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# Millimetre-sized hollow spheres of lead zirconate titanate by a sol–gel method

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Hollow spheres of lead zirconate titanate (PZT) [chemical formula $Pb(Zr_{0.52}Ti_{0.48})O_3$], with outer diameter of 1–2 mm and a wall thickness of about 100 μm, were fabricated by gellation of a PZT sol inside solid polymer spheres and then burning the polymer out. Monomodally sized polyacrylamide spheres, with diameter 1.40–1.90 mm, were soaked in a PZT sol, prepared by dissolving $Pb(NO_3)_2$, zirconium *n*-butoxide and titanium isopropoxide in *N*, *N*-dimethylformamide. The absorbed sol was then gelled beneath the surface of the polymer sphere by the action of $NH_3$. Upon calcination of the spheres at 850 °C for 4 h in air, hollow spheres of pure PZT perovskite phase (as identified by X-ray diffraction patterns) were obtained. The density of the hollow spheres was 1.13 g cm$^{-3}$, while that of the wall of the spheres was 3.10 g cm$^{-3}$. The scanning electron microscopic examination of the broken spheres showed that the inner surface of the spheres contained rib-like structures, which provided strength to the hollow spheres. The planar coupling factor, $k_p$, of six hollow spheres, placed at a close-packed arrangement in a plane, was 0.22, indicating the possibility of fabrication of low-density transducer arrays.

## 1. Introduction

Hollow spheres of piezoelectric ceramics have potential uses in medical ultrasound, non-destructive testing and low-density transducer arrays. Piezoelectric sensors and actuators made of tiny hollow spheres can lead to miniaturization, which can help achieve better resolution and high power densities. Tiny hollow spheres can provide high frequencies and excellent acoustical impedance matches, which are useful in underwater transducers and biomedical ultrasonics. Lead zirconate titanate (PZT) [1] is widely used as a piezoelectric material because of its large electromechanical coupling coefficients, ease of fabrication, temperature stability and high resistance to depolarization. Hollow spheres of PZT have been prepared by a coaxial nozzle technique [2], in which the slurry of PZT is injected through a coaxial nozzle with air passing through the centre. Owing to surface tension and hydrostatic forces, bubbles of PZT slurry are formed, the diameters of which can be uniformly varied from 1–6 mm, and the wall thickness varies from 30–100 μm. Yang and Chaki [3] prepared hollow PZT microspheres by a sol–gel/emulsion technique in which polymer microspheres were coated with PZT gel and then the polymer was burnt out. The outer diameter of the spheres prepared by this technique typically ranged from 20–100 μm and the wall thickness was about 2 μm. In this paper we describe fabrication of millimetre-sized hollow spheres (1–2 mm outer diameter and about 100 μm wall thickness) by impregnating polymer spheres with a PZT sol. We also describe a way of making a planar array of the tiny hollow spheres and poling them.

## 2. Experimental procedure

First, polyacrylamide latex solid microspheres were prepared by a sedimentation polymerization method [4]. In this method 7.1 g (100 mmol) of monomer acrylamide ( > 99%) and 1.54 g (10 mmol) cross-linker *N*, *N*′-methylene*bis*acrylamide ( > 99%) were dissolved in an aqueous solution of $(NH_4)_2S_2O_8$($1.6 \times 10^{-2}$ g in 20 ml water) inside a beaker placed in ice. The solution was then introduced dropwise (about 2 mm in size) with a syringe into heated (90 °C) mineral oil, kept in a cylinder of height 50 cm and diameter 8 cm. During the sedimentation process, which lasted 7–9 s, partial polymerization of the drops took place. The droplets were kept at the bottom of the cylinder, where the temperature was about 50 °C, for 2 h so that polymerization could be completed. The soild polymer spheres were taken out of the mineral oil by filtering with the help of a perforated funnel. The spheres were then rinsed three times with acetone. The polymer spheres were dried in air at 50 °C for 24 h.

