J Mater Sci (2007) 42:6742–6748
DOI 10.1007/s10853-006-1477-6

Fabrication and properties of thin-shell monolithic piezoelectric ceramic transducers

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Received: 14 September 2005 / Accepted: 21 December 2006 / Published online: 26 April 2007

Abstract Monolithic piezoelectric ceramic transducers with hollow thin shell forms (sphere, cylinder, tube and cone) were successfully fabricated from lead zirconate titanate using slip casting method. Stable and well dispersed water based slurries were prepared under basic conditions with 35–45 vol% solid loading using 0.25–0.50 wt% dispersant. Various characteristic vibration modes, such as length extension, radial expansion, etc., were obtained from the thin shell transducers at 50–200 kHz frequencies. The resonance frequencies of these modes were engineered by changing the shape and dimensions of the shells. Comparison of the numerical calculations and experimental results indicates that slip casting is a viable method to obtain hollow thin shells with reasonable electrical properties.

Introduction

Piezoelectric ceramics find use in a wide range of applications such as biomedical and underwater transducers, and in-air actuators [1]. However, typical piezoelectric strain of a bulk ceramic is limited to 0.1%, and therefore an amplification is required to obtain the required large displacements for low frequency underwater operation or for actuator applications. Flextensional transducers with flexing, compliant metallic shells and an active ceramic driving element provide such an amplification mechanism [2]. Such mechanical amplification schemes add additional complexity and cost, and raise reliability issues in the long-term use of the transducers. Additionally, these compliant shells are not piezoelectric and therefore they are not active.

The ideal case would be to reliably obtain larger displacement and better electroacoustic performance from piezoelectric ceramic itself with a simple and robust design that can be fabricated easily. These requirements point to a monolithic ceramic structure with built-in amplification mechanisms obtained through the shape and geometry of the transducer. In fact, there have been examples of monolithic ceramic transducers that have built-in internal displacement or stress amplification mechanisms. A thin-wall hollow sphere transducer structure redistributes the stress and effectively amplifies incoming stress, like a flextensional transducer, by a ratio of radius/thickness (r/t) of the sphere to provide large hydrostatic piezoelectric charge coefficients [3]. Rainbow transducers, prepared by chemically reducing one surface of a piezoelectric ceramic wafer at high temperature, thereby producing a stress-biased, dome-shaped structure, provide high axial displacements and sustain moderate pressures [4].

Piezoelectric ceramic transducers are usually fabricated in simple shapes such as discs, rectangular bars, open ended tubes (cylinders) and hemispheres using the dry pressing method. New or improved ceramic processing techniques such as injection moulding, extrusion, solid free-form fabrication and gel-casting, and more time-tested approaches such as slip casting provide new routes to obtain complex ceramic bodies with intricate details.

This paper describes the design and fabrication of monolithic piezoelectric ceramic transducers based on hollow thin-shell structures using slip casting method. The

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thin shell forms that have been investigated in this study are hollow *cylinder*, *tube*, *cone* and *sphere*. The main objective is to investigate the feasibility of preparing piezoelectric ceramic transducers with engineered vibration modes and frequencies, and built-in amplification mechanism using the slip casting method. Slip casting method was selected to obtain the thin shells due to several reasons. First of all, since these transducers are intended to be used mainly for underwater applications they have to withstand hydrostatic pressures of several MPa (depending on the depth). They, therefore, have to be fabricated with an appropriate wall thickness of at least 1 mm. This thickness requirement effectively makes methods such as vapor deposition, sputtering or sol-gel coating unusable. Other methods such as extrusion can be used for cylinders, and injection molding can be used for cones and tubes. However, both of these methods require costly equipment. Compared to these two methods slip casting uses only plaster-of-Paris moulds and, therefore, requires minimal investment. This was the second main reason for choosing slip casting method. Finally, machining these shells from bulk ceramics of simpler shapes would cause material losses, and again, requires equipment investment. For all these reasons explained above, slip casting was deemed to be the ideal method to fabricate hollow thin shells.

Experimental procedure

Starting materials

A commercial grade lead zirconate titanate (PZT)–Pb(Zr,Ti)O_3 powder (APC 850 from APC International Ltd.) was used in the preparation of ceramic slurries. Ammonium polyacrylate based Darvan 821 A (R.T. Vanderbilt Company, Inc.) was used as a dispersing agent to obtain a stable ceramic slurry. Surfynol 104E (Air Products and Chemicals, Inc.) was used as a surfactant to prevent foaming in the slurry. Finally, Glycerol was used as a plasticizer.

