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Dielectric and Piezoelectric Properties of PZT Composite Thick Films with Variable Solution to Powder Ratios

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Abstract

The use of PZT films in sliver-mode high-frequency ultrasonic transducers applications requires thick, dense, and crack-free films with excellent piezoelectric and dielectric properties. In this work, PZT composite solutions were used to deposit PZT films >10 μm in thickness. It was found that the functional properties depend strongly on the mass ratio of PZT sol–gel solution to PZT powder in the composite solution. Both the remanent polarization, P_r, and transverse piezoelectric coefficient, $e_{31,f}$, increase with increasing proportion of the sol–gel solution in the precursor. Films prepared using a solution-to-powder mass ratio of 0.5 have a remanent polarization of 8 μC/cm^2, a dielectric constant of 450 (at 1 kHz), and $e_{31,f} = -2.8$ C/m^2. Increasing the solution-to-powder mass ratio to 6, the films were found to have remanent polarizations as large as 37 μC/cm^2, a dielectric constant of 1250 (at 1 kHz) and $e_{31,f} = -5.8$ C/m^2.

I. Introduction

Integrating PZT films into MEMS devices is a promising solution for miniaturized sensors, actuators, filters, and high-frequency (>30 MHz) ultrasonic transducers.[1–4] In some of these devices, thick, dense, and crack-free piezoelectric layers (> 10 μm) with good piezoelectric and dielectric properties are necessary to produce large generative forces with fast response speeds. However, it is difficult to process crack-free PZT films thicker than 10 μm on Si substrates using either chemical solution deposition[5,6] or most vapor deposition methods.[7]

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Techniques such as screen-printing,[8–10] tape-casting,[11,12] and aerosol deposition[13,14] have been used to fabricate thick films (> 15 μm).

On the other hand, the composite ceramic sol–gel film technique has been proved a successful technique to fabricate thick PZT films on various substrates in which, a chemical sol is generally loaded with appropriate concentrations of ceramic powers.[15–17] The resultant slurry type composite sol–gel will be spun onto the substrates followed by optimized pyrolysis and annealing steps. This approach enables to fabricate controllable, crack-free PZT thick films (>10 μm) with minimized stress levels between various layers. These advantages of composite ceramic sol–gel technique are due to the formation of a strongly bonded network between the sol–gel and ceramic particles along with enhanced adhesion with the substrates minimize the cracks in the resultant thick films. The success of this process was summarized initially by Barrow *et al.*[17], in ferroelectric PZT thick films having piezoelectric properties ($d_{33} \sim 325$ pC/N and $d_{31} \sim -80$ pC/N) comparable with those of the bulk PZT ceramics. However, controlling film porosity in this method is a serious issue to obtain superior dielectric and piezoelectric properties in thick PZT films. Later attempts by Corker *et al.*,[16] and Huang *et al.*,[18] improved partially the functional properties of thick PZT films by adding a Cu_2O/PbO liquid-phase sintering aid along with pH adjustments in the composite ceramic sol–gels. Recently, Dorey *et al.*,[19] demonstrated that the PZT sol–gel solution infiltration into the PZT composite films, processed following Corker *et al.*'s[16], work, could reduce partially the porosity in thick PZT films. The relative permittivity of the thick PZT films was found to be increased by both sol infiltration and the addition of sintering aid, with a slight reduction in dielectric loss values. However, a correlation between the effect of ceramic powder loading into sol–gel on the microstructure and electrical properties needs to be addressed to optimize viable processing conditions for thick PZT films for various ultrasonic biomedical imaging applications.

In this work, the effect of sol–gel solution to loading powder mass ratio of PZT composite solutions on the properties of thick composite PZT films were mainly investigated. For this purpose, a set of PZT films were prepared following composite ceramic sol–gel method with variable solution-to-powder mass ratios and without liquid phase sintering aids for the sake of film densification. Our work demonstrates that density of the thick PZT films can be increased to ~ 90% of the bulk PZT ceramics using appropriate solution-to-powder mass ratios combined with sol infiltrations without liquid phase sintering aid assistance. In addition, the microstructure, density, transverse piezoelectric, and dielectric properties of these films were compared and correlated systematically with the mass ratios in the composite ceramic sol–gels to obtain superior properties.