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Next, a sol for PZT was prepared from lead nitrate ($Pb(NO_3)_2$), zirconium *n*-butoxide ($Zr(C_4H_9O)_4$) and titanium isopropoxide ($Ti(OC_3H_7)_4$), taken in amounts of the cation ratio in the chemical formula $Pb(Zr_{0.52}Ti_{0.48})O_3$. All the chemicals were of ACS grade and were inexpensive. 2.08 g $Pb(NO_3)_2$ was dissolved in 5 ml *N*, *N*-dimethylformamide (DMF) at room temperature. Then 1.545 ml $Zr(C_4H_9O)_4$ and 0.855 ml $Ti(OC_3H_7)_4$ were poured into $Pb(NO_3)_2$ solution and stirred in an ambient atmosphere for 45–60 min to obtain the sol for PZT. Recently, high-quality PZT powder has been prepared by this solution technique [5].

3.45 g polyacrylamide spheres were poured into 7 ml PZT sol and gently stirred for 12 h. Almost all the sol was absorbed by the spheres. Then 2 ml $NH_3$ aqueous solution (28%–30%) was poured into the spheres to cause gellation. The spheres were shaken for a few minutes and then left for 12 h in a closed beaker. The spheres were filtered with a perforated funnel and dried in air at room temperature for 12 h.

The polyacrylamide spheres containing PZT gel were placed in an alumina boat, heated in air at a rate of 100 °C $h^{-1}$ and fired for 4 h at various temperatures (namely 500, 600, 700 and 850 °C). The polymer was burnt out, leaving PZT hollow spheres. The phases in the spheres fired at various temperatures were examined by X-ray powder diffraction of ground spheres using Cu$K_\alpha$ radiation in transmission mode. Scanning electron and optical microscopes were used to characterize the morphology and microstructure of the PZT hollow spheres. The average outer diameter of the sphere was measured with the help of a micrometer.

Two pieces of glass plates, each with area 5 mm × 5 mm, were cut from a microscope glass slide (0.35 mm thick). A piece of conducting carbon tape (with adhesive on both sides) was pasted on one side of each of the glass plates. A few PZT spheres (three to six), fired at 850 °C, were placed in contact with one another on the carbon tape attached to the glass plate. The hollow spheres were pushed with a tweezer until they were arranged in close-packed contact, sticking on to the carbon tape. Another glass plate was placed on the top of the spheres, with the carbon tape sticking to the upper parts of the spheres. For electrode connections, silver wires were connected to the top and bottom carbon tapes with silver paint. Thus, a transducer array of hollow PZT spheres was constructed. To avoid breakage or displacement of the spheres, the transducer array with the glass plates was embedded in polypropylene. The thickness of the surrounding polypropylene layer was about 4 mm. The transducer array was poled inside silicone oil maintained at 90 °C under an electric field of 2 kV $mm^{-1}$ for 30 min. The planar coupling factor, $k_p$, was determined by measuring resonant and antiresonant frequencies of the poled array of the hollow spheres, following the IRE Standards [6]. $k_p$ was calculated by using the relation [7]

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

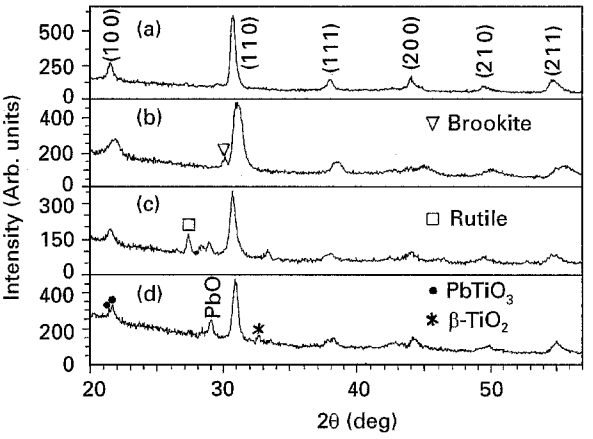


*Figure 1* X-ray powder diffraction patterns of hollow PZT spheres prepared by firing in air for 4 h at various temperatures: (a) 850 °C, (b) 700 °C, (c) 600 °C, (d) 500 °C.

where $f_r$ and $f_a$ are resonant and anti-resonant frequencies, respectively.