Suspension preparation and transducer fabrication

A water based slurry was prepared by adding 35–45 vol% PZT powder accompanied with dispersant (0.05–1.25 wt%), surfactant (0.065 wt%) and plasticizer (0.4 wt%). The slurry was then ball milled for 24 h using zirconia milling media to break up the agglomerates and obtain a uniform mixture. Rheological properties of slips were investigated by viscosity measurements using a rotating-spindle viscometer (Brookfield RVT DV-II). The slurry stability was evaluated through gravity sedimentation tests by pouring 50 mL of suspension into a Pyrex glass cylinder. Sediment heights were measured after 10 days as a percentage of the total suspension height. The optimum solid loading and dispersant addition was determined based on the results of these measurements.

The PZT thin shell structures were obtained by slip casting into multicomponent plaster-of-Paris moulds that allow easy removal of the green bodies. The casting rate was measured by slip casting into identical moulds and keeping the slurry inside the mould for a different time period (1–10 min). After the determined casting time, slurry was drained from the mould and the wall thickness of each green ceramic part was measured. The thickness of the thin shells in our study was, therefore, controlled by the casting time. The drying was done at room temperature under atmospheric conditions for 24 h. Sintering was done at 1,285 °C for 90 min in closed alumina crucibles in the presence of $PbZrO_3$ buffer powders to provide a PbO rich sintering atmosphere. The cooling rate was left to the furnace characteristics.

Inner and outer surfaces of the sintered thin ceramic shells were painted with fire-on silver paste. Firing of the electrode was done at 600 °C for 30 min. Electrical poling of the transducers were done at 115 °C in an oil bath by applying an electric field of 25 kV/cm for 10 min. The microstructural features of the sintered ceramic pieces were examined by scanning electron microscopy. Resonance–antiresonance vibration frequencies were measured using an HP 4194A, Impedance/Gain-Phase Analyzer.

Results and discussion

Rheological properties

Particle agglomerates and lower solid loading in slurries can result in surface and bulk defects in the finished ceramic parts. A high solids loading, homogeneous and well-dispersed powder in the suspension and the stability of suspension is imperative in obtaining dense ceramics with uniform and defect free microstructures. This can be achieved through electrostatic and steric stabilization by changing the acidity of the suspensions and using appropriate dispersants [5].

In this study, an ammonium polyacrylate based polyelectrolyte (Darvan 821 A, R.T. Vanderbilt Company, Inc.) was used as a dispersing agent to obtain a stable ceramic slurry. This dispersant was chosen because it is most often used in aqueous solutions and its thermal decomposition temperature by depolymerization is below 400 °C, allowing clean burnout with little residual carbon [6]. This is beneficial for electrical properties of electronic ceramics.

In our previous study [7] zeta potential measurements of PZT suspensions with ammonium polyacrylate based polyelectrolytes indicated that the best dispersion can be obtained under basic conditions (pH > 8.5). In this study, measurements showed that all the slurries have pH > 8.8.

Viscosity measurements and sedimentation tests were carried out to examine the rheological properties and determine the optimum preparation and casting conditions of the PZT slurries. Fig. 1(a) shows the variation of apparent viscosity with respect to solid loading and dispersant concentration of the slurries (measured at 50 rpm spindle rotation speed). From these curves, a dispersant concentration range was determined for each solid loading within which a minimum slurry viscosity was observed. The minimum viscosity range becomes narrower and the viscosity value becomes higher as the slurry solid content is increased. This range can be considered as the optimum concentration for deflocculation and slip casting. The lowest viscosity value (13.1 mPa.s) was observed in the 35 vol% solid containing slurry at 0.25 wt% dispersant concentration. The optimum value of 26.2 mPa.s was determined for 40 vol% solid loading at 0.50 wt% dispersant concentration, and finally, 0.25 wt% dispersant concentration was found to be sufficient for slurries with 45 vol% solid loading, resulting in a minimum viscosity value of 57.8 mPa.s.