II. Experimental Procedure

In this work, a 2-methoxyethanol-based sol–gel $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) precursor was used as the matrix. To compensate for lead loss during heat treatments, a 20 mol% excess PbO was added to the solution adjusting its concentration to 0.3*M*. A PZT 5H powders were procured from Piezoelectric Technology Inc.,[20] to use as the loading powder in the composite sol–gel. However, the as-received powder has an average particle size of ~ 5 μm and hence, these ceramic powders were ball milled initially in an ethanol medium for 20 h at 200 rpm using a Fritsch Pulverisette (Fritsch GmbH, Idar-Oberstein, Germany) milling machine. After ball milling, the resultant powders were found to have an average particle size of ~ 400 nm using a particle size analyzer. Subsequently, these powders were mixed with PZT sol–gel precursor and subjected to further ball milling for 20 h to obtain well-dispersed composite solution. Finally, composite solutions with solution to powder mass ratios of 0.5, 1, 2, 4, and 6 were prepared. To estimate the particle sizes of the ball-milled PZT powders, Particle size distribution (PSD) analyzer (Particle Sizing Systems Inc., Santa Barbara, CA) was used. It was found that the average diameter of PZT particles decreased from 411 to 320 nm after a 20 h

milling in the composite solution with a mass ratio of 0.5. All other mass ratio composite solutions show similar average particle sizes (~ 250 nm) after 20 h milling.

The prepared composite solutions were spun at 2000 rpm for 30 s on platinum-coated silicon substrates using a Chemat spinner. Each PZT layer was subjected to a two-step pyrolysis scheme, one at 200°C for 2 min in air followed by second step at 400°C for 2 min in air. Subsequently, each layer was annealed at 750°C for 1 min in a rapid thermal annealer. The above process was repeated multiple times until the desired thickness of 15 μm was achieved. The structure of the films was examined using a Rigaku X-Ray diffractometer (Rigaku Corporation, Tokyo, Japan). As can be seen in the Fig. 1, the film has a well-crystallized pure perovskite phase. All other samples have similar patterns. The grain sizes in the films were monitored using a scanning electron microscope (SEM, S-3500N, Hitachi, Tokyo, Japan). As shown in Fig. 2, the average grain size in composite films was about 300–350 nm for a mass ratio of 0.5 and was ~ 200–250 nm for a mass ratio of 6. In addition, it was also clear that the films had some porosity. To minimize or reduce the voids for higher dense thick PZT films, we followed a vacuum infiltration of the PZT sol–gel solution process into the as prepared PZT composite thick films.[19] For this process, pure PZT precursor solution was evenly dispersed onto the film surface after each composite PZT layer was deposited. Subsequently a slight vacuum (~ 30 psi) was drawn on the film surface for 30 s. The vacuum may serve to improve the solution penetration into the pores.[21] Afterwards the sample was subjected to the spinning and pyrolysis procedures as mentioned above.

III. Results and Discussion

Circular Cr/Au electrodes with a diameter of 1.5 mm were deposited by sputtering as top electrodes onto the films for a quantitative comparison of the functional properties of these films. Dielectric properties were measured using an Agilent 4294A impedance analyzer and polarization field ($P-E$) hysteresis properties were evaluated using Radiant precision materials analyzer (Radiant Technologies, Albuquerque, NM). Figure 3 shows a comparison of the ferroelectric hysteresis of the films fabricated using composite solutions with solution-to-powder mass ratio of 0.5 and 6, respectively. In addition, the dielectric constant and remanent polarization values as a function of solution-to-powder mass ratio are shown in Fig. 4. The dielectric constant and remanent polarization values increased with the increasing proportion of PZT solution. With a solution-to-powder mass ratio of 0.5, the film exhibited ~8 μC/cm^2 remanent polarization value and this increased to ~37 μC/cm^2 for a mass ratio of 6. Similarly, the dielectric constant increased from 450 to 1250 at 1 kHz (the dielectric loss is about 0.03 at 1 kHz), which is much higher than the previously reported results (300).[1] These results are comparable with earlier works[16,19]; and indicate that comparable dielectric properties can be achieved with optimized solution-to-powder ratios combined with sol-infiltration procedure with no sintering aids.