## 3. Results and discussion

### 3.1. X-ray diffraction

Fig. 1a–d show X-ray powder diffraction patterns of PZT hollow spheres prepared by firing at 850, 700, 600 and 500 °C, respectively for 4 h. In addition to PZT perovskite phase, the hollow spheres fired at 500 °C contained $PbTiO_3$, PbO and β-$TiO_2$ phases, as identified by the presence of their peaks in the diffraction pattern (Fig. 1d), but did not contain any pyrochlore phase of PZT. In contrast, PZT powder and films prepared by some other sol–gel routes [8, 9] contained pyrochlore even after firing at 650 °C. Upon firing at 600 °C, the PZT hollow spheres contained rutile ($TiO_2$), PbO and β-$TiO_2$ (Fig. 1c). Upon firing at 700 °C, the PZT hollow spheres still contained brookite ($TiO_2$) (Fig. 1b). Finally, upon firing at 850 °C, the hollow spheres contained only PZT perovskite phase (Fig. 1a). It should be noted that no excess lead was added to the initial sol to compensate for possible lead loss during subsequent firing. A rather low firing temperature (850 °C) in the sol–gel processing of the hollow PZT spheres reduced the chance of lead loss, and consequently, pure perovskite phase could be obtained (Fig. 1a).

### 3.2. Morphology

Fig. 2a and b show a whole and a partially broken PZT sphere, respectively, both fired at 500 °C for 4 h. Non-PZT phases appeared as coloured spots in polarized light (Fig. 2). When the spheres were fired at 850 °C for 4 h, they appeared uniform in colour, indicating a single-phase material. Fig. 3 shows a scanning electron micrograph of a PZT hollow sphere fired at 850 °C. Small cracks and pores were present on the surface of the sphere.

The mean diameter (measured using a micrometer) of the starting polyacrylamide spheres was 1.64 ± 0.13 mm. The measurement was done on 20 randomly selected

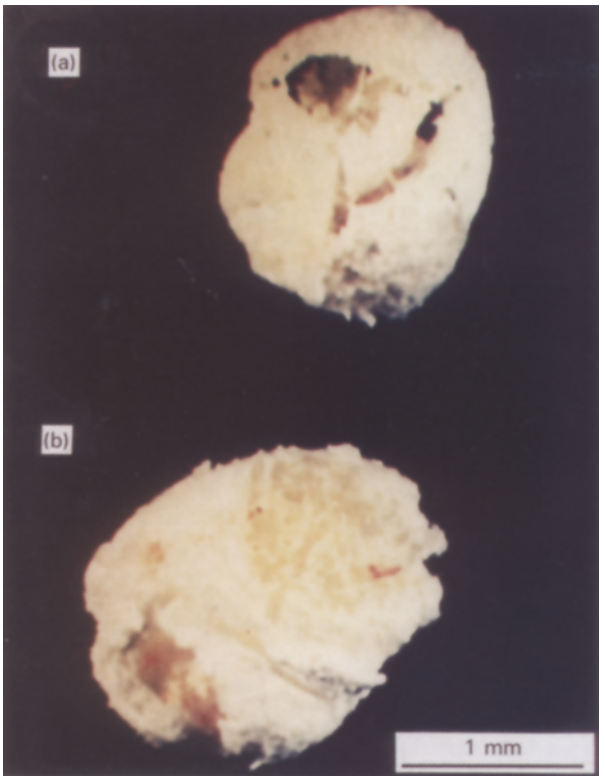


*Figure 2* Optical micrograph of hollow PZT spheres prepared by firing at 500 °C for 4 h, showing (a) a whole sphere and (b) a partially broken sphere.