Figure 1(b) shows the results of slurry stability observations obtained through 10 days-long gravity sedimentation tests as a function of dispersant concentration and solid loading. The sedimentation ratio in this figure is a relative value that is defined as the sediment height after 10 days as a percentage of the highest sediment height observed at the lowest dispersant concentration. The stability of the slurries was found to follow the same trend observed in the viscosity measurements. The lowest sediment height, i.e., the highest stability, was observed in the 35 vol% solid containing slurry at 0.25 wt% dispersant concentration. These results also confirm the viscosity measurements and point out the optimum conditions for slip casting of PZT slurries.

Ceramic slurries are known not to exhibit Newtonian flow behaviour (i.e., constant viscosity, independent of the shear rate) [8]. Accordingly, the PZT slurries prepared in this study exhibited pseudoplastic (shear-thinning) behaviour, i.e., a reduction in apparent viscosity with increasing shear rate (Fig. 1c). The results presented in Fig. 1(c) are obtained from slurries with the optimum dispersant concentrations.

Resonance frequency of thickness vibration mode in a thin shell structure is directly related to the wall thickness. However, wall thickness also affects the stress amplification ratio and additionally, it has cross coupling with the volume expansion vibration modes [3]. Precise control of the wall thickness of the thin shell transducers is, therefore, essential for the device performance. The thickness of the final pieces was controlled by using casting rate calibration curves, taking into consideration the shrinkage that occurs during sintering (≈16%). The casting rate was measured by slip casting into identical moulds and keeping the slurry

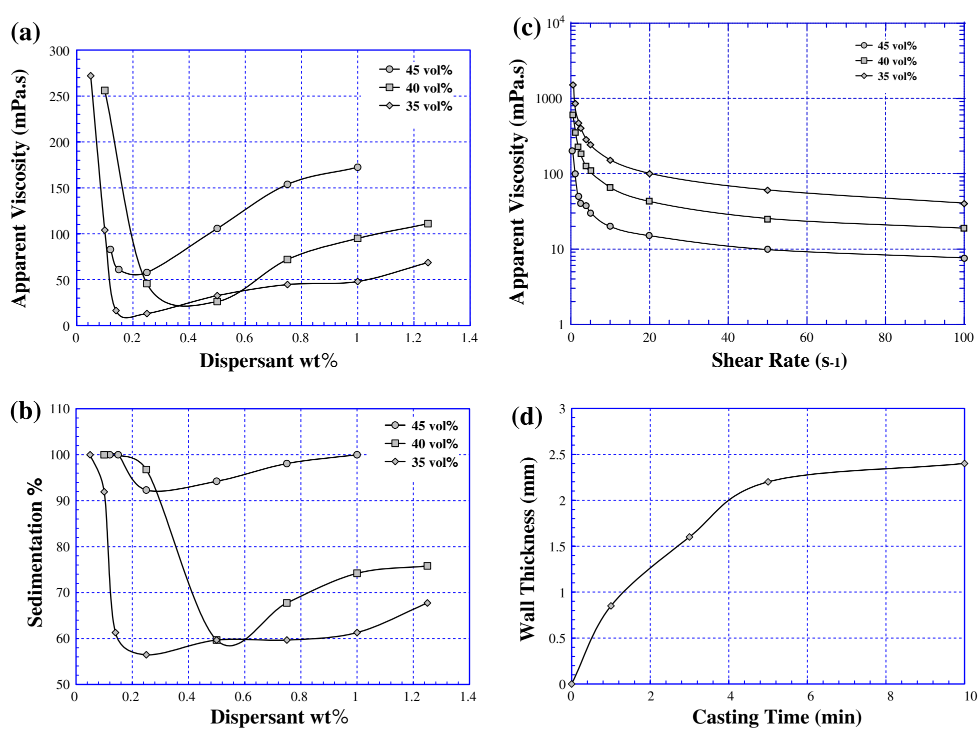

Fig. 1 Rheological properties of the PZT slurries. Effect of (**a**) solid loading and dispersant concentration on slurry viscosity (measured at 50 rpm), (**b**) solid loading and dispersant concentration on sedimentation ratio, (**c**) solid loading and shear rate on slurry viscosity. (**d**) Casting rate

inside the mould for a different time period (1–10 min). After the determined casting time, slurry was drained from the mould and the wall thickness of each green ceramic part was measured. The casting rate shown in Fig. 1(d) is obtained for 35 vol% solid containing slurries with optimum dispersant concentration.

