Article

Effects of Powder Phase Properties on Pb(Zr, Ti)O_3/Pb(Zr, Ti)O_3 Sol-Gel Composites

Makiko Kobayashi [1,*], Hiroto Makino [2] and Kei Nakatsuma [1]

[1] Faculty of Advanced Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan; e-mail@e-mail.com
[2] Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan; e-mail@e-mail.com
* Correspondence: kobayashi@cs.kumamoto-u.ac.jp; Tel.: +81-96-342-3628

Abstract: The effects of the dielectric constant of the powder phase on lead zirconate titanate (PZT)/PZT sol-gel composite films were investigated to tailor their electrical properties. Three types of PZT powders were used to fabricate three different PZT/PZT sol-gel composite films. The PZT powders had the same electromechanical coupling coefficient but different relative dielectric constants. The PZT/PZT films were fabricated on a 3 mm-thick titanium substrate using an automatic spray coating system, and their properties were investigated. The relative dielectric constants of the PZT/PZT films were successfully controlled by tailoring the properties of the PZT powder phase. However, the piezoelectric constants showed a tendency different to those of the raw powders, because of the poor poling degree. This was overcome by conducting poling at a high temperature.

Keywords: piezoelectric material; dielectric constant; piezoelectric constant

1. Introduction

Sol-gel composite materials have been developed to fabricate thick films without cracks [1]. The thick porous films have helped realize ultrasonic transducers with a relatively low center frequency (in the range of 2–20 MHz); such transducers are suitable for non-destructive testing (NDT) applications. Owing to the porosity of sol-gel composite films, ultrasonic transducers fabricated using the sol-gel spray technique exhibit high-temperature durability, curved surface applicability, reasonable signal strength, and high signal-to-noise ratio (SNR), in addition to the suitable frequency range for NDT. Therefore, sol-gel composite-based ultrasonic transducers have a good potential for industrial and medical applications [1–9].

Sol-gel composite materials are prepared using two raw materials: a sol-gel solution and a piezoelectric powder. Each phase affects the overall properties of the composite. Various sol-gel composites have been investigated. For example, sol-gel composites made of lead zirconate titanate (PZT) powders and PZT sol-gel solution, namely the PZT/PZT composite, are expected to be useful in many applications, as they exhibit a high sensitivity among sol-gel composites with poling facility [1–4]. Although the relatively low maximum operating temperature (up to 200 °C) of PZT/PZT composites is a disadvantage, many applications do not require operating temperatures above 85 °C, and it is preferable to have a certain temperature stability [10–12]. Therefore, PZT/PZT composites seem attractive for applications such as imaging and structural health monitoring.

The dielectric properties of PZT/PZT composites should be controlled to tailor the electrical impedance depending on the application for a high electrical output power. It is difficult to obtain reproducible results using the conventional manual spray coating technique. Therefore, an automatic spray coating system has been developed for better reproducibility [13-15]. However, controlling the dielectric properties of PZT/PZT composites remains challenging. Previous studies

have failed in this regard because of the particle size difference and top electrode quality difference The dielectric constant of PZT/PZT films was controlled through the PZT powder phase by maintaining the fabrication conditions as much as possible [16], though in the past report, ultrasonic measurement results were mainly discussed and there was no dielectric property discussion. In this paper, the difference in the electrical properties due to the PZT powder phase was evaluated.

2. Sample Fabrication

Three types of PZT powders, namely HIZIRCO A(A), HIZIRCO L(L), and HIZIRCO MPT(MPT), were purchased from Hayashi Chemical Industry Co., Ltd. The particle size was specified as 0.6 μm. Table 1 lists the material properties of each powder.

Table 1. Properties of PZT powders.