*Figure 3* Scanning electron micrograph of a hollow PZT sphere prepared by firing at 850 °C for 4 h.

polymer spheres and the size ranged from 1.42–1.93 mm. The polyacrylamide spheres swelled upon absorption of solvent DMF with up to 90% increase in the diameter. Upon drying, however, the polymer spheres shrank back to the original size. The mean diameter of dried polymer spheres upon gellation was 1.57 ± 0.14 mm (measured over another random set of 20 spheres). There was no gelled powder on the outer surface of the polymer spheres. In other words, the gellation took place inside the polymer spheres. Even though the polyacrylamide spheres were initially ductile, they became brittle upon gellation and drying, and broke at any attempt of compaction. The initial swelling in DMF made the polyacrylamide spheres porous and helped deep penetration of the PZT sol into the polymer sphere. The depth of penetration of the sol determined the wall thickness of the PZT spheres, obtained upon firing. The outer diameter of hollow PZT spheres fired at 850 °C for 4 h was 1.43 ± 0.15 mm (measured over 20 randomly selected spheres) and the wall thickness (measured by scanning electron microscopy of broken spheres) was 100 ± 20 μm.

TABLE I. Density of hollow PZT spheres fired for 4 h at various temperatures

| | 500 °C | 600 °C | 700 °C | 850 °C |
|---|---|---|---|---|
| Density (g cm$^{-3}$) | 1.078 | 1.136 | 1.138 | 1.129 |

The density of hollow PZT spheres (including air inside) was determined by measuring the outer diameter of five spheres and the total weight of five spheres together, and then dividing the total weight by the total volume of five spheres. Table I shows the density of hollow spheres fired at various temperatures. The density upon firing at 500 °C was 1.078 g cm$^{-3}$. The density increased to 1.136 g cm$^{-3}$ at the firing temperature of 600 °C and then remained approximately steady with the further increase in the firing temperature. The density of hollow PZT spheres fired at 850 °C for 4 h was 1.129 g cm$^{-3}$ and the density of the material in the wall was calculated to be 3.10 g cm$^{-3}$. The theoretical density of PZT is about 8.0 g cm$^{-3}$. Thus, the PZT spheres prepared by the present technique were not only hollow, but the wall was also porous.

## 3.3. Microstructure

The microstructure of the outer surface of a hollow PZT sphere prepared by firing at 850 °C for 4 h is shown in Fig. 4a and b. Micropores as well as some larger pores were seen on the surface (Fig. 4a). The grain size on the surface was about 0.8 μm (Fig. 4b). The cross-section of the wall of a broken PZT sphere is shown in Fig. 5. The wall thickness was not uniform, but varied from place to place. Fig. 6 shows the fracture surface of the wall: fracture was intergranular and the fracture surface contained pores. Fig. 7a and b show the microstructure of the inner surface of the hollow PZT sphere. The inner surface was rough (Fig. 7a) due to non-uniform penetration of the PZT sol into the polyacrylamide sphere. The inner surface also contained rib-like structures (Fig. 7b), which provided strength to the hollow PZT spheres.