Structural and microstructural features

Figure 2(a) and (b) show some of the thin shell ceramic transducer samples prepared in this study by slip casting. Schematic drawings with main dimensional parameters of these transducers are presented in Fig. 2(c). The main differences of fabricating thin shells using this method are the ease of fabrication, low cost, flexibility of the method to prepare shells with various sizes and thicknesses, and feasibility of obtaining the entire shells in one single step (for example; spherical transducers are not prepared as two hemispheres and bond together as it is normally done commercially, but instead they can be cast as an intact spherical shell with a small inner electrode access hole).

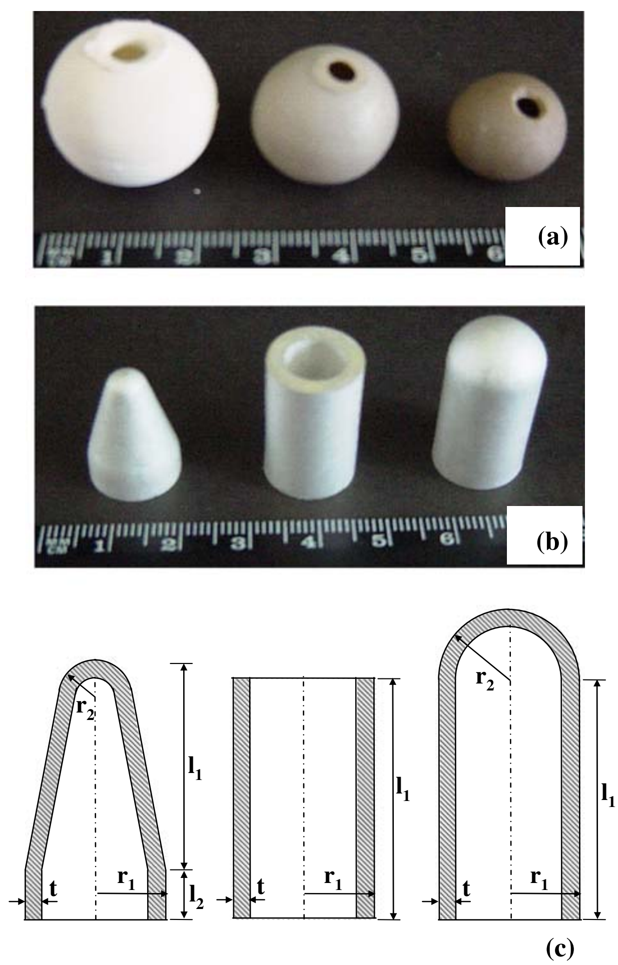

Fig. 2 Thin shell PZT ceramic transducers (**a**) hollow spherical shells (from left: green; sintered and electroded; sintered smaller size spheres), (**b**) conical, cylindrical and tube shape hollow shells. (**c**) Schematic drawings of thin shells

The scanning electron micrographs of sintered thin shell PZT ceramics are shown in Fig. 3. From the thermally etched shell surface and fracture surface micrographs it is clearly seen that the shells have a dense and uniform microstructure with no apparent porosity. The grain size was found to be less than 10 μm.

Vibration modes and resonance characteristics

The most basic thin shell structure with the highest symmetry is a hollow sphere with a centre of symmetry. Vibration modes and associated resonance frequencies of such a structure for given dimensions have been investigated analytically [9], as well as experimentally and using finite element analysis [3] and reported in the literature. Therefore, results for hollow spheres prepared in this study are not presented here, but will be discussed in order to form a basis for further discussion of other shells. An electrically driven piezoelectric hollow sphere has two-dimensional parameters; a radius and a wall thickness. Accordingly, such a structure has two fundamental vibration modes; lower frequency mode is a volumetric expansion and contraction of the sphere, i.e., increase and

