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Structure and electrical properties of multilayer PZT films prepared by sol–gel processing

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Abstract

Multilayer PZT(Zr:Ti = 52:48) films were prepared by the repeated process of spin-coating and firing at 600°C of a PZT sol with various heating rates between 20 and 200°C min^{-1}. Their structural and dielectric properties were examined. The multilayer film prepared with the heating rate of 50°C min^{-1} shows the highest dielectric constant and a smooth surface with no surface cracks. High-resolution TEM (HRTEM) observations of an as-deposited PZT film indicate nucleation of perovskite and pyrochlore crystals in the amorphous matrix. The perovskite crystals are found to form through the initial construction of {110} planes.

1. Introduction

PZT (lead zirconate titanate, $Pb(Zr,Ti)O_3$) films with a thickness of a few micrometers and more are often required in the field of piezoelectric actuators and sensors [1,2]. Through stacking of thin layers by repetition of the spin-coating and firing process of a PZT sol with a fast heating rate of 100°C min^{-1}, thick PZT films on MgO substrates could be prepared without formation of surface cracks [3]. This result was considered to be caused by a soft porous part formed in the bottom part of each layer which was revealed by a cross-sectional TEM observation [4,5]. In order to make the fabrication process of the multilayer films more efficient, each heating and firing time should be selected as short as possible not to degrade their electrical properties. This paper reports the dielectric property of multilayer PZT films prepared with different heating rates, and also detailed microstructural characterizations performed by high resolution transmission electron microscopy (HRTEM).

2. Experimental procedures

Lead acetate trihydrate ($Pb(CH_3COO)_2{\cdot}3H_2O$, LA), titanium tetraisopropoxide ($Ti(iso\text{-}OC_3H_7)_4$, TIP) and zirconium tetra *n*-propoxide ($Zr(O\text{-}n\text{-}C_3H_7)_4$, ZNP) were used as organic precursors to obtain a 0.4 M PZT (Zr:Ti = 52:48) solution. Firstly, 3 ml of diethanolamine (DEA) was dissolved into 75 ml of isopropyl alcohol (IP) in a 200 ml-beaker in an Ar atmosphere at room temperature, and then ZNP and TIP were added and mixed by a magnetic stirrer. Next, LA with an excess of 10 mass% was slowly and completely dissolved into the solution. Finally, the total volume of the solution was adjusted to 100 ml with IP and stirred for two days at room temperature.

The PZT sol was spin-coated on a SiO_2/Si substrate (15 mm×15 mm) with a sputter-deposited Pt(0.15 μm)/Ti (0.05 μm) layer at 5000 rpm for 20 s in air, and then fired at 600°C for 10 min in air, in about 5 min after the spin-coating, using a furnace with infrared heating sources (QHC-P610C, Shinku-Riko Inc., Japan). Heating rates of 50, 100 and 200°C min^{-1} were used. The cooling rates were set to be −50, −100 and −200°C min^{-1}, corresponding to the above heating rates. One specimen was prepared by a heating rate of 20°C min^{-1} through a conventional furnace. The multilayer PZT films were prepared by 8–15 times repetition. The

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change of dielectric and structural properties by heat treatment for 2 h at 700°C in air was further examined.

The structural analysis was done by XRD (CuK_α, 40 kV, 200 mA), FE-SEM (Hitachi S4200) and high-voltage electron microscope (HVEM, JEM-ARM1250, 1250 kV, University of Tokyo). The dielectric properties of the films were analyzed by a LCR meter (Ando AG-4306, Japan).

3. Results and discussion

3.1. XRD analysis and surface observation of the multilayer PZT films

XRD patterns are shown in Fig. 1 for the films with 15 coating layers prepared with heating rates of 50, 100 and 200°C min^{-1}. The pyrochlore phase (Py) is found in the film (a), while only the perovskite phase (Pv) is observed in the film (c). A small amount of pyrochlore phase [Py (440)] is present in the film (b). The tetragonality of perovskite phase is larger in Fig. 1(a) than in Figs. 1(b) and (c). Fig. 2 shows constituent phases for the films prepared at heating rates of 20 and 200°C min^{-1}. A considerable amount of pyrochlore phase is found in Fig. 2(b), while the perovskite phase is dominant in Fig. 2(a). The above results show that too slow or too fast heating rates should be avoided in preparing the PZT films composed of the desirable perovskite phase.