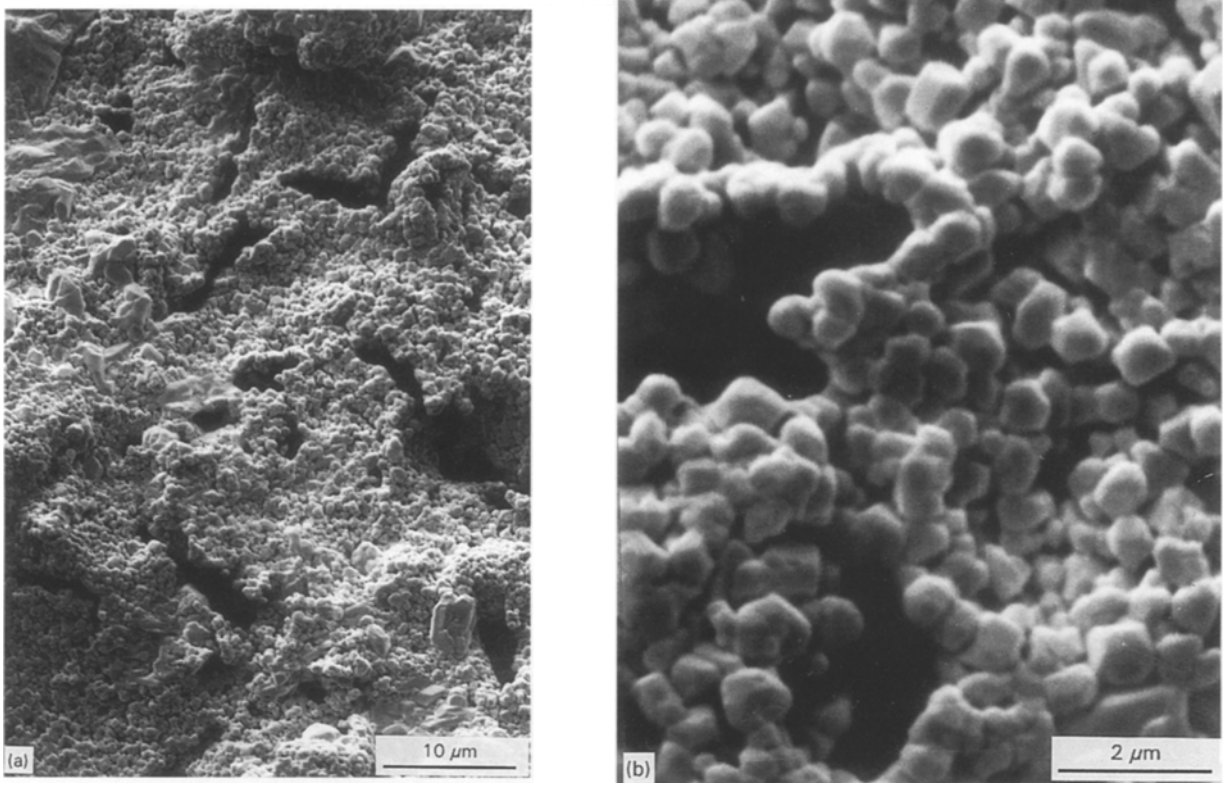


*Figure 4* Scanning electron micrographs of the outer surface of a hollow PZT sphere fired at 850 °C for 4 h, showing (a) porosity and (b) grains.

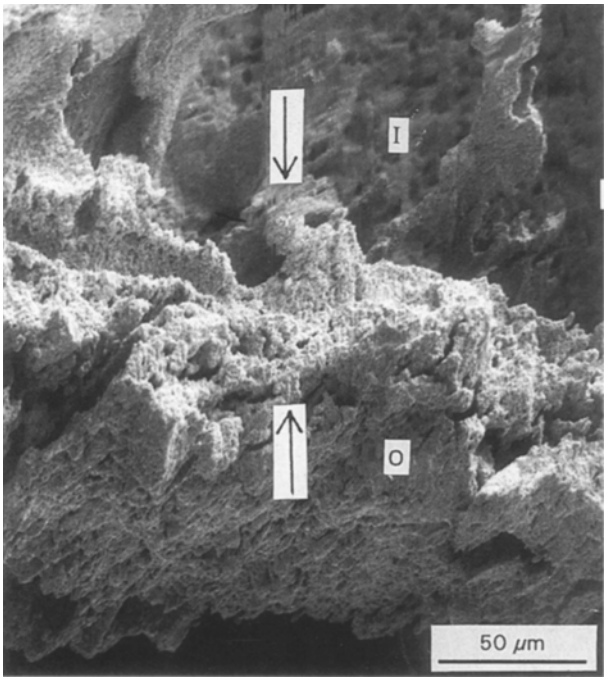


*Figure 5* Scanning electron micrograph of a broken PZT sphere fired at 850 °C for 4 h, showing the cross-section of the wall. The regions O and I correspond to the outer and inner surfaces of the sphere, respectively. The thickness of the wall is indicated by two arrows.