Material property	HIZIRCO A	HIZIRCO L	HIZIRCO MPT
ε_r	5500	1800	1300
k_{33}(%)	70	70	70
d_{33} (×10^{-12} m/V)	660	400	290
g_{33} (×10^{-4} Vm/N)	136	251	252

The piezoelectric constant (d_{33}) values of A, L, and MPT are high, medium, and low, respectively, whereas there is no significant difference in the electromechanical coupling coefficient k_{33}. The piezoelectric constant (g_{33}) values of L and MPT are higher than that of A. The three PZT powders were mixed in a laboratory-made PZT sol-gel solution. After ball milling, the mixture was sprayed onto titanium substrates with a thickness of 3 mm, a length of 30 mm, and a width of 30 mm. An automatic spray coating system was used for the spray coating process to achieve a uniform coating in all cases. Subsequently, a thermal treatment, a drying process, and a firing process were conducted at 150 °C using a hot plate and at 650 °C using an electrical furnace. The spray coating and thermal treatment were repeated until the film reached the desired thickness. The film thickness was confirmed using a micrometer. After fabricating the films, poling was conducted through a positive corona discharge process to impart piezoelectricity for the sol-gel composite films. The output voltage was approximately 23 kV. It is difficult to measure the electrical field applied to the film, because electrical devices are easily destroyed by corona discharge. After poling, a 10-mm square silver top electrode was fabricated on each sample by a dispenser system to reduce the top electrode quality difference. Figure 1 shows the typical optical images of each sol-gel composite material. Except for the film color difference because of the piezoelectric powders, no significant difference was observed.

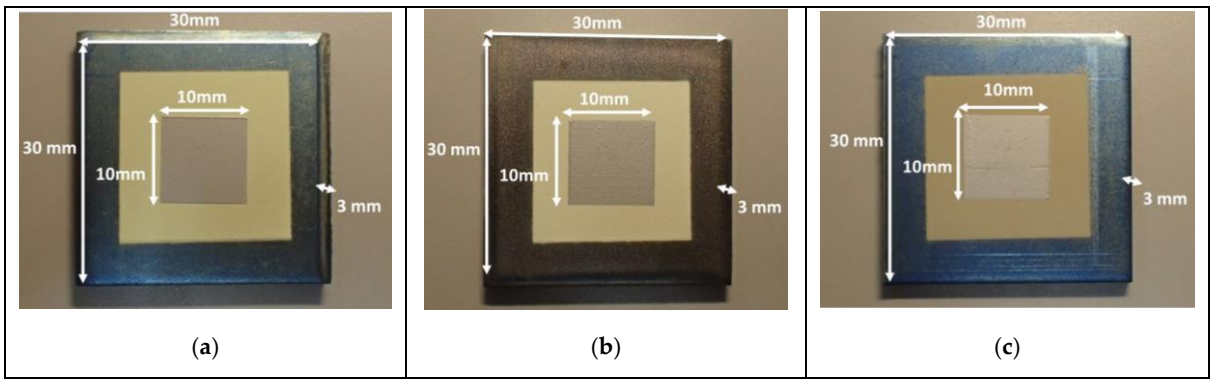

Figure 1. (Color online) Optical images of (**a**) A/PZT (**b**) L/PZT, and (**c**) MPT/PZT films grown on 30 mm × 30 mm × 3 mm titanium substrates.

3. Results and Discussion

The capacitance was measured using an LCR meter, and the relative dielectric constant ε_r was calculated using the following equation:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A}, \quad (1)$$

where C is the capacitance, d is the film thickness, ε_0 is the dielectric constant of vacuum, and A is the area of the top electrode. The ε_r values of the A/PZT, L/PZT, and MPT/PZT films were found to be 516, 465, and 326, respectively, as shown in Table 2, showing a similar tendency with those of the piezoelectric powders; the difference was due to the porosity.

The average method [17] can be used for sol-gel composite properties, though the properties of pure sol gel materials cannot be reliably measured. A cube model was proposed to determine the properties of 0–3 composites using parallel and series equations, and in previous studies, the theoretical values from the cube model showed reasonable agreement with the experimental values concerning the dielectric constant of PZT/PZT films [1,3]. The dielectric constant of the PZT/PZT sol-gel composites was calculated using the following equation:

$$\varepsilon_r = \frac{\varepsilon_{r1}\varepsilon_{r2}}{(\varepsilon_{r2}-\varepsilon_{r1}){V_1}^{-1/3}+\varepsilon_{r1}{V_1}^{-\frac{2}{3}}} + \varepsilon_{r2}\left(1-{V_1}^{\frac{2}{3}}\right), \quad (2)$$

where ε_{r1} is the relative dielectric constant of the PZT powder phase, ε_{r2} is the relative dielectric constant of the PZT sol-gel phase, and V_1 is the volume fraction of the PZT powder phase.