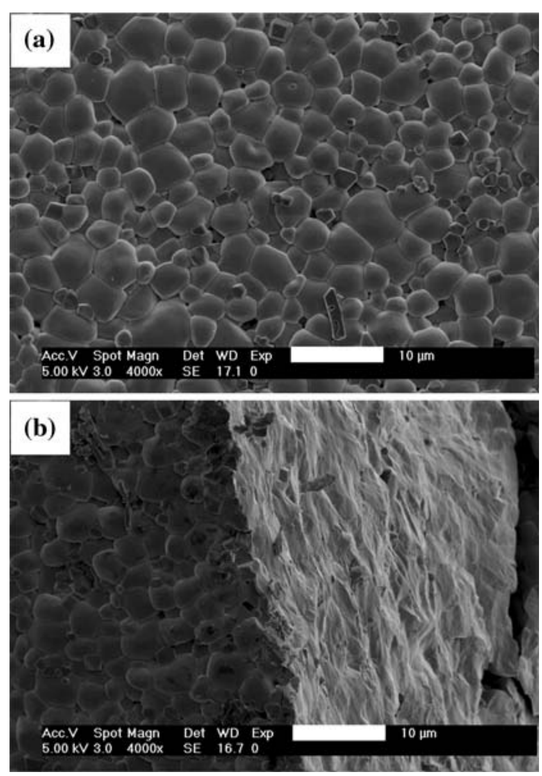

Fig. 3 Scanning electron micrographs of sintered ceramic pieces (**a**) thermally etched surface (**b**) fracture surface

decrease of the sphere radius, and can be called as the *breathing mode*. Higher frequency vibration mode is the increase and decrease of the wall thickness, the so-called *thickness mode*.

Thin shell shapes with increasing complexity and lower symmetry would have more dimensional parameters. They would, therefore, have more fundamental vibration modes, as well as some coupled vibration modes. The main objective of this study is to engineer these vibration modes and their frequencies by controlling the shape and dimensions of the shells such that the underwater acoustic performance (transmitting voltage response, band-width, directional properties, etc.) can be fine tuned to desired values. The results of the admittance vs. frequency measurements for thin shell piezoelectric ceramic transducers prepared in this study are presented in Fig. 4 and the vibration modes are discussed below.

Figure 4(a) shows the lower frequency (10–200 kHz) and Fig. 4(b) shows the higher frequency (0.2–5 MHz) admittance spectra of cylindrical thin shell transducers with two different dimensions. The details are given in Table 1. Cylinder is an axisymmetric structure and there are three main dimensional parameters associated with a cylindrical shell (Fig. 2c); length (l_1), radius (r_1) and thickness (t). Accordingly, there would be three fundamental vibration modes; extension and contraction of the cylinder along the symmetry axis, i.e., increase and decrease of the length of the cylinder, and can be called as the *length extension mode*. The second vibration mode would be associated with radius of the cylinder, a radial expansion and contraction of the cylinder perpendicular to the symmetry axis, the so-called *radial expansion mode*. Finally, the third mode would be the *thickness mode*. These three fundamental vibration modes are indicated on the figures. However, these modes are not expected to be pure modes but would include couplings with each other. As clearly seen in Fig. 4(a) and (b), changing the dimensions of the cylinder changes the resonance frequencies of these characteristic vibration modes (Table 2).

Figure 4(c) shows the lower frequency (10–200 kHz) admittance spectrum of thin shell tube transducers (Fig. 2c) with two different dimensions. Such an axisymmetric structure would have four-dimensional parameters; length (l_1) and radius (r_1) of the cylindrical section, radius of curvature of the dome (r_2) and shell thickness (t). As a result, this structure would have an additional vibration mode that is related to the radius of curvature of the dome. This vibration mode would be a radial expansion and contraction of the dome that is similar to the breathing mode of a hemisphere with limited degrees of freedom. Again, in this case, varying the dimensions resulted in a shift in the resonance frequencies (Table 2).

The final thin shell structure that was investigated in this study is a cone. The main difference of this axisymmetric structure from the previous ones is the gradually changing dimension (diameter) of the conical section (Fig. 2c). As a