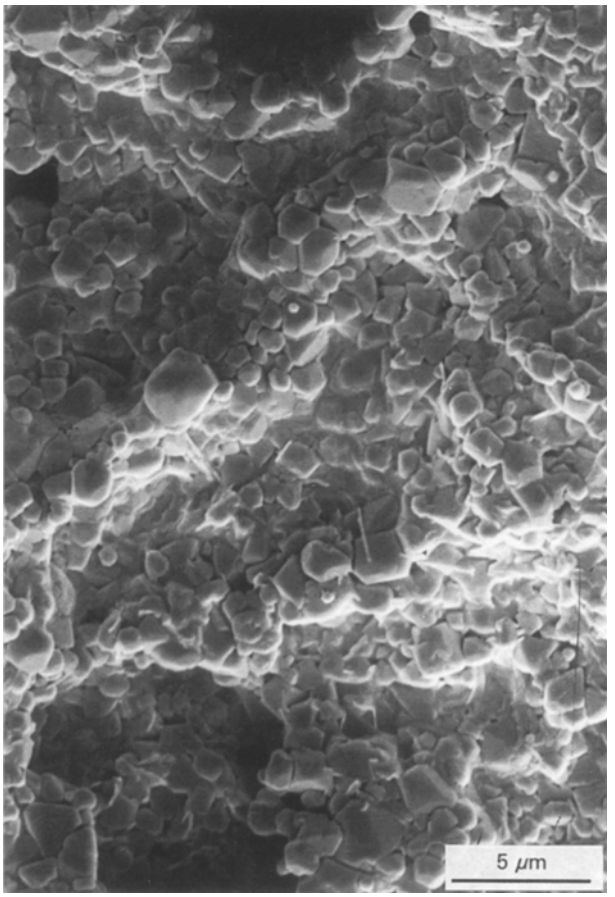


*Figure 6* Scanning electron micrograph of fracture surface of the wall of a PZT sphere fired at 850 °C for 4 h.