The effective transverse piezoelectric coefficient ($e_{31,f}$) of these films were measured by a modified wafer flexure method.[22]

Figure 5 shows the calculated $e_{31,f}$ values of various PZT thin films with the method as a function of solution-to-powder mass ratio. As shown in the figure, the $e_{31,f}$ values increased with the solution-to-powder mass ratio increase in these films up to −6.0 C/m^2 which is very close to our earlier work (−6.5 C/m^2) of PZT thick films derived by pure sol–gel process,[20] but is somewhat less than the values (e.g., $e_{31,f} = -8.4$ C/m^2) obtained by other workers in thick films produced by a pure sol–gel process in 5 mm PZT40/60 films.[23]

To investigate the cause of above improvements in film properties, densities of the films with different ratios were measured. For this purpose, the PZT films were first cut into 10 mm × 10

mm squares by a dicing saw. The thickness of the films (over 10 μm) was determined using a SEM (S-3500N, Hitachi), so that the volume could be determined. Then, the parts were immersed in a 20% KOH solution at a temperature of 80°C. This resulted in the PZT films peeling off from the silicon substrates in ~10 min causing a slight damage to the films.[24] Finally the mass of the films was measured using a precision electronic balance (OHAUS Corp, Pine Brook, NJ) after clearing $Pt/Ti/SiO_2$ debris and drying. Earlier, Nelson detailed various sets of dielectric mixture equations considering the dielectric constant and density of different materials and can often be used to predict the density of films from its dielectric constant value or *vice versa*.[25] In our case, an approximate linear relationship between film densities and the square root of the film dielectric constants was noticed indicating a complex refractive index mixture rule applies fairly well at various mass ratios. As shown in the Fig. 6, the density of the fabricated film increased for a larger solution-to-powder ratio in the composite solution. At a mass ratio of 0.5, the average density of the film is only 5900 kg/m^3, increasing to 6700 kg/m^3 at a mass ratio of 6, which is about 90% of bulk PZT-5H material (7500 kg/m^3). The increase in $e_{31,f}$ values with higher concentrations of loaded power mass ratios is definitely due to decrease in film porosity thereby increasing the d_{31}.[26] Moreover, Maki *et al*.[27] found that decrease in PZT thick film density leads to reduction in the remanent polarization values. Therefore, the improvements in the PZT film dielectric and piezoelectric properties were mainly due to increased density with reduced porosity. The porosity of the film, as discussed above, can be reduced by using a larger mass ratio composite solution combined with a vacuum infiltration procedure. Our experimental results indicate that a mass ratio of around 4 is an optimal value to obtain thick (> 10 μm), dense, and crack-free PZT films with superior piezoelectric and dielectric properties in this process. There are mainly three reasons: (i) The dielectric constant (1200) and transverse piezoelectric values (−6 C/m^2) in the films with mass ratios around 4 are comparable to typical randomly oriented PZT thin film values.[14,16] (ii) In the thick films with mass ratio > 4, the remanent polarization (P_r) values of the films were observed to be saturated. (iii) The viscosity of the composite solution decreases with an increase in the proportion of PZT sol–gel. This results in that the higher the proportion of the PZT solution in the composite; the larger the number of spin/infiltration steps would be needed to obtain thick films (~10–20 μm). For example, each layer thickness was ~2 μm with a composite solution of mass ratio equals to 1, whereas, only 0.5-μm-thick film could be obtained with a mass ratio of 4. This implies that the quality of the films will be more difficult to be maintained with higher proportion of the PZT solution in the composite since each extra layer has the risk of impairing the films quality. In addition, the higher dielectric constant of the thick films can be obtained by loading high dielectric constant powder and using as same composition sol–gel solution as ceramics.

IV. Summary

In summary, it has been shown in this study that increasing of mass ratio of PZT sol–gel solution to PZT powder in the composite solution gives rise to improved piezoelectric and dielectric properties without using any liquid-phase sintering aids. PSD analysis experiments confirmed that particle size of the composite solution has an insignificant role for the improvements. The improvements are primarily due to homogeneity in the slurry composition that reduced both cracking and elimination. Moreover, vacuum infiltration of sol–gel solution into films after each layer deposition reduced void density. As a result, the overall film density increased with enhanced piezoelectric and dielectric properties in thick PZT films. The improved properties make PZT composite films promising candidates for high frequency ultrasound transducers. Moreover, the relative low density of the PZT films (~70%–90%) results in low acoustic impedances. This property makes the films better matching to human tissues, which is favorable to thickness-mode broadband transducers capable of medical imaging applications.