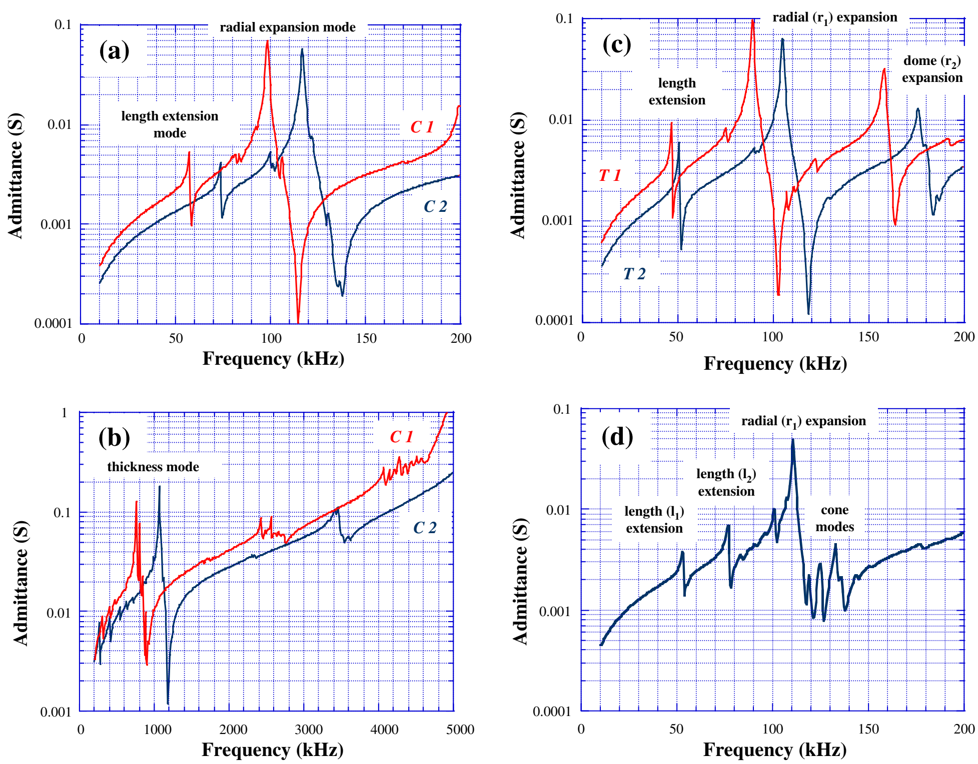

Fig. 4 Admittance vs. Frequency spectra of thin shell transducers showing resonance frequencies for various vibration modes. (**a**) Cylinder—length extension and volumetric expansion modes (**b**) Cylinder—thickness mode (**c**) Tube—length extension and volumetric expansion modes (**d**) Cone—length extension and volumetric expansion modes

Table 1 Dimensional parameters of thin shell piezoelectric ceramic transducers

Sample ID	l_1 (mm)	l_2 (mm)	r_1 (mm)	r_2 (mm)	t (mm)
Cylinder (C1)	24.0	–	6.8	–	2.3
Cylinder (C2)	18.3	–	5.5	–	1.8
Tube (T1)	24.0	–	7.0	7.0	1.9
Tube (T2)	22.6	–	6.0	6.0	1.9
Cone	22.0	5.0	7.0	3.5	1.7

Table 2 Vibration modes and resonance frequencies of thin shell piezoelectric ceramic transducers

Sample ID	Resonance frequency (kHz)			
	Length (l_1) extension	Length (l_2) extension	Radial (r_1) expansion	Dome-cone expansion
Cylinder (C1)	57.2	–	98.6	–
Cylinder (C2)	73.9	–	116.7	–
Tube (T1)	47.1	–	89.4	158.2
Tube (T2)	50.9	–	105.0	176.0
Cone	53.1	76.7	110.6	120–140

result of this variation, thin shell cone structure displayed a complex admittance spectrum (Fig. 4d) where the radial expansion and contraction of the conical section has several resonance frequencies (Table 2).

Comparison of the experimental and numerical results

Numerical calculations were conducted using the materials properties reported in the manufacturer's catalogue and compared with the experimental results in order to estimate and discuss the validity of the slip casting method to obtain hollow thin shells. The cylindrical thin shells were selected for this evaluation due to their higher symmetry and the existence of analytical solutions in literature to predict the resonance frequencies of fundamental vibration modes. Only the sample (C1) was used in these calculations.

The capacitance of a cylindrical capacitor can be calculated using the following equation:

$$C = \frac{2\pi\varepsilon_0\varepsilon_r r_a l}{t} \tag{1}$$

where ε_0 is the permittivity of free space (=8.854 × 10^{-12} F/m), ε_r is the dielectric constant (=1,900 for APC 850) [10], t is the wall thickness of the shell, r_a is the average radius of the cylinder [$r_a = r-(t/2)$]. Using t = 2.3 mm, r_a = 5.65 mm, l = 24 mm, the capacitance of the cylindrical sample (C1) was calculated to be 6,150 pF. The measured capacitance was 5,650 pF, which in turn gives a dielectric constant of 1,722 using Eq. (1).