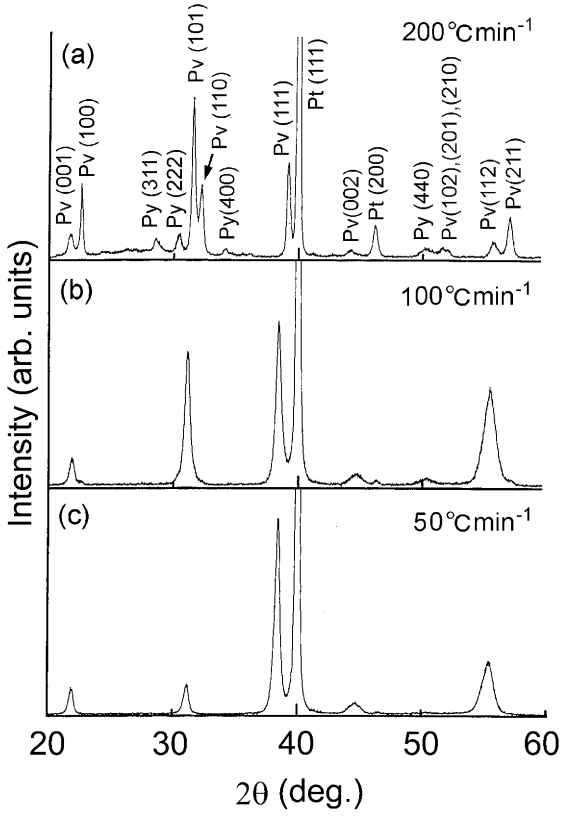

Fig. 1. XRD patterns of the as-deposited multilayer PZT films with 15 coating layers.

The lattice constants are collected in Table 1.

As shown by Fig. 3, the heat treatment at 700°C little affects the transformation of the pyrochlore phase to the perovskite phase.

Surface appearances are shown in Fig. 4 for the as-deposited films of Fig. 2. Cracks are observed in the film (a) prepared with the slowest heating rate of 20°C min^{-1}, while no cracks are found in the film (b) prepared with the fastest heating rate of 200°C min^{-1}. The surface of film (b) is, however, rough. This image indicates that the structure is porous like the structure observed in our previous experiments [4,5]. The heating rate of 50°C min^{-1} [Fig. 1(c)] also yields no cracks in the surface as shown in Fig. 5.

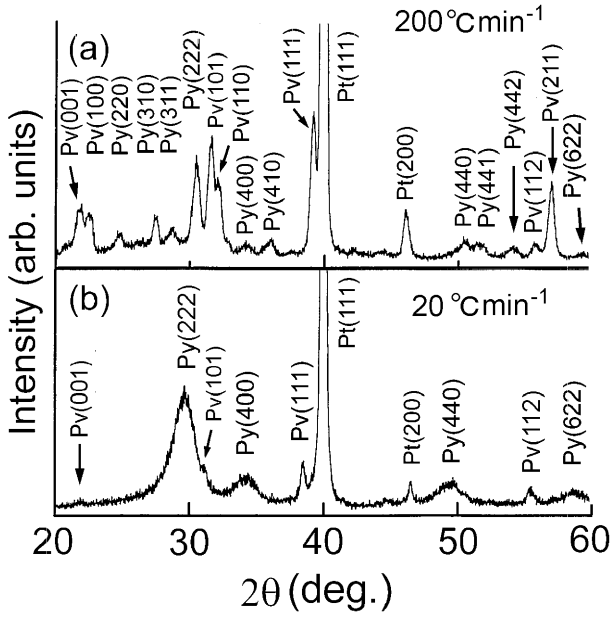

Fig. 2. XRD patterns of the as-deposited multilayer PZT films with eight coating layers.

Table 1
Lattice constants calculated from Figs. 1 and 2

Figures	Perovskite phase	Pyrochlore phase
Fig. 1(a)	a = 0.393 nm, c = 0.410 nm, c/a = 1.04, $(a^2c)^{1/3}$ = 0.398 nm	–
Fig. 1(b)	a = 0.406 nm	–
Fig. 1(c)	a = 0.406 nm	–
Fig. 2(a)	a = 0.394 nm, c = 0.407 nm, c/a = 1.03, $(a^2c)^{1/3}$ = 0.398 nm	a = 0.103 nm
Fig. 2(b)	–	a = 0.104 nm