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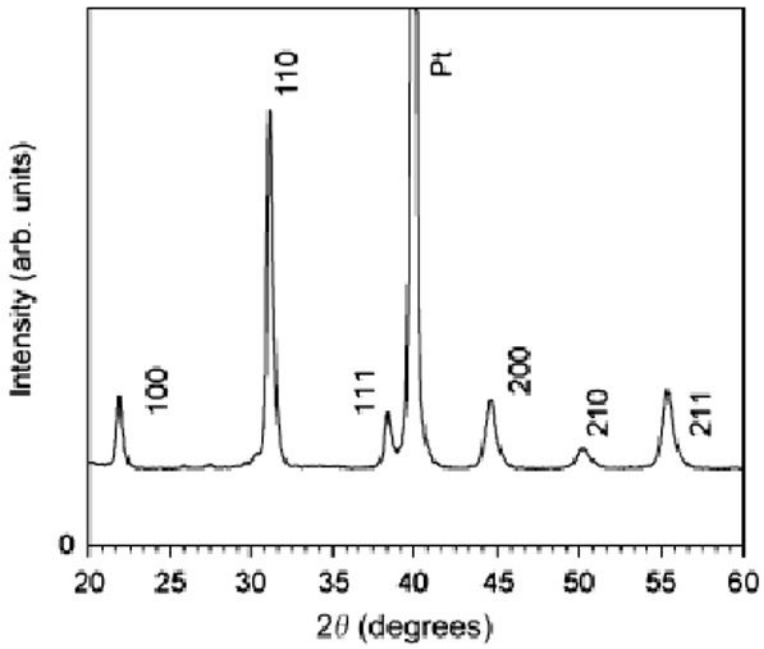

Fig. 1.
X-Ray Diffractometer pattern of a PZT thick film fabricated from the PZT composite with the solution to powder mass ratio of 2.

