently, a sort of ultra-stable wet foams was utilized

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to produce porous ceramics [10,11]. In the method, partial hydrophobization is first achieved by modifying the ceramic particle surface with short-chain carboxylic acids that adsorb with the carboxylate group onto particles, leaving the hydrophobic tail in contact with the aqueous solution. Then the modified particles adsorb onto the air–water interface of freshly incorporated air bubbles and reduce the foam overall free energy by removing part of the highly energetic gas–liquid interfacial area to form ultra-stable wet foams. The stability of wet foams is mainly determined by the surface properties of the resulting modified particles, which can be affected by the concentration of adsorbed amphiphilic molecules or the pH value of suspension.

In order to fabricate solid porous PZT ceramics from particle-stabilized wet foams, shaping, drying, and sintering have to be accomplished. Gelcasting, first developed by Omatete and Janney during the 1990s, has been applied not only to the fabrication of dense ceramics, but also to porous ceramics and complex-shaped ceramic parts [12–15]. The gelcasting process involves a suspension of ceramic powders in an aqueous monomer solution creating a 3D network by in situ polymerization, which holds ceramic powders in the shape of the mold cavity.

Our group, recently, successfully produced porous PZT ceramics with excellent piezoelectric properties by combining the particle-stabilized foams and the gelcasting technique [16]. However, there have been few investigations carried out to understand the effects of foam composition on the properties of porous PZT ceramics. In the present work, the concentration of adsorbed amphiphilic molecules and pH values of final suspension were investigated for structural, dielectric, and piezoelectric properties such as foaming capacity, density, microstructures, relative permittivity, etc.

2. Experimental procedure

2.1. Materials

PZT-5H powders (BaoDing HongSheng Acoustics Electron Apparatus Co. Ltd., Hebei Province, China) with a mean particle size of 1.87 μm and a density of 7.6 g/cm^3 were employed in the experiment. Valeric acid ($C_5H_{10}O_2$, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was selected for the short-chain amphiphilic molecules to hydrophobize the particle surface. Acrylamide (AM, $C_2H_3CONH_2$) and *N*,*N*′-methylenebisacrylamide (MBAM, $(C_2H_3CONH)_2CH_2$) were selected as the organic monomers. Ammonium persulfate solution (APS, $(NH_4)_2S_2O_8$, 35 wt%) as an initiator and *N*,*N*, *N*′,*N*′-tetramethylenediamine (TEMED) as a catalyst were employed for the gelation process.

2.2. Sample preparation

Suspensions containing valeric acid were produced as follows: a premix solution of monomers was prepared by adding into deionized water AM and MBAM with concentrations of 14.5 wt% and 0.5 wt% respectively, then PZT powder was added stepwise to the solution to obtain a suspension with a solid loading of 15 vol%. Homogenization and deagglomeration were carried out on a ball mill for 4 h. An aqueous solution containing valeric acid was then slowly added dropwise to the ball-milled slurry under slight stirring to avoid local particle agglomeration. The concentration of valeric acid was determined by PZT suspension and set to 10, 30, 50, 70 and 90 mmol/L in this research. Afterward, the pH was set to its desired value (pH = 1, 3, 5, 7 and 9) employing HCl aqueous solution. In order to minimize the influence of water brought in by HCl solution, different concentrations of HCl aqueous solution (1, 3 and 5 mol/L) were employed in the experiment. Then the slurry was ball-milled again for 4 h to enable valeric acid to modify the surface of PZT particles sufficiently.

Foaming of suspensions was carried out using a household mixer at 300 r/min for 5 min. Meanwhile, the catalyst and initiator were added to the particle-stabilized foams with the amounts of 0.5 vol% and 1 vol% respectively; then the polymerization of AM started with an obvious increase in temperature in several minutes. The wet foams were then cast into a mold while in situ polymerization continued. After about 12 h, wet green parts were removed from the mold and dried at 40 °C. The dried bodies, which had no obvious shrinkage in the drying process, were subsequently sintered in a corundum crucible containing $PbZrO_3$ powder to produce an excess PbO atmosphere at 1150 °C for 2 h.

2.3. Characterization

Each test in our research led to 3–4 samples and all samples were subjected to simple machining to be disc-shaped with a typical size of 10 mm in diameter and 1.5 mm in height. The porosity of sintered sample was obtained from the ratio of the measured bulk density, measured by using the water displacement method based on the Archimedean principles, to the theoretical one of this PZT material (7.6 g/cm^3). The microstructures of porous PZT ceramics were observed using SSX-550 scanning electron microscopy (SHIMAZU, Shimazu Corp., Kyoto, Japan). Cell size was measured from the obtained SEM photographs using the image analysis software (Image J) [17]. For dielectric and piezoelectric testing, both surfaces of the samples were coated with a thin silver layer, followed by heat treatment at around 550 °C for 20 min to form electrodes. To minimize the penetration of silver into porous ceramic bodies, the silver paste was made highly viscous by adding ethyl cellulose (EC). Thereafter, the samples were poled by applying a dc field of 10 kV/cm for 10 min in a bath of silicone oil at 120 °C, and subsequently aged for 24 h before testing. The longitudinal piezoelectric strain coefficient (d_{33}) was measured by a direct method based on a Quasti-static d_{33}-meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science, Beijing, China). The relative permittivity (ε_r) was calculated from the capacitance by the formula

$$\varepsilon_r = \left(\frac{1}{\varepsilon_0}\right)\frac{C_0 d}{S} \quad (1)$$

where ε_0 is the vacuum permittivity, C_0 the capacitance at 1 kHz measured under constant (zero) stress by using an