The results might not be accurate, as the phase of the pores was ignored. If spherical pores are homogeneously dispersed throughout the PZT sol-gel phase, the PZT sol-gel phase can be considered as another air/PZT 0–3 composite. Therefore, the relative dielectric constant of the modified sol-gel phase was first calculated using Eq. (2), taking ε_{r1} as the relative dielectric constant of the air phase, ε_{r2} as the relative dielectric constant of the PZT sol-gel phase, and V_1 as the volume fraction of the air phase against the PZT sol-gel phase. The relative dielectric constant of the modified sol-gel composite was then calculated using Eq. (2), taking ε_{r1} as the relative dielectric constant of the PZT powder phase, ε_{r2} as the relative dielectric constant of the modified sol-gel phase, and V_1 as the volume fraction of the PZT powder phase. Thus, with the double-cube model, the effect of pores is considered, and the accuracy of the calculation can be improved. Figure 2 shows the typical results. The solid line indicates the fitting curve derived from the three experimental values, and the dashed line indicates the curve obtained using Eq. (2) (best fitting method). For the best fitting method, the volume fraction of the air phase, the relative dielectric constant of the PZT sol-gel phase, and molar ratio of the PZT powder to the PZT sol-gel were estimated to be 0.25, 400, and 7:3, respectively. Figure 2 shows that the calculation results are in good agreement with the best fitting results. However, the simulation results are not in good agreement with the experimental results. Following are the possible reasons for the same: measurement errors of film thickness due to surface roughness, measurement errors of capacitance due to the thick silver paste top electrode,

uncertainty in the volume fraction of the air phase, relative dielectric constant of the PZT sol-gel phase, and/or molar ratio of the PZT powder to the PZT sol-gel. However, the volume fraction of the air phase reasonably agreed with previous SEM cross-sectional measurement results. Owing to the automatic spray coating system, the surface roughness was within ±5 μm. This value is less than that realized when using the manual spray system, resulting in an efficient dielectric control, even though the error increases with the increase in the dielectric constant of the powder.