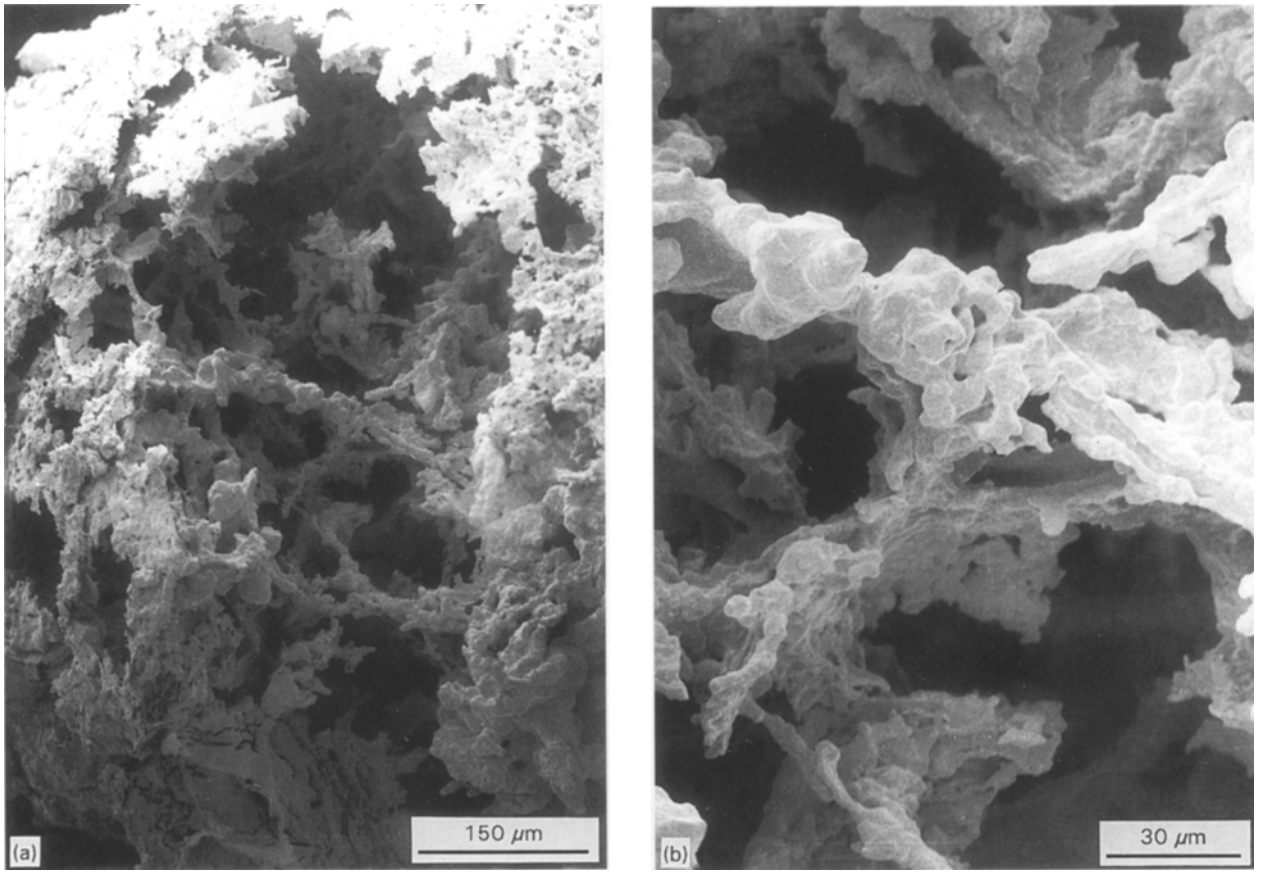


*Figure 7* Scanning electron micrographs of the inner surface of a hollow PZT sphere fired at 850 °C for 4 h. (a) Roughness on the inner surface, (b) rib-like structures.

TABLE II Planar coupling factor, $k_p$, of the transducer arrays made of hollow PZT spheres fired at 850 °C for 4 h

| | Number of spheres | | |
|---|---|---|---|
| | 3 | 5 | 6 |
| $k_p$ | 0.16 | 0.19 | 0.22 |

### 3.4. Planar coupling factor

The values of the planar coupling factor, $k_p$, of the transducer arrays fabricated by placing various numbers of hollow PZT spheres (fired at 850 °C for 4 h) at close-packed contacts in a plane are listed in Table II. For the array made of three PZT spheres (arranged in a triangular form), $k_p$ was 0.16. For six spheres, $k_p$ increased to 0.22. Although these $k_p$ values were lower than $k_p$ (typically about 0.5) of dense PZT discs, the arrays of hollow PZT spheres offer the possibility of development of light-weight transducers.

## 4. Conclusion

Hollow PZT spheres, 1–2 mm in size, have been prepared by using a simple, inexpensive sol–gel method. The PZT sol was absorbed by polyacrylamide spheres, inside which gellation took place. Upon firing at 850 °C for 4 h, hollow spheres of pure PZT perovskite phase were obtained. Close-packed, planar arrays of PZT hollow spheres were constructed and they can be useful as light-weight transducers in medical ultrasonics and underwater applications.

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