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Fabrication and electrical properties of porous BS–0.64PT high temperature piezoceramics using polystyrene microsphere

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Abstract

Porous $BiScO_3$–$0.64PbTiO_3$ (BS–0.64PT) ceramics were fabricated by using burnable plastic sphere technique (BURPS). Self-synthesized polystyrene microsphere (PS, φ360 nm) was used as pore forming agent (PFA). Porosity of the porous ceramics was regulated by adjusting sintering temperature and volume fraction of PFA. The porous ceramics were characterized by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). All samples were pure tetragonal perovskite. Properties of the porous ceramics, including porosity, piezoelectric coefficient (d_{33}) and dielectric properties (ε_r) were measured. Electromechanical coupling coefficients (k_p, k_t, k_{31}), mechanical quality factor (Q_m), piezoelectric coefficient (d_{31}, d_h), hydrostatic voltage coefficient (g_h), acoustic impedance (Z), hydrostatic figure of merit (HFOM) were derived from impedance spectrum. Sintering temperature and volume fraction of PFA were optimized to bring out porous ceramics with highest g_h and HFOM. Porous ceramic with 50 vol% PS microspheres sintered at 1000 °C possessed porosity of 17.12%, with g_h and HFOM to be 0.024 V/m Pa and 6087×10^{-15}/Pa, respectively.

Keywords: B. Porosity; C. Piezoelectric properties; Polystyrene; BS–0.64PT

1. Introduction

Porous piezoceramics with lower relative permittivity and acoustic impedance have been widely used in ultrasonic transducers for applications like hydrophones, medicine imaging and geothermal prober [1–4]. For the application in hydrophones, their efficiency is determined by the acoustic matching between the piezoceramics and the investigated medium [5], while their sensitivity is depend on the hydrostatic figure of merit (HFOM $= d_h \cdot g_h$) of the piezoceramics, where d_h ($d_{33}+2d_{31}$) is the hydrostatic charge coefficient, g_h ($d_h/(\varepsilon_r \cdot \varepsilon_0)$) is hydrostatic voltage coefficient. In brief, high sound velocity and high HFOM are required for high performance of the devices.

It is well known that electrical and acoustic properties of porous piezoelectric materials are strongly dependent on pore properties, such as porosity, pore size, pore morphology, pore alignment and pore connectivity (0–3, 1–3, 3–3) [6–9]. The two digitals in 0–3 represent the steric connectivity of pore and matrix material, respectively. The main processing routes for high HFOM porous piezoceramics with tailored microstructure include burning plastic spheres (BURPS) [10,11], gel-casting [12,13] and freeze-casting [14–16]. While different methods directly control the microstructure features, pores properties ultimately determine the performances of the porous materials.

Yang et al. fabricated porous PZT ceramics with 3–3 pores using *tert*-butyl alcohol-based gel-casting [13]. With increasing sintering temperature, the porosity usually decreases, thus leading to increase in ε_r and hence decrease in HFOM. They found that highest porosity of 57.6% was achieved at 1150 °C, which led to the highest HFOM of $22{,}299 \times 10^{-15}$/Pa, with d_{33} and ε_r of 454 pC/N and 502, respectively. Lee et al. reported porous PZT–PZN piezoceramics with a high porosity of 90% by using directional freeze casting [16]. There were three pore configurations, with orientation angles of 0°, 45°,

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and 90° with respect to the poling direction. As the orientation angle was varied from 90° to 0°, the d_{33} value as notably increased from 302 to 450 pC/N, while the hydrostatic piezoelectric properties were increased significantly.

BURPS process offers advantages, such as the ability to control pore configuration and production at large scale with ease. Kumar et al. reported porous PZT ceramics developed by using the BURPS process with varied contents of PMMA (10, 20, 30, 40 and 50 vol%) as a pore-forming agent (PFA) [17]. The porosity was increased with increasing content of PMMA. The PZT porous ceramics with 50 vol% PMMA had HFOM and g_h of 3306×10^{-15}/Pa and 0.057, respectively. The formation of the pores in BURPS process can be controlled by many factors, such as the shape [18], size [19–21] and volume [22,23] of PFA and sintering temperature [24–26]. All the influence factors can be used to control the properties of the pores, thus optimizing electrical properties of the porous piezoceramics.