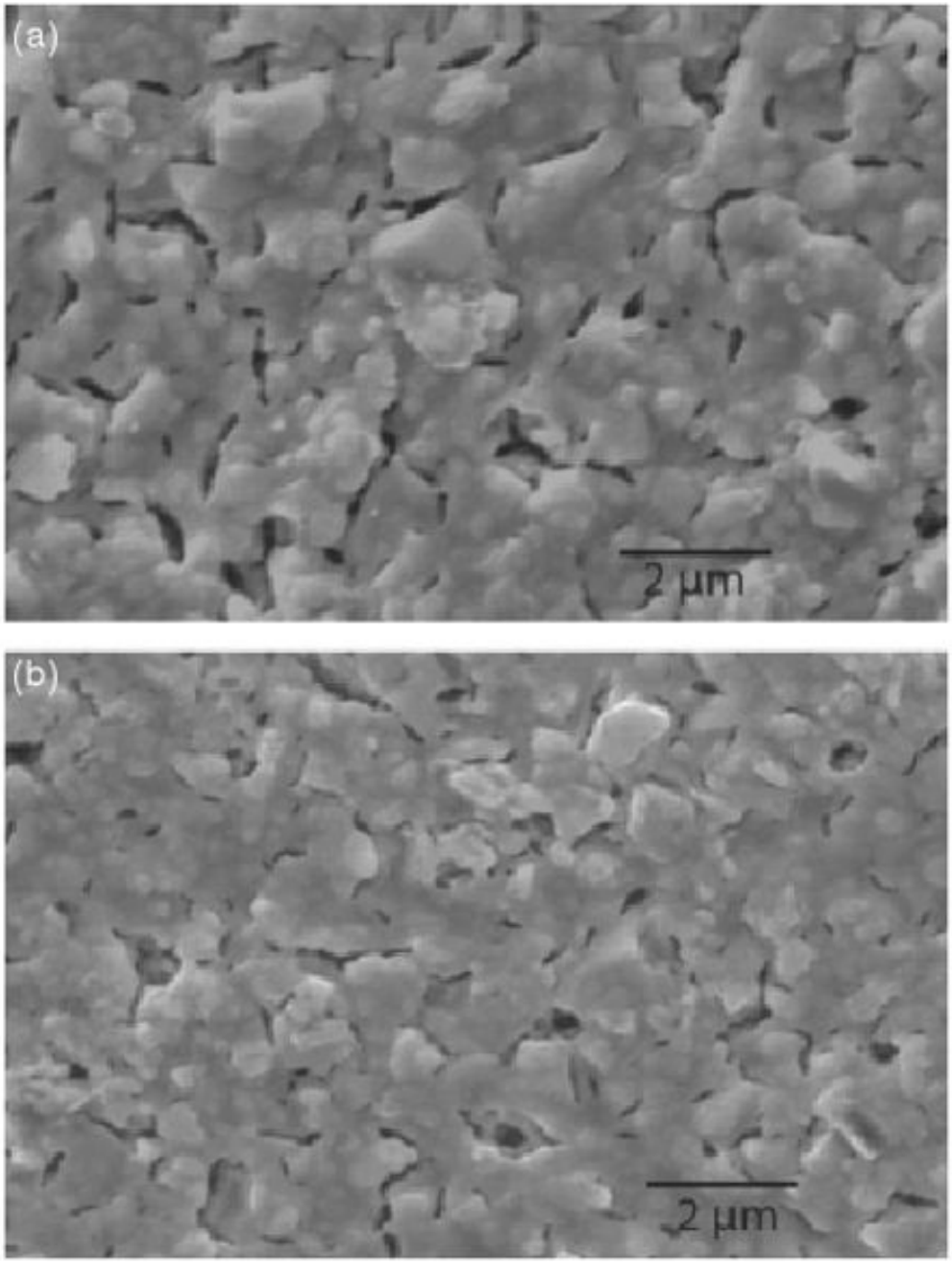

Fig. 2.
Scanning electron microscope pictures of PZT thick films fabricated from the PZT composites with solution to powder ratio of 0.5 (a) and 6 (b).