One of the fundamental modes of vibration in a radially poled cylindrical shell is the radial expansion mode, as discussed in the previous section. The resonance frequency of this mode has been studied theoretically by Haskins and Walsh [11] and formulized by the following equation for short ($l/r \ll \pi$) cylinders:

$$f_r = \frac{1}{2\pi r_a}\sqrt{\frac{1}{\rho s_{11}^E}} \tag{2}$$

where ρ is the density, and s_{ij}^E is the tensor component of compliance. In the present study, the aspect ratio (l/r) of the cylinders were greater than π, therefore, the equation for the resonance frequency was modified as follows [11]:

$$f_r = \frac{1}{2\pi r_a}\sqrt{\frac{1}{\rho s_{11}^E(1-\sigma^2)}} \tag{3}$$

where σ is the Poisson's ratio at constant electric field and can be calculated using:

$$\sigma^E = -\frac{s_{12}^E}{s_{11}^E} \tag{4}$$

The Poisson's ratio was calculated as 0.35 using $s_{12}^E = -5.74 \times 10^{-12}$ m^2/N and $s_{11}^E = 16.4 \times 10^{-12}$ m^2/N for the PZT composition used in this study [12]. Assuming a 100% dense ceramic with $\rho = 7{,}700$ kg/m^3 [10] and using Eq. (3), the resonance frequency of the fundamental radial expansion vibration mode was calculated as 84.6 kHz. This value is lower than the measured value of 98.6 kHz (Fig. 4a).

The final parameter evaluated for the cylinder is the planar coupling coefficient, k_p. This coefficient can be calculated numerically from the material's properties using the following equation [12]:

$$k_p = \sqrt{\frac{2}{1-\sigma^E}}\frac{d_{31}}{\sqrt{\varepsilon_{33}^T s_{11}^E}} \tag{5}$$

where d_{31} is the piezoelectric charge coefficient and ε_{33}^T is the permittivity ($\varepsilon_r \times \varepsilon_0$). Using the reported material's properties [10] with d_{31} = –175 × 10^{-12} C/N, the coupling coefficient was calculated as 0.58. Coupling coefficient can also be determined from the measurements using the following relationship:

$$k_p^2 = 1 - \frac{f_r^2}{f_a^2} \quad (6)$$

where f_r and f_a are the resonance and antiresonance frequencies, respectively. The coupling coefficient was calculated to be 0.51 from Eq. (6) using the measured values of $f_r = 98.6$ kHz and $f_a = 114.4$ kHz, determined from Fig. 4(a). The piezoelectric charge coefficient was back-calculated as $d_{31} = -152 \times 10^{-12}$ C/N using Eq. (5) and substituting $k_p = 0.51$ and $\varepsilon_r = 1{,}722$, which were obtained from the measurements.

The comparison of the electrical properties obtained from numerical calculations and from the measurements indicates that shells fabricated using the slip casting method has slightly (10–15%) lower values than the ones reported for bulk ceramic. The difference is believed to be due to the porosity that might be present in the ceramic, slight variations in the dimensions of the transducers and the quality of the electrodes. However, the results clearly demonstrate that slip casting is a viable method to obtain hollow thin shells with engineered vibration modes and resonance frequencies.

Conclusions

Monolithic piezoelectric ceramic transducers were prepared in hollow thin shell forms with various shapes and sizes using the slip casting method. Investigation of the rheological properties indicated that stable and well-dispersed water based lead zirconate titanate slurries can be prepared under basic conditions with 35–45 vol% solid loading using 0.25–0.50 wt% dispersant. Slip casting of the slurries resulted in dense ceramics with uniform microstructure and dimensions. The hollow shell forms that were investigated in this study were sphere, cylinder, tube and cone. Characteristic vibration modes associated with the dimensions (length, radius, thickness) of the thin shells were obtained from the transducers at 50–200 kHz frequencies.

In accordance with the main objective of this study, it was demonstrated that the vibration modes and associated resonance frequencies of the thin shell transducers can be engineered by varying the shape and dimensions of the shells. The slip casting method was also proved to be a very flexible, easy and cost effective method to achieve this objective.

Acknowledgements The author would like to acknowledge the financial support of the Scientific and Technical Research Council of Turkey (TUBITAK) for this research project (Project #: MISAG 202).

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