In this paper, porous BS–0.64PT piezoceramics (d_{33}=460 pC/N and T_c=450 °C) were fabricated with PS microsphere as PFA [27]. Volume fraction of PS microsphere and sintering temperature were optimized to control the porosity. Electrical properties dependent on the porosity have been investigated.

2. Experimental procedure

$BiScO_3$–0.64$PbTiO_3$ was synthesized by using the conventional mixed oxides method. Bi_2O_3 (99.0%), Sc_2O_3 (99.99%), TiO_2 (99.5%), and PbO (99.9%) powders were used as starting raw materials. The powder mixtures were ball-milled for 4 h in alcohol, followed by oven drying. Then, the dried powders were calcined at 750 °C for 2 h in an alumina crucible and re-milled for 4 h. PS was synthesized by using the procedure described Ref. [28]. PS powders of 10, 30, 50 and 60 vol% were mixed with the BS–0.64PT powder with liquid stirring in ethanol medium. Then, the mixed powders were pressed into disks (~10 mm in diameter and ~1.5 mm in thickness) at 60 MPa. After the PFA was burn out at 450 °C for 2 h [29], the disks were sintered in a sealed alumina crucible at 1000–1150 °C for 2 h. Then all the samples were annealed at 800 °C for 5 h. The sintered samples were polished before measurement and sample sizes are about 1 mm in thickness and 7.2–7.9 mm in diameter for porous ceramics and 9.1 mm for dense ceramic.

Phase structures were characterized by using X-ray diffraction (XRD) (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). Surfaces of the sintered samples after polishing and hot corrosion were observed by using scanning electron microscopy (SEM, Quanta F520; JEOL, Tokyo, Japan). Bulk density of the sintered samples was measured with Archimedes method and porosity of the sample was calculated according to the ratio of the measured bulk density to the theoretical one of BS–0.64PT (ρ=7.8 g/cm^3) [28].

To measure piezoelectric and dielectric properties, electrodes were made by sputtering gold layer on two sides of the samples. The samples were poled in a silicone oil bath at 120 °C and electric field of 3 kV/mm for 10 min, which were aged for 24 h before testing. Longitude piezoelectric coefficient (d_{33}) was measured by a quastic-static d_{33}-meter (ZJ-6A, Institute of Acoustics, Chinese Academy of Science, Beijing, China). Impedance spectrum (including the resonant vibration frequency f_r and the antiresonant vibration frequency f_a) (Agilent 4294A, America). The temperature dependence of the permittivity were measured from room temperature to 550 °C (Agilent E4980A, CA). The values of piezoelectric coefficient (d_{31}) were calculated using the following formulas:

$$k_{31}^2 \approx \frac{\pi^2}{4}\frac{f_a - f_r}{f_r} \tag{1}$$

$$k_{31} = \frac{d_{31}}{\sqrt{s_{11}^E \varepsilon_{33}^T}} \tag{2}$$

$$s_{11}^E = \frac{1}{c_{11}^E} \tag{3}$$

$$f_r = \frac{B}{\pi D}\sqrt{\frac{c_{11}^E}{\rho(1-\mu^2)}} \tag{4}$$

$$\mu = \frac{5.332 f_r - 1.867 f_{r1}}{0.6054 f_{r1} - 0.191 f_r} \tag{5}$$

In these formulas, k_{31}, s_{11}^E, c_{11}^E, D, μ and ρ are electromechanical coupling factor, elastic constant, elastic stiffness constant, diameter, and density of the samples, respectively. The coupling factor of the thickness vibration mode (k_p and k_t) is expressed as

$$k_p = 1/\sqrt{\frac{0.395 f_r}{(f_a - f_r)} + 0.574} \tag{6}$$

$$k_t = \sqrt{\frac{\pi}{2}\frac{f_r}{f_a}\tan\left(\frac{\pi}{2}\frac{f_a - f_r}{f_a}\right)} \tag{7}$$

The magnitudes of HFOM and Z were calculated from the measured values and other parameters as follows:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 S} \tag{8}$$

$$d_h = d_{33} + d_{31} \tag{9}$$

$$g_h = \frac{d_h}{\varepsilon_r \varepsilon_0} \tag{10}$$

$$\text{HFOM} = d_h g_h \tag{11}$$

$$Z = \rho D f_r \tag{12}$$

In these formula, ε_r is relative permittivity, ε_0 the permittivity of vacuum, C is the capacitance of samples, S and d are the area and thickness of samples, respectively.