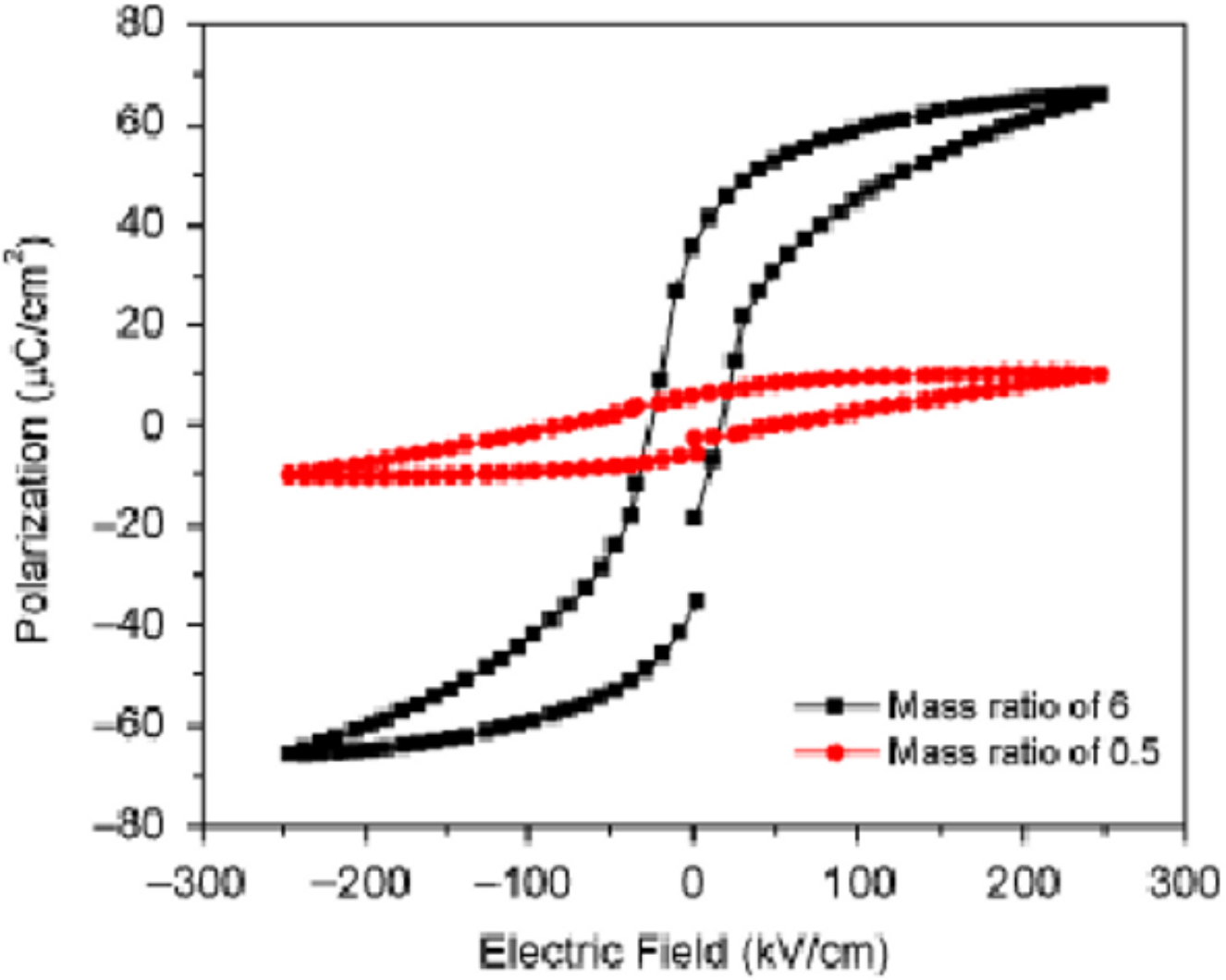

Fig. 3.
Ferroelectric (P-E) hysteresis loops of the PZT thick films fabricated from the composites with solution-to-powder mass ratio of 0.5 and 6.

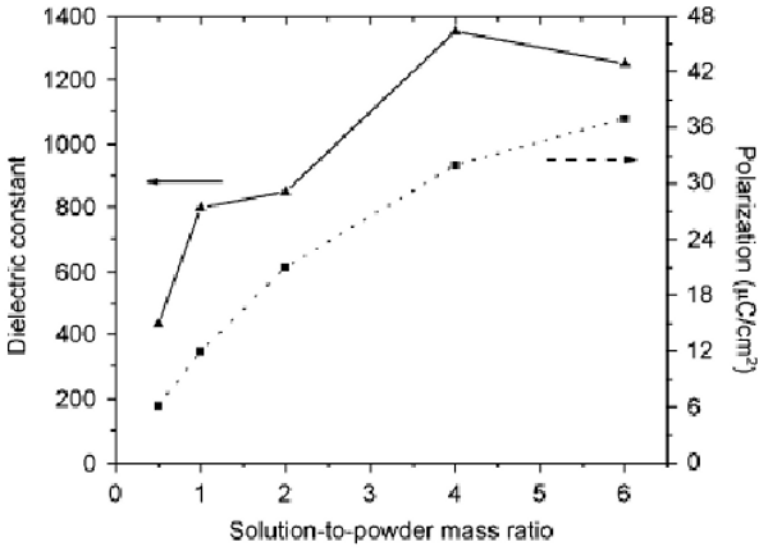

Fig. 4.
Variation of dielectric constant and remanent polarization of the thick films with solution-to-powder mass ratios.

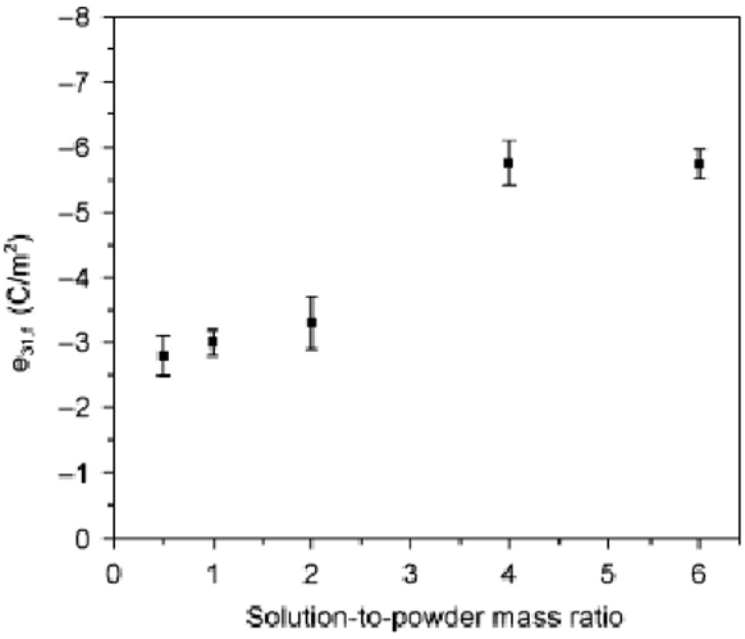

Fig. 5.
Variation of $e_{31,f}$ values with solution-to-powder mass ratios.