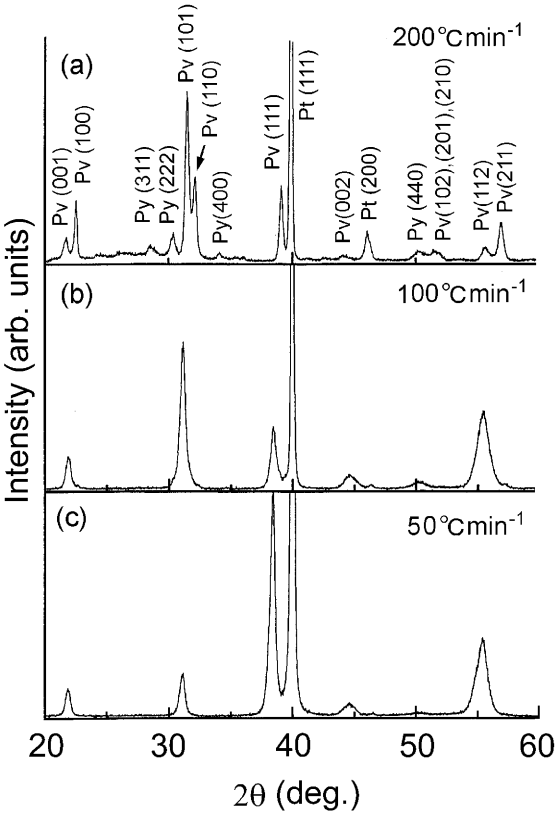

Fig. 3. XRD patterns of the multilayer PZT films heat-treated at 700°C for 2 h after the deposition of 15 coating layers.

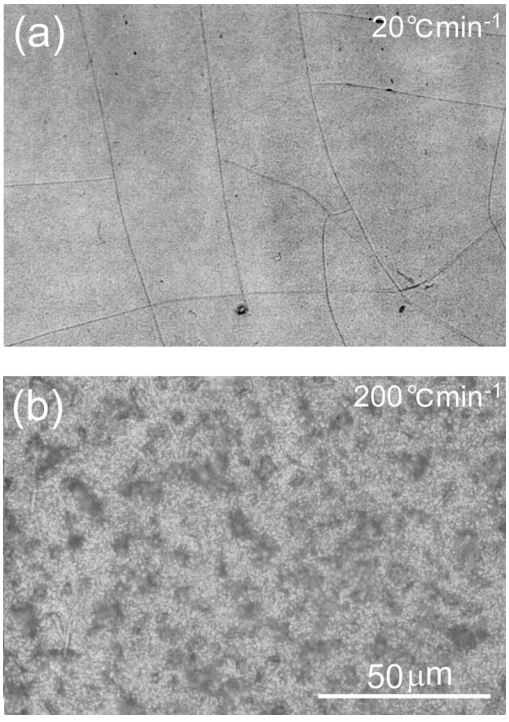

Fig. 4. Surface optical micrographs of the as-deposited multilayer PZT films with eight coating layers.

3.2. SEM and TEM observations

A cross-sectional SEM observation of the as-deposited PZT film prepared at a heating rate of 50°C min^{-1} shows that the coating structure is dense (Fig. 6). From the SEM observation, the average film thickness was measured to be 1.84 μm, which corresponds to the thickness of 0.123 μm for each single layer.

From an electron diffraction pattern of a region containing both phases (Fig. 7), the lattice constants of the pyrochlore and perovskite phases were determined to be a = 1.02 nm and a = 0.411 nm, respectively, using Si for the calibration of camera length. The pyrochlore crystals and the perovskite crystals show close lattice plane spacings, but Py(400) (0.256 nm) and Pv(111) (0.237 nm) can be distinguished from each other, within the

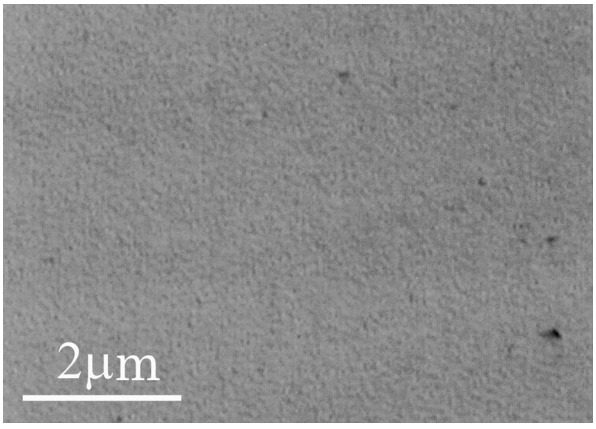

Fig. 5. Surface optical micrograph of the as-deposited PZT film with 15 coating layers prepared with a heating rate of 50°C min^{-1}.