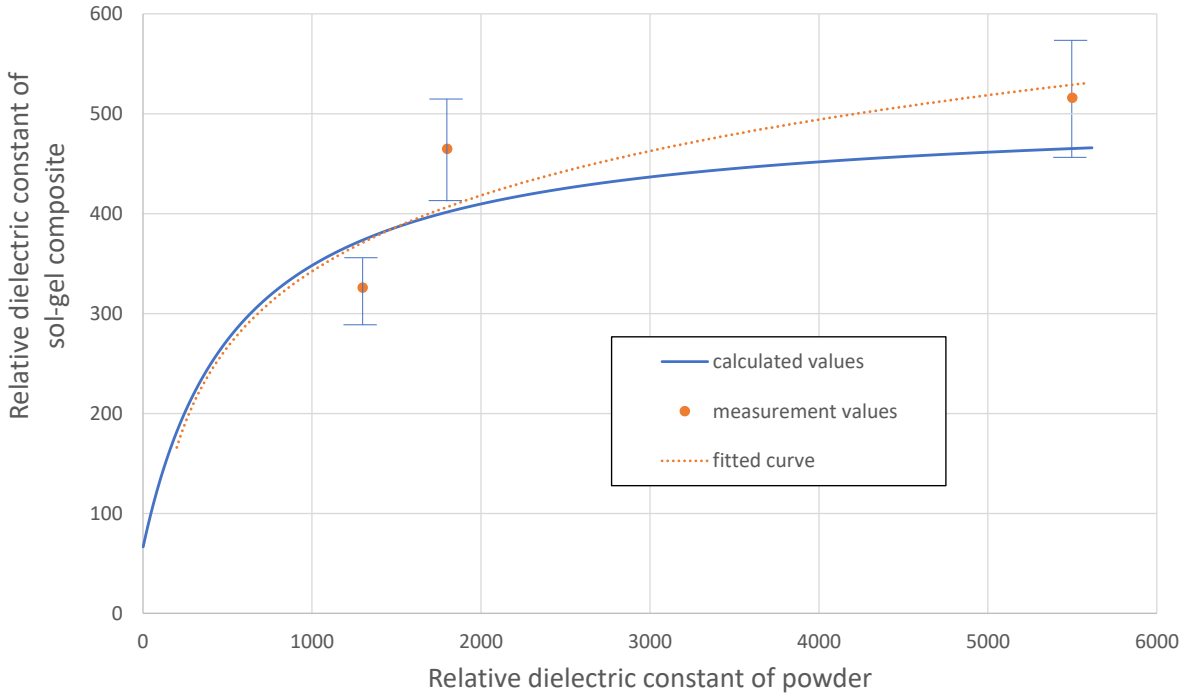

Figure 2. (Color online) Typical relative dielectric constant calculation results of PZT/PZT films from the double-cube model considering the effect of pores, as a function of the relative dielectric constant of the powders.

The piezoelectric constants were also measured and calculated. Table 2 lists the measured film properties. The piezoelectric constant of the L/PZT film is the highest, even though the piezoelectric constant of A is higher than that of L. This tendency was reproducibly observed, and as the dielectric constant of PZT sol-gel is much lower than those of bulk ceramics [18] (decreasing further as it becomes porous), the electrical field might not have been sufficiently applied to the PZT powders during the poling process when the dielectric constant of the PZT powder is too high. The piezoelectric constants of the PZT/PZT films showed a better agreement with those of the PZT powders because of the low dielectric constant. The piezoelectric constant of the A/PZT film can be improved by modifying the poling conditions. With the automatic spray coating system, 20 μm-thick PZT/PZT films were fabricated on 30 mm × 30 mm × 3 mm titanium substrates by poling at 150 °C; the previous samples were poled at room temperature. Other poling conditions, such as the poling voltage and distance between the sample and the needle, were unchanged. Table 3 lists the results of the measured piezoelectric constant. The dielectric constant of the A/PZT film is comparable to that of the L/PZT film, thus proving our hypothesis. Poling is often conducted at a high temperature, e.g., approximately half the Curie temperature, to achieve a sufficient poling degree, even though domain wall switching theory is still under investigation. The results might have been influenced by

the critical size reduction for nucleus formation during domain growth.

Table 2. Properties of PZT/PZT films with the top electrode fabricated using a dispenser.

Film property	A/PZT	L/PZT	MPT/PZT
Thickness (μm)	47	49	49
Capacitance (nF)	9.71	8.40	5.88
ε_r	516	465	326
d_{33} (×10⁻¹² m/V)	44.8	51.1	34.9
g_{33} (×10⁻⁴ Vm/N)	98.2	124	121

Table 3. Properties of PZT/PZT films poled at high temperature.

Film property	A/PZT	L/PZT	MPT/PZT
Thickness (μm)	20	20	20
d_{33} (×10⁻¹² m/V)	24.4	24.0	17.8

4. Conclusions

Three types of PZT powders with different dielectric constants were used to fabricate PZT/PZT sol-gel composite films on a 3 mm-thick titanium substrate using an automatic spray coating system. The effects of powder phase properties on the fabricated films were investigated. The relative dielectric constants of the PZT/PZT films were successfully controlled by tailoring the properties of the PZT powder phase, showing a reasonable agreement with the simulated results obtained using the double-cube model considering the presence of air inside the films. The piezoelectric constant of the films was lower than expected when the dielectric constant of the PZT powder phase was too high. This was overcome by poling at a high temperature (instead of room temperature).

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