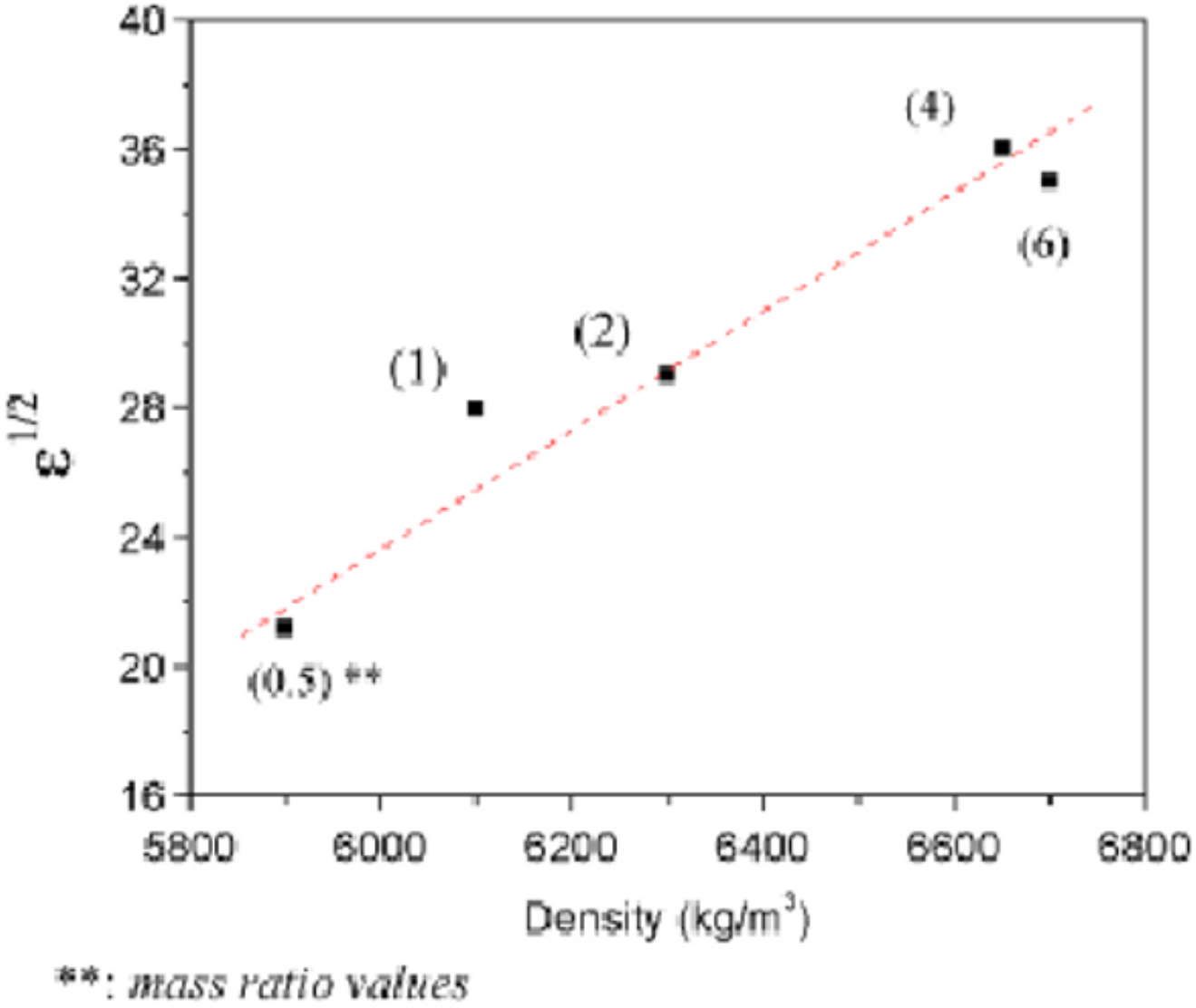

Fig. 6.
Variation of film dielectric constants with film densities.