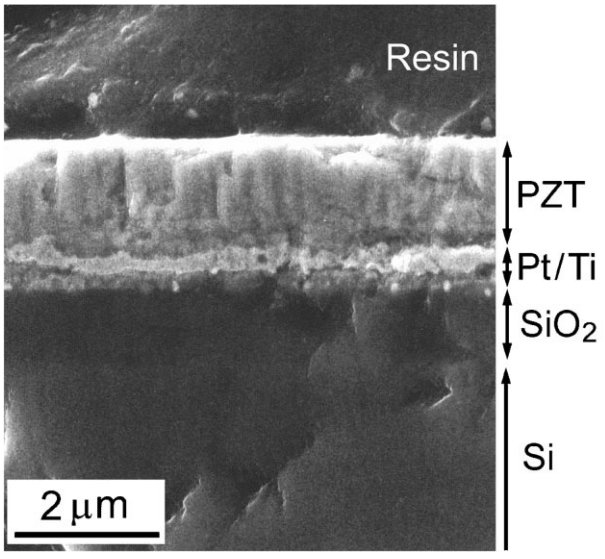

Fig. 6. Cross-sectional SEM image of the multilayer PZT film shown in Fig. 5.

experimental error of a few percent. HRTEM micrographs in Fig. 8 show the place where the pyrochlore and perovskite grains are adjacent. The marks of Pv and Py are assigned to the grains by analyzing the plane spacings.

In Fig. 8(b), the Pv (211) lattice planes (0.16 nm) are found to be parallel with the Py (400) lattice planes (0.26 nm), which suggests that the grain A is growing into the grain B through the rearrangement of constituent atoms in the lattice planes running parallel to each other.

Fig. 9 shows that a perovskite crystal, marked by the arrow 'A', is directly nucleating from the amorphous matrix. In the place marked by the arrow 'C', the (101) planes (0.29 nm) of grain A is growing into the amorphous matrix. This observation indicates that the perovskite crystals form through the initial construction of the closest packed planes. Although the place marked by the arrow 'B' has a crystal structure different from perovskite, the formation of lattice planes (0.27 nm)

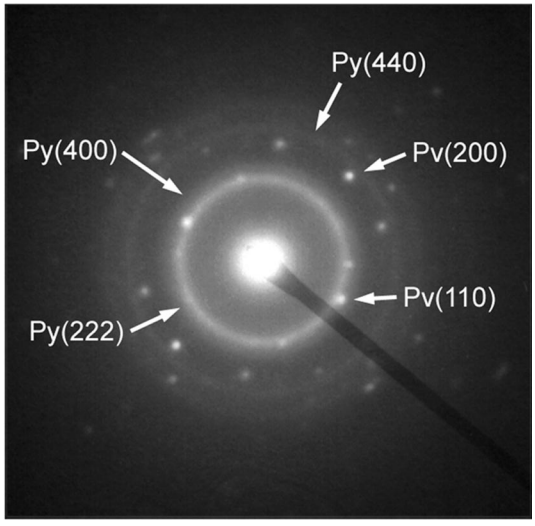

Fig. 7. Electron diffraction pattern of a film prepared with a heating rate of 100°C min^{-1}.

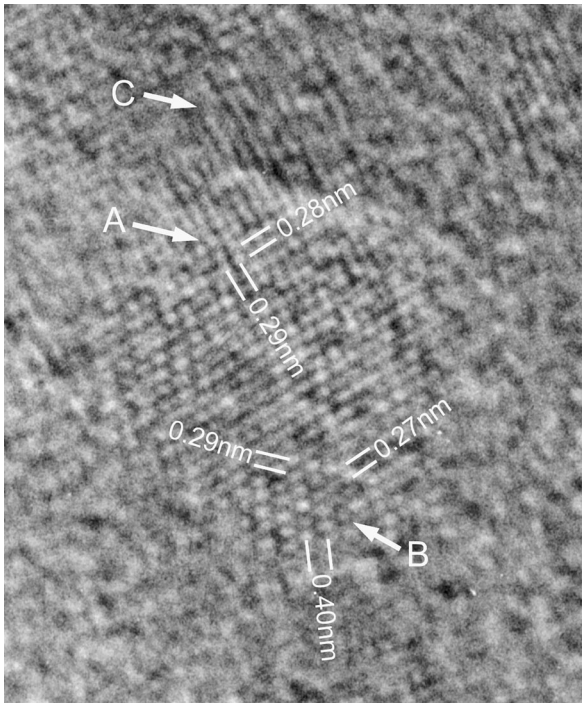

Fig. 9. HRTEM image of an as-deposited PZT film prepared at 600°C in air.

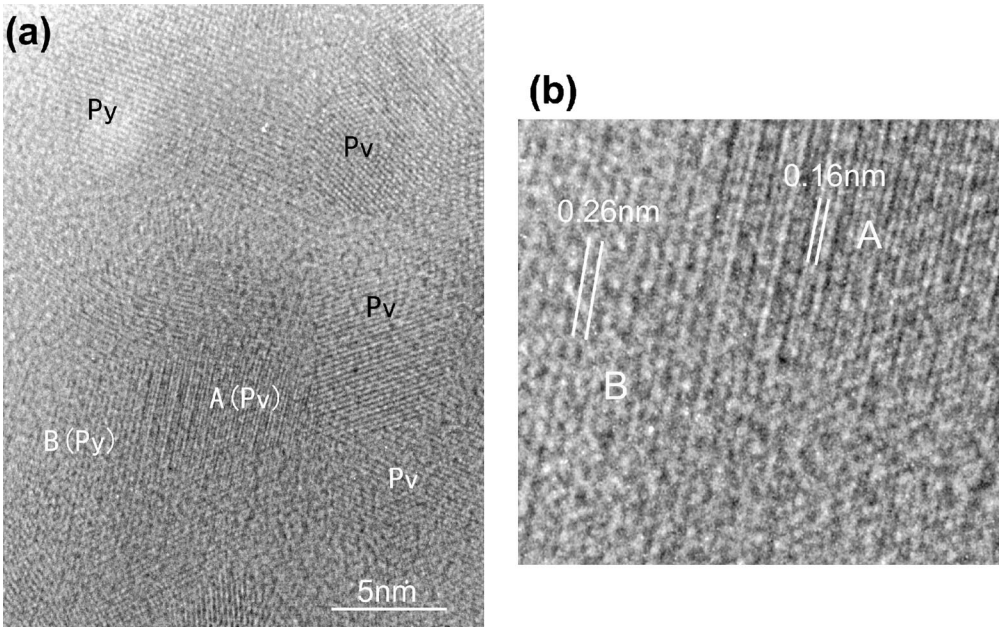

Fig. 8. HRTEM images of a part of PZT multilayer film prepared at 600°C. (b) Shows an magnified image of the place marked by A(Pv) and B(Py) in (a).

parallel with the (110) planes (0.28 nm) of grain A is observed.

3.3. Dielectric properties of the multilayer PZT films

The dielectric constant (ε_r) is shown in Fig. 10, where 'Film A' is the as-deposited film prepared at a heating rate of 50°C min^{-1}, 'Film B' is the 'Film A' heat-treated at 700°C, 'Film C' is the as-deposited film prepared at a heating rate of 100°C min^{-1}, and 'Film D' is the 'Film C' heat-treated at 700°C. The as-deposited films show higher ε_r values, while the films heat-treated at 700°C have lower ε_r values. On the other hand, the value of ε_r is shown to decrease with increasing heating rate. These results are explainable if the film porosity is increased by the increase of heating rate or by the heat treatment at 700°C as shown in our previous experiments [4,5]. The constant ε_r increases with increasing applied field as shown by Fig. 11, indicating the increase of oriented dipole moments.

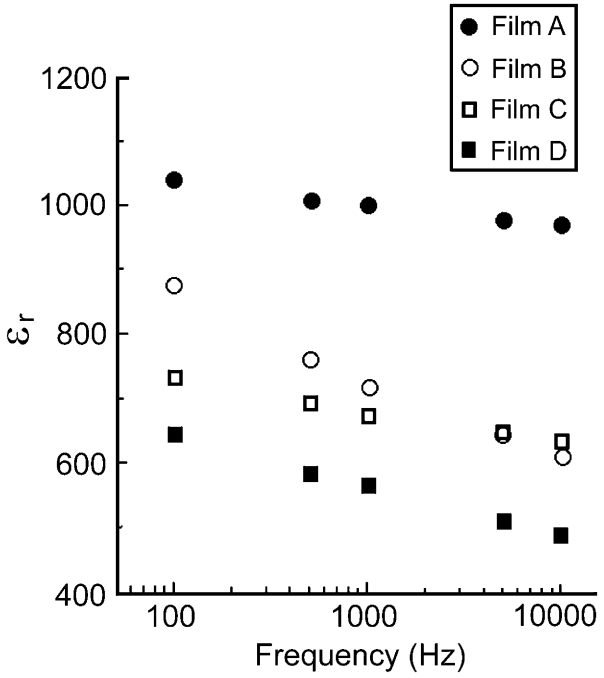

Fig. 10. Dielectric constant ε_r of the multilayer PZT films with 15 coating layers measured with an applied field of 0.11 kV mm^{-1}.

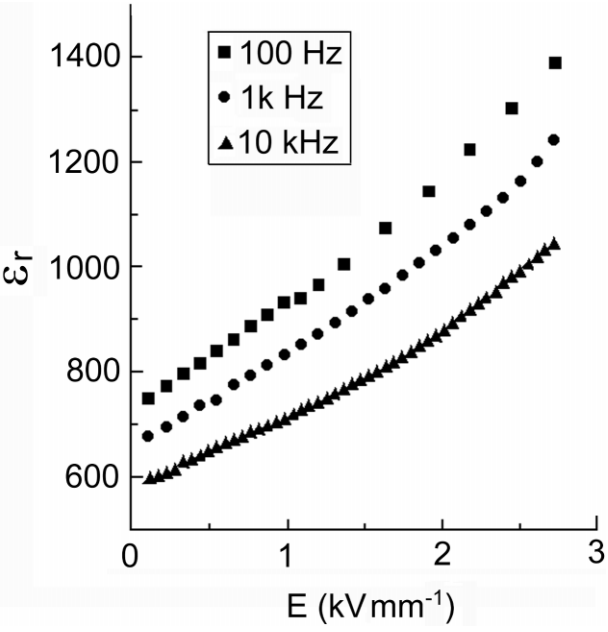

Fig. 11. Dielectric constant ε_r of the as-deposited multilayer PZT film prepared at a heating rate of 50°C min^{-1} measured as a function of applied field.

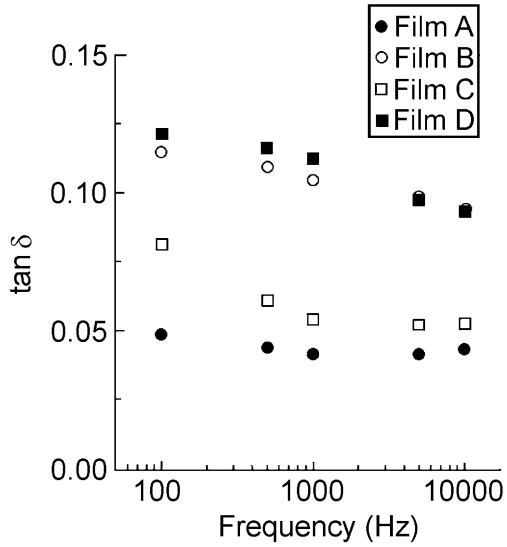

Fig. 12. Dielectric loss (tanδ) of the multilayer PZT films plotted as a function of frequency under an applied field of 0.11 kV mm^{-1}.

Fig. 12 shows the dielectric loss (tanδ) of the same specimens as Fig. 10. It is found that the value of tanδ is increased by the increase of heating rate, or, by the heat treatment at 700°C. The above results show that optimization of heating rate is required in order to fabricate multilayer PZT films with superior dielectric properties.

4. Conclusions

1. A PZT multilayer film with a tetragonal structure can be obtained with a heating rate of 200°C min^{-1}, while the films fired with heating rates of 50 and 100°C min^{-1} show a cubic structure.
2. The pyrochlore phase is dominant in the PZT film prepared with a heating rate of 20°C min^{-1}.
3. Surface cracks are not observed in the films prepared with heating rates of 50, 100 and 200°C min^{-1}, while cracks appear in the film prepared with a heating rate of 20°C min^{-1}.
4. Pyrochlore and perovskite crystal grains with a size of several nanometers are observed to nucleate from the amorphous film matrix. A perovskite

crystal is facetted with {110} planes in the amorphous matrix.

5. The dielectric constant ε_r decreases, while the dielectric loss tanδ increases with increasing the heating rate. The as-deposited film prepared at a heating rate of 50°C min^{-1} yields the highest ε_r value and the lowest tanδ value.
6. The film with 15 coating layers prepared at a heating rate of 50°C min^{-1} shows the best dielectric